"Development of Holistic Remediation Alternatives for the Catholic 40 and Beaver Creek"

Spring 2000 Environmental Capstone Project
Civil Engineering and Environmental Science
University of Oklahoma

Submitted to
Governor Frank Keating's
Tar Creek Superfund Task Force

April 28, 2000

Submitted by

Kim Wahnee
Kimberlie Coursey
Ashley Norton
Mathew Jefferson
Matt Cogburn
Michael Kimbro
Stephanie Lipe
Kelly Rhoney
Terrie Biles
Ashley Pankop
Megan Sprowls
Justin Suiter
Shu-Mei Tsai
Colleen Gillespie
Denae Athay
Todd Wolfard
Andrew Alcazar
Crystal Stearns
Vihn Pham

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

I. Scope of Work

The overall objective of this study was to develop a Remedial Investigation/Feasibility Study (RI/FS) for the Catholic 40 (Quapaw Waste) site. The study results are based on a review of the current literature and field and laboratory data collected as a result of two field sampling trips.

The literature review initially focused on descriptive information regarding the geomorphology/geology, climate, hydrology and history of the Picher Mining Field and the evolution of the Tar Creek Superfund site. In addition, general information regarding the environmental impacts and human health hazards associated with the abandoned mines was collected. Most importantly, the current literature was surveyed to identify candidate technologies for remediating the land and surface waters of the Catholic 40 site. Process information including performance data and design parameters were collected and synthesized for the most promising remediation technologies.

The environmental sampling data were utilized to assess the water quality conditions of Beaver Creek, the chemical characteristics of the discarded chat, and the impacts of the chat on the surface soils of the Catholic 40 site. The analytical data were used in combination with the available process information to evaluate the alternative technologies as to their technical and economic feasibility. The overall remediation plan for the Catholic 40 site had to meet the following criteria:

- improve the water quality of the stream traversing the Catholic 40 recreational area such that it will support warm water fishing and body contact recreation activities
- re-contour the surface topography to accommodate overnight camping and associated recreational activities
- restore vegetative cover
- address use and/or disposal of the accumulated volumes of chat material
- include a cost estimate for each component of the overall plan.

Deliverables

Project deliverables included 35% and 65% progress reports and a Final Project report. The contents of each deliverable and schedule of activities are outlined below:

1. 35% Progress Report (Due 2/16/00)
    - overview of the literature
    - discussion of field activities
    - identification of environmental impacts
2. 65% Progress Report (Due 3/30/00)
    - identify alternative remediation technologies
    - advantages/disadvantages
3. 100% Final report (Due 4/7/00)
    - overview of the literature
    - discussion of field activities
    - identification of environmental impacts
    - identify alternative remediation technologies
    - advantages/disadvantages
    - identify preferred alternative
        - scope design
        - cost estimate

This document and the attached appendices represent the Final Report for the project. Information contained in the report was developed from documents submitted by the following three student project teams:

Team 1 – Enviro-Corp	Team 2 – Sooner Sweep	Team 3 - Sagpaw Remediation
Kim Wahnee (Leader)	Stephanie Lipe (Leader)	Colleen Gillespie (Leader)
Kimberlie Coursey	Kelly Rhoney	Denae Athay
Ashley Norton	Terry Biles	Todd Wolford
Mathew Jefferson	Ashley Pankop	Andrew Alcazar
Matt Cogburn	Megan Sprowls	Crystal Stearns
Michael Kimbro	Justin Suiter	Vihn Pham
	Shu-Mei Tsai	

It is important to acknowledge the efforts of Mr. Dennis Patton and Mr. Marshall Brackin from Surbec-ART, LLC. In addition, Surbec-ART, LLC subsidized the costs of chat sampling, chat product development, and laboratory testing of the chat product.

This report was co-edited by Dr. Robert C. Knox PE, Samuel Roberts Noble Presidential Professor, Dr. Robert W. Nairn, Assistant Professor, and Dr. Keith A. Strevett, Assistant Professor, School of Civil Engineering and Environmental Science, University of Oklahoma.

II. Background Information

Site History

The Picher Mining Field is part of a former lead and zinc mining area known as the Tri-State Mining District covering parts of Oklahoma, Kansas and Missouri (Figure II-1). Significant quantities of lead and zinc were produced from the Tri-State District from about 1900 to the 1960s. Peak production occurred in the early 1920s when the mines accounted for over 55% of total U.S. zinc production. Although production decreased, the area continued to be an important ore-producing region throughout the 1930s and 1940s. During World War II, tailings were reprocessed two or three times to facilitate zinc recovery. Ore production through the early 1960s was over 7 million tons of zinc and slightly less than 2 million tons of lead. However, by the late 1950s, depressed global markets resulted in the suspension of most mining operations. Mining ceased by the early 1970s (McKnight and Fischer, 1970).

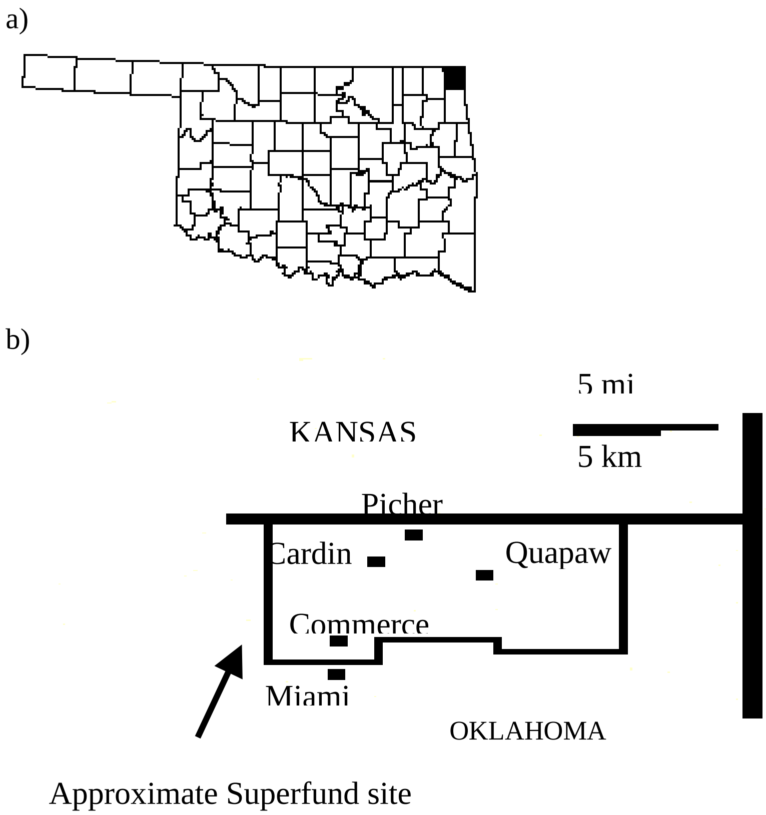

Figure II-1. a) Location of Tar Creek Superfund site in Ottawa County, OK; b) Approximate boundary of, and several local communities, located in the Superfund site.

Approximately 1,000 hectares (2,500 acres) are underlain by underground mines in all or part of 47 sections in northeastern Oklahoma (Luza,1983). During mining, large capacity dewatering operations pumped approximately 50,000 cubic meters (over 13 million gallons) of water per day (Reed et al., 1955) from the mines. Upon cessation of mining, groundwater began to accumulate in the mine voids. Approximately 94 million cubic meters (76,000 acre-feet) of contaminated water exist in the underground voids. In late 1979, acidic metal-rich waters began to discharge into Tar Creek from natural springs, boreholes and abandoned mine shafts. Two major discharge points developed. In general, water quality of the discharges was originally characterized as follows: pH 3.6-5.7, 80 μg Pb/L, 154,000 μg Zn/L, 80 μg Cd/L and 331,000 μg Fe/L (USEPA, 1999).

Over the course of the approximately 70 years that mines in the Picher Field operated, 10.3 km^2 (2,540 acres) of land were undermined in Ottawa County (USEPA, 1997). The mining operations left large quantities of mining waste on the surface as piles of chat and tailings pond sediment. According to Frank J. Cuddeback,general manager of Eagle-Picher's Tri-State operations, the chat pile at the central mill near Commerce, OK was about 91.4 m (300 ft) high and contained 12 million metric tons of chat (Tulsa Tribune, 1976). Approximately 37 million cubic meters (48 million cubic yards) of chat now litter the land surface in large piles. Also, approximately 325 hectares (800 acres) of tailings ponds exist on site. Typical concentrations of metals found in the chat and tailings ponds are shown in Table II-1.

Table II-1. Metals Concentrations in Chat and Tailings Ponds

Source	Pb (mg/kg)	Zn (mg/kg)	Cd (mg/kg)
Chat	750	8,300	46
Tailings Pond	3,800	21,600	124

The chat piles that remain, besides being unsightly, are a source of heavy metal contamination to surface water and stream sediments (Spruill, 1987). Carroll et al. (1998) report median in-stream Tar Creek sediment concentrations of 3.59 weight % for Fe, 1.76 weight % for Zn, as well as 433 mg Pb/kg and 58 mg Cd/kg. Significant reductions in native macroinvertebrate and fish populations in Tar Creek have been documented (Aggus et al. 1983).

The near surface aquifer, the Boone Formation, was mined and is severely contaminated. The Roubidoux Formation, a deeper aquifer at 325 m (1100 feet) below the surface, serves as a drinking water supply and has demonstrated limited contamination due to boreholes and leaky abandoned wells connecting the aquifers (USEPA, 1999).

The site was proposed for the Comprehensive Environmental Response, Compensation and Liability Act (Superfund) National Priorities List (NPL) on July 27, 1981, and received final listing on September 8, 1983. The site Hazard Ranking System (HRS) score of 58.15 made Tar Creek number one on the NPL for many years. The Tar Creek Superfund site encompasses approximately 104 square kilometers (40 square miles), including the towns of Miami, Picher, Cardin, Quapaw and Commerce. Approximately 70% of the land is owned by Native Americans, primarily Quapaw. Adjacent are the Cherokee County Superfund Site (Kansas) and the Oronogo-Duenweg Mining Belt Superfund Site (Missouri).

Several remedial actions have been conducted at the Tar Creek site (USEPA, 1999). Initial actions included the provision of emergency water supplies by the Oklahoma National Guard in 1985 during plugging of contaminated production wells. EPA drilled new wells and re-established the water supply. In addition, 83 other wells were plugged by late 1986. An attempt was made to decrease acid water impacts from two collapsed shafts discharging into Lytle Creek by construction of a diversion dike at a cost of approximately $20 million. However, this attempt failed to decrease impacts to the receiving waters. Beginning in 1994, EPA examined residential areas for lead contamination. Indian Health Service data had indicated approximately 35% of children tested had elevated blood lead levels. Since then, EPA has concentrated on residential remediation at more than 1,300 home sites at costs approaching $30 million (USEPA, 1997).

In 1995, the Oklahoma Department of Health conducted blood screening for lead in children living in the mining area. The results show that 21 percent of the children had elevated blood lead levels (> 10ug/dL) (USEPA, 1999c). As a result of those findings, a list of suggested measures were issued in order to limit the exposure of children to lead contamination. These included having children wash their hands thoroughly before eating; not allowing them to eat or drink in areas with known contamination; disallowing them to play in areas with known contamination; washing their toys and discouraging them from putting toys into their mouths; washing pacifiers and bottles if they should fall on the floor; washing all garden-grown vegetables and fruits before consuming; cleaning, vacuuming, and dusting often to remove contaminants; wiping the feet before entering the home; and feeding children foods rich in iron and calcium (USEPA, 1999a).

In addition to the Tar Creek watershed, mining activities have impacted adjacent watersheds, including Beaver Creek to the east. The focus of this investigation is a 162,000 m^2 (40 acre) plot of land in Ottawa County known locally as the Catholic 40 (or Quapaw Waste site). The acreage derived its name from the Catholic mission that one time owned the land. The first mining in Ottawa County began in 1891, near Peoria, Oklahoma, in what is called the Peoria District of the Picher Field. The first mine shaft was sunk on Quapaw tribal lands in 1904 (Weidman et al., 1932). The Mission mine on the Catholic 40 was one of the two most important mines in the Peoria District.

The Catholic 40 is in the Beaver Creek watershed and has piles of mine waste (chat), abandoned tailings ponds and mine shafts characteristic of the Picher Mining Field. Like much of the Picher Mining Field in Oklahoma, the Catholic 40 is on Native American land; in this case, the Quapaw land. Beaver Creek flows through the Catholic 40, then through the Quapaw Pow Wow grounds, eventually discharging into the Spring River. In January 1999, the EPA approved funding for a RI/FS study of the impacts of the waste sites in the Beaver Creek watershed (USEPA, 1999a). To date, that study has not been initiated.

The Catholic 40 site presents an exposure problem for local residents, in part, due to dust blown off the chat piles. In fact, the Center for Disease Control (CDC) noted that concentrations of lead in soil or dust exceeding 500-1000 ppm can be responsible for blood levels in children increasing above background levels (CDC, 1985). A study from the Community Health Action & Monitoring Program (CHAMP) program in Ottawa County, including the Quapaw tribe, found that 41.1 % of young children in 39 separate homes had blood lead levels (BLLs) greater than 9 μg/dl. Factors that added to the risk of elevated BLLs in Ottawa County were low incomes, poor diets high in sugar and low in calcium, and having a pet that spent time outdoors. Sources for lead contamination cited were high soil and lead dust concentrations, soldering, making bullets in the home, and homes built before 1965 (when home construction was changed to reduce or eliminate lead use) (CHAMP, 1997).

Environmental Impacts

Effects on Water Quality

The mining process exposes underlying rocks to water and air. Initial oxidation results in dissolution of reduced metal-sulfides, which are subsequently oxidized and hydrolyzed upon discharge from mine seep upwellings. The oxidation and hydrolysis of Zn, Pb, and Cd are shown in reactions I-1 to I-3. These metals tend to remain in solution in their ionic form at low and circum neutral pH levels.

$$2ZnS + 7/2\ O_2 + H_2O \rightarrow 2\ Zn^{+} + 2SO_4^{2-} + 2\ H^{+} \qquad \text{(I-1)}$$

$$2PbS + 7/2\ O_2 + H_2O \rightarrow 2\ Pb^{+} + 2SO_4^{2-} + 2\ H^{+} \qquad \text{(I-2)}$$

$$2CdS + 7/2\ O_2 + H_2O \rightarrow 2\ Cd^{+} + 2SO_4^{2-} + 2\ H^{+} \qquad \text{(I-3)}$$

Iron is a common metal in mine drainage due to a reaction that naturally occurs when pyrite (FeS_2) is exposed to water.

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^{+} \qquad \text{(I-4)}$$

$$Fe^{2+} + ¼\ O_2 + H^+ \rightarrow Fe^{3+} + ½\ H_2O \quad \text{(I-5)}$$

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+ \quad \text{(I-6)}$$

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \quad \text{(I-7)}$$

$$4FeS_2(s) + 15\ O_2(g) + 14\ H_2O\ (l) \rightarrow 4\ Fe(OH)_3(s) + 8\ SO_4^{2-}\ (aq) + 16\ H^+\ (aq) \quad \text{(I-8)}$$

The above reactions are catalyzed by bacteria. For pyrite, iron-oxidizing bacteria such as *Thiobacillus* ssp. greatly increase the rate of acid production (Skousen et al., 1998). As shown in the net reaction (I-8), iron solids precipitate out of solution forming an armor over the sediments. This can result in the smothering of aquatic life.

Acidity is added to the water through mineral dissolution processes (reactions I-2,I-4 and I-6). The acidity may be neutralized by the presence of bicarbonate ion, creating discharges that are net alkaline. Alkalinity comes from bicarbonate in the water due to the dissolution of dolomite ($CaMg(CO_3)_2$) or limestone ($CaCO_3$):

$$CaMg(CO_3)_2 + 2\ H^+ \rightarrow Ca^{+2} + Mg^{+2} + 2\ HCO_3^+ \quad \text{(I-9)}$$

$$CaCO_3 + H^+ \rightarrow Ca^{+2} + HCO_3^+ \quad \text{(I-10)}$$

At the Catholic 40 site, galena (PbS) and sphalerite (ZnS), acid-producing minerals, were exposed through mining, but limestone and dolomite in the geological substrate were capable of neutralizing the acidity, resulting in discharge of alkaline water high in metal ion concentrations.

Other impacts from mining at the Catholic 40 site include changes in topography and exposure of large volumes of waste rock to wind and water, leading to problems with erosion. Subsidence of undermined areas has also been known to be a problem in Ottawa County.

Effects on Aquatic Communities

The impacts of heavy metals on the aquatic ecosystem vary depending on the background environmental characteristics, concentrations of metals present, and how tolerant the species of plants and animals are to pollution. The EPA has set maximum allowable levels for concentrations of metals in fresh water to protect aquatic life (USEPA, 1999b).

Waters impacted by mine drainage are expected to show a decrease in species richness and diversity of fish and macroinvertebrate populations. Polluted waters should also show a shift towards a more pollution tolerant species distribution.

Plants that are not tolerant to heavy metals cannot grow easily on metal-contaminated soil or mine wastes. Heavy metal toxicity in these plants causes a decrease in photosynthesis, transpiration, growth, and reproduction. Plant cover is expected to be sparse because of metal toxicity along with the physical properties of the soil or chat, such as pH, organic content, moisture content, nutrients, and substrate particle size (Gibson, 1981a; 1981b).

Human Health Hazards

The three metals that pose the greatest human health risks at the Catholic 40 site are cadmium, lead, and zinc. Although all three metals may not necessarily be toxicants when acting alone, they can act synergistically to produce health problems for people who live in the area.

Cadmium

Based on several epidemiological studies, there is sufficient evidence that cadmium and cadmium compounds have human carcinogenic effects. Cadmium enters the blood via absorption from ingestion and inhalation. Usually only 1-5% of what is ingested is absorbed, while 30-50% of what is inhaled is absorbed (Robbins et al., 1989). Chronic cadmium poisoning manifests itself with bone pain, radiological decreases in bone density, high calcium concentrations in the urine, and renal stones (Gosselin et al., 1984). Cadmium replaces calcium in the bones and flushes calcium from the body. Pulmonary effects of prolonged exposure to cadmium are emphysema, and other lung diseases (USEPA, 1981). Long-term exposure to levels of 0.1 mg/m^3 of cadmium through inhalation or ingestion may increase the risk of lung disease or kidney damage. Although cadmium is a teratogen, it does not cross the placental-fetal barrier, or the blood-brain barrier (Robbins et al., 1989).

Zinc

Most zinc enters the environment as the result of anthropogenic activities such as mining. In the air, zinc is present as fine dust particles, and in water most zinc settles in the sediments. Zinc enters the body through inhalation and ingestion. Harmful effects begin at levels in the range of 100 to 250 mg/day. Zinc causes short-term lung irritations and has not been classified as a human carcinogen. Ingestion of high levels can cause pancreas damage (Robbins et al., 1989).

Cadmium and zinc have similar structures and functions inside the human body. The zinc-cadmium ratio in the human body is extremely important since cadmium toxicity and storage is greatly increased with zinc deficiency (Robbins et al., 1989). Cadmium is known to compete with zinc for binding sites and can therefore interfere with enzyme reactions and uptake and utilization of nutrients.

Lead

Lead enters the human body through ingestion and inhalation. Airborne lead particles have an approximate aerodynamic diameter of 0.1 – 1.0 um, with a predicted airway deposition of 35% (Friberg et al., 1996). Once in the body, lead is distributed to the liver and kidneys and is subsequently stored in the bones. Lead affects the red blood cells and can cause damage to the liver, kidneys, heart, reproductive systems, and immune system. Elevated lead concentrations in the blood can cause irreversible damage to the central nervous system. Reduced IQ, learning, and behavioral problems can manifest in children with elevated lead concentrations in their bodies. Elevated lead levels in the body of a pregnant woman can cross the placental-fetal barrier causing a reduced birth weight, reduced motor activity, and skeletal deformity. These malformations have shown a tendency to be compounded by the presence of cadmium (Robbins et al., 1989).

III. Field and Laboratory Procedures

Safety and Health Plan

Safety concerns at the Catholic 40 site include uneven terrain due to the irregular chat piles, open mine shafts, and boreholes. In addition, there are elevated metals concentrations in the water, soil, chat, and air. Precautions were taken to minimize the risks for personnel working in the area. In the zone of contamination, all personnel were required to wear gloves, proper work clothing, dust masks, and proper footwear. All equipment was properly cleaned with deionized water in the field and upon return to the laboratory.

Site Survey

On 5,6, February 2000, a survey was conducted on the Catholic 40 site using a GTS-2111 Total Station. Over 200 side shots were taken to establish the relative location and elevation of the soil and chat sampling points and other features. The site survey encompasses the general area inscribed by Beaver Creek, the west-side wood line, the north side ridgeline, and the east-side wood/ridge line. The actual land area affected by chat piles is approximately ten acres.

Chat and Soil Sampling

Chat and soil samples were collected at 14 locations within the 10-acre site on the Catholic 40 on 5,6, February 2000. At each chat-sampling site, the ground was initially cleared of debris and chat was removed with a coated aluminum trowell. The sampling depth for chat was approximately 6 inches. Two 1-gallon plastic bags of chat were collected at each sample location using the trowel, which was cleaned with deionized water between sites. Chat samples were collected from all of the sites except for the tailings pond and site A4, which did not contain any surface chat. After each chat sample was collected, the remaining chat was cleared using a shovel until the underlying soil was reached.

Soil samples were taken at 6-inches and 24-inches (if possible) below the soil surface using a steel bucket auger, which was cleaned with deionized water between each sample collection. At several locations (A1, A2, B2, B5, C1) the overlying chat was too deep for the soil to be sampled. The soil color at each site was recorded using a Munsell soil chart. A small amount of concentrated HCl was added to the soil and chat samples at each site to determine whether carbonates were present. Bulk density samples were also collected at each soil sampling site except for B3 and C5, which were accidentally covered with chat before samples could be collected. Bulk density samples were collected using a slide hammer and a stainless steel sleeve of known volume.

A second chat sampling episode was conducted on 26 March 2000. Chat material was retrieved from 12 of the 14 sample locations shown in Figure III-1. Three composite samples were developed by randomly combining the chat material from four individual sample locations.

The Catholic 40 site also contains at least one abandoned mill tailings impoundment. Soil samples were retrieved from the tailings pond at two different locations, and one location was sampled at two different depths. The soil sample retrieval, storage and cleaning procedures described above were used for the tailings pond samples.

Primary Water Quality Indicators

The definition of water quality indicators for mine discharge impacted water bodies differs from traditional metrics. The variables selected to characterize water quality at the Catholic 40 site were selected based on the type of mining activities that occurred in Ottawa County. The primary minerals in this mining area are sphalerite (ZnS), galena (PbS), and greenockite (CdS). Additionally, past studies of the mining area have shown elevated levels of zinc (Zn), lead (Pb), cadmium (Cd), and iron (Fe). Based on this information, these metals were targeted for analysis. Manganese (Mn) concentrations were also determined for the Beaver Creek and mine discharge samples. Manganese limits are often used to regulate metal removal treatment processes. Manganese is usually the last heavy metal to come out of solution during chemical treatment. Therefore, it is often assumed that if the manganese concentration is reduced to regulatory limits through a treatment process, the other metals will also be reduced proportionally.

Water Sampling and Analysis

In-situ parameters were measured for Beaver Creek on 12,13, February 2000. The ten stream sampling sites were located either in Beaver Creek or at a mine drainage discharge site that flows into Beaver Creek (see Figure III-2). Sites BC1 through BC5 are upstream of the Catholic 40 and downstream of the City of Quapaw wastewater outfall; sites BC6 and BC7 are downstream of the Catholic 40. Dissolved oxygen, pH, conductivity, and temperature were measured in-situ with calibrated meters (Appendix A). The probes were rinsed with deionized water between each reading.

Three water samples were collected from each of the ten sites using 250-ml plastic bottles that were rinsed with sample water three times prior to collection. Two water samples were collected for subsequent laboratory analyses for macronutrients (phosphate, nitrate, and sulfate), acidity, and bioassay toxicity tests. The third sample was collected for atomic absorption (AA) analysis of metals (Fe, Mn, Pb, Zn, and Cd) content and was preserved in the field using approximately 1 ml of concentrated HCl. Grab samples were collected for field measurements of turbidity, alkalinity, ammonia, and hardness (Appendix B).

Sediment samples were also collected at each stream sampling location shown in Figure III-1. Sediment samples were collected using a dredge and/or hand trowels and placed in plastic bags for transport to the laboratory.

Water Quantity/Discharge

The volumetric flow rate (discharge) was also measured at several locations along Beaver Creek (see Figure III-2). At each location, the stream cross-section was divided into sub-sections of uniform width. The velocity in each subsection was measured using a Global Water Flow Probe. Discharge was calculated by multiplying the sub-section area by the average velocity; total discharge at each location is the sum of all sub-section discharges (Appendix F).

Bioassessment

Bioassessment studies were performed at stream sampling sites BC4, BC5, BC6, and BC7. The bioassessment study covered a distance of 100 m upstream or downstream of the exact stream sampling location. Each 100-m reach was divided into two 50-m segments for the habitat-scoring portion of the bioassessment. The riparian zone width of each bioassessment segment was also assessed (Appendix D).

Macroinvertebrate and fish samples were collected for the entire 100-m reach. If the site reach had adequate riffles, macroinvertebrate samples were collected using a kicknet. A d-frame net was used to collect samples along the banks if adequate riffles were not present or if there was significant leaf litter present. A seine was used to gather fish and invertebrates, which were preserved in alcohol for identification. When multiple individuals of the same species of fish were collected, a few were preserved and brought back to the lab for identification and the rest were returned to the stream. The approximate number of individuals returned was recorded at

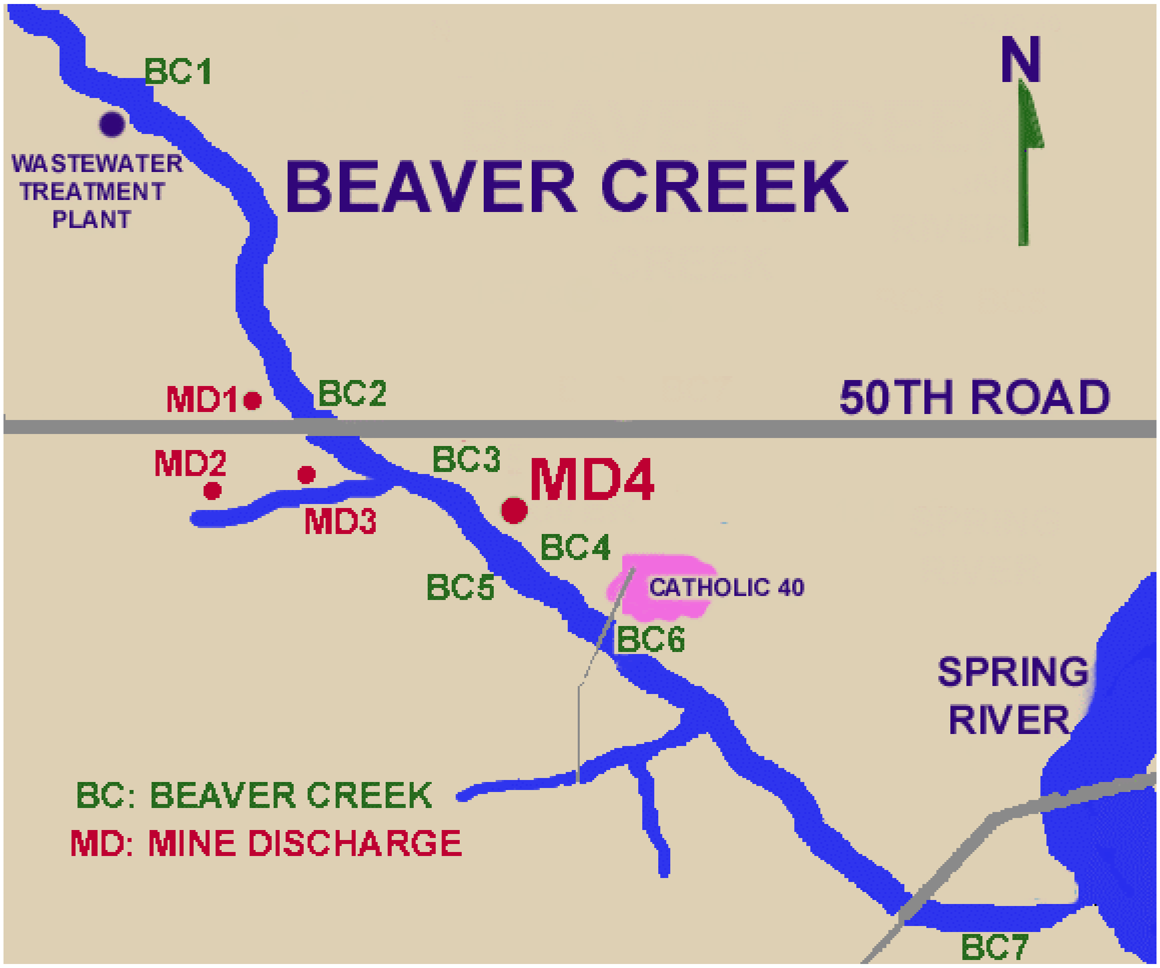

Figure III-1. Map of Catholic 40 Site and Stream Sampling Locations.

each site. Algae were observed along each reach and the quantity and color of periphyton or free-floating algae were noted and used for comparison between sites.

Laboratory Analyses

The bulk density soil samples were weighed before and after drying. Sample weights and volumes were used to calculate bulk density and moisture content of each sample. The organic content of the soil was measured using the loss on ignition procedure (Appendix H).

Chat samples from the first sampling episode were sieved for particle size analysis using sieve numbers 40 (6350*u*m), 100 (254*u*m), and the pan. Laboratory analytical procedures require 100g of each sample, therefore only three-size fractions were utilized in the particle size analyses. The specified fractions were selected due to the potential health implications associated with their particle sizes. The 1997 Record of decision (ROD) determined that the primary exposure route for lead in children was ingestion from hand to mouth. The size distribution of dust adhering to the hand was used as a surrogate for the ingested fraction of dust in children, which is approximately 200 um (Adgate et al., 1998). Sieve number 100 is therefore used as the potentially ingested fraction. The smaller particles in the pan are considered potentially airborne. The individual and composited chat materials from the second sampling were also analyzed for particle size distribution. The composited materials were used as aggregate in asphalt and concrete mix design studies. The samples were then tested for select engineering properties and chemical characteristics (Appendix I).

The Toxicity Characteristic Leaching Procedure (TCLP, USEPA, 1983a)) was utilized to extract the leachable metals in the soil (Appendix H), chat (Appendix I), and sediment samples (Appendix G). The chat samples retrieved during the second sampling episode were sent off to a commercial laboratory for analysis of both TCLP and total metals concentrations (Appendix J).

The water samples and the extracted soil, chat, and sediment samples were digested prior to AA analysis for metals content (American Public Health Association, *et* al., 1995). The concentrations of iron, zinc, manganese, lead, and cadmium in all of the samples were analyzed using a Perkin-Elmer 5100 PC Flame Atomic Absorption Spectrophotometer. Calcium and magnesium concentrations were measured on the water samples in order to determine total hardness. Standards, calibration curves, and detection limits were calculated according to the manufacturer's suggested methods (Perkin Elmer Corporation, 1996).

Acidity measurements (Appendix C) were also performed in order to study the inorganic nature of the collected samples. Ion chromatography using a Perkin-Elmer Ion Chromatograph was used to measure macronutrient content (USEPA, 1983a).

Bioassay tests were performed on the water samples in the laboratory using metals sensitive lettuce seeds (*Lactuca sativa)*. The lettuce seeds were soaked for 20 minutes in a 10% bleach solution to kill fungus, then rinsed with deionized water before use. Water from each stream sampling location was used, along with 50% and 25% dilutions and a deionized water blank. Three petri plates lined with filter paper and 10 to 11 lettuce seeds were soaked with 2 ml of each sample concentration. The plates were incubated for one week in plastic bags in the dark. After 5 days, some of the plates were drying out, so 2 ml of deionized water was added to all of the plates. After one week, two experimental endpoints were recorded: number of seeds germinated and root length of germinated seeds (Appendix E).

IV. Results

Chat

The Catholic 40 site survey data were loaded into Eagle Point and AutoCAD v.14 software to create the topographic map shown in Figure IV-1. The survey data indicate that the area affected by mining waste (chat) is approximately 4.17 ha (10.3 acres). The change in elevation from the highest point to the lowest point is 15m (49.3 feet). The survey data were used in combination with chat thickness measurements at each sampling location to estimate the volume of chat covering the site, which is approximately 48,000 m^3 (65,000 yd^3).

For the second chat sampling episode material was retrieved from twelve of the sample locations shown in Figure IV-1. Three composite samples were developed by randomly combining the chat material from four individual sample locations. The individual and composite samples were analyzed for particle size distribution. A typical particle size distribution curve for the chat material on the Catholic 40 site is shown in Figure IV-2. On average, the chat is comprised of 65% sand, 29% gravel and 6% fines.

The individual size fractions of composite chat sample #1 were analyzed for both total and TCLP extractable metals. Figure IV-3 depicts the total concentrations of cadmium, lead, and zinc for the various size fractions in composite sample #1. From Figure IV-3 it is clear that the highest concentrations of total metals are found in the smaller-sized chat particles. This is of particular concern given that the smallest chat particles are most likely to become mobile and move offsite. The breathable dust fraction of the chat material (< 75 um) contains high enough levels of lead and cadmium to be considered a regulatory health hazard.

Figure IV-4 shows the concentrations of TCLP extractable metals for each size fraction in composite chat sample #1. Once again, the highest concentrations of TCLP extractable metals are found in the smaller-sized chat particles. The TCLP hazardous substance criteria for lead and cadmium are also shown on Figure IV-4. In general, chat particle sizes less than 4 mm would be classified as hazardous substances based on leachable metals. Combining the TCLP levels (Figure IV-4) with the particle size analysis (Figure IV-2) shows that approximately 20% of the total chat material on the Catholic 40 site is hazardous. This material should be separated out and handled properly in order to eliminate further contamination of the area and reduce potential exposure.

It is important to note the difference in heavy metals concentrations derived from whole samples (i.e., not size separated) versus the concentrations in the various size fractions. Figures IV-5 and IV-6 show the concentrations of total metals and TCLP metals, respectively, for the three composite chat samples and the average values for the 12 individual chat samples. The averaging influence of the non-hazardous portion of the chat is evidenced in the total metals concentrations of the whole samples (Figure IV-5). The maximum concentrations of lead, zinc, and cadmium in the whole samples are well below the maximum values found in the smaller size fractions (Figure IV-3). However, the averaging effect of the non-hazardous size fraction is diminished when examining the TCLP metals concentrations. Although the maximum TCLP metals concentrations for the whole samples (Figure IV-6) are lower than the values for the smaller size fractions (Figure IV-4), they still exceed the TCLP leachability criteria for lead and cadmium.

These data are conclusive evidence that the unprocessed chat material is a hazardous substance. Engineering controls to reduce human exposure and/or control off-site migration of the chat material need to be implemented. Moreover, uncontrolled use of the chat material (e.g., road base, asphalt, concrete) will result in increased mobility and potential exposure to the hazardous fractions within the chat.

Figure IV-1. Topographic Map of the Catholic 40 Site (omitted for web viewing)

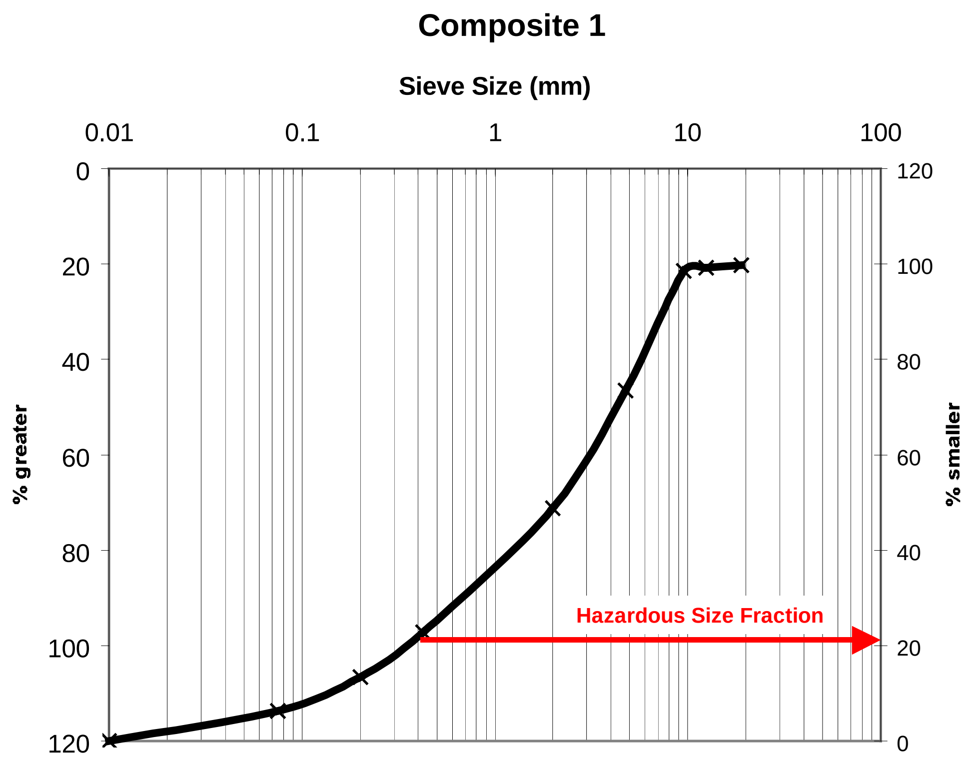

Figure IV-2. Particle Size Analysis for Chat Composite Sample #1

Tailings Ponds

The results of TCLP leachability tests conducted on the tailings pond samples are depicted in Figure IV-7. The figure shows higher concentrations of zinc and cadmium in the surface samples. Zinc concentrations are lower in the tailings pond than in the chat. This is probably due to the fact that historical processing operations targeted zinc for removal from the raw ore. Cadmium concentrations in the tailings pond samples are higher than in the chat and exceed the TCLP criterion; thus, the material in the tailings pond should be considered hazardous. The tailings pond materials should be excavated and properly disposed to reduce potential exposure to cadmium.

Soil

Soil samples were retrieved from two depth intervals (where possible) at each sample location shown on Figure IV-1. In addition, a background soil sample was taken from a location across Beaver Creek that did not have any visible accumulation of chat. Figure IV-8 depicts the concentration of leachable zinc and lead in each of the soil samples. It is readily apparent that metals have been leached out of the overlying chat materials and migrated down into the surface soils on the Catholic 40 site. In fact, some of the zinc concentrations found in the soils are over 300 times higher than the background concentration.

There are two important trends associated with the data in Figure IV-8. First, it appears that the metals leached from the chat reside mainly in the upper reaches of the underlying soil (compare Zn for location B3). This seems to indicate that these metals are not highly mobile through the soil system. Of more importance is the obvious elevated concentrations found along the “A” sampling transect, which is located in the flatter land area closest to Beaver Creek (see Figure IV-1). These data indicate that runoff from precipitation has transported the leachable

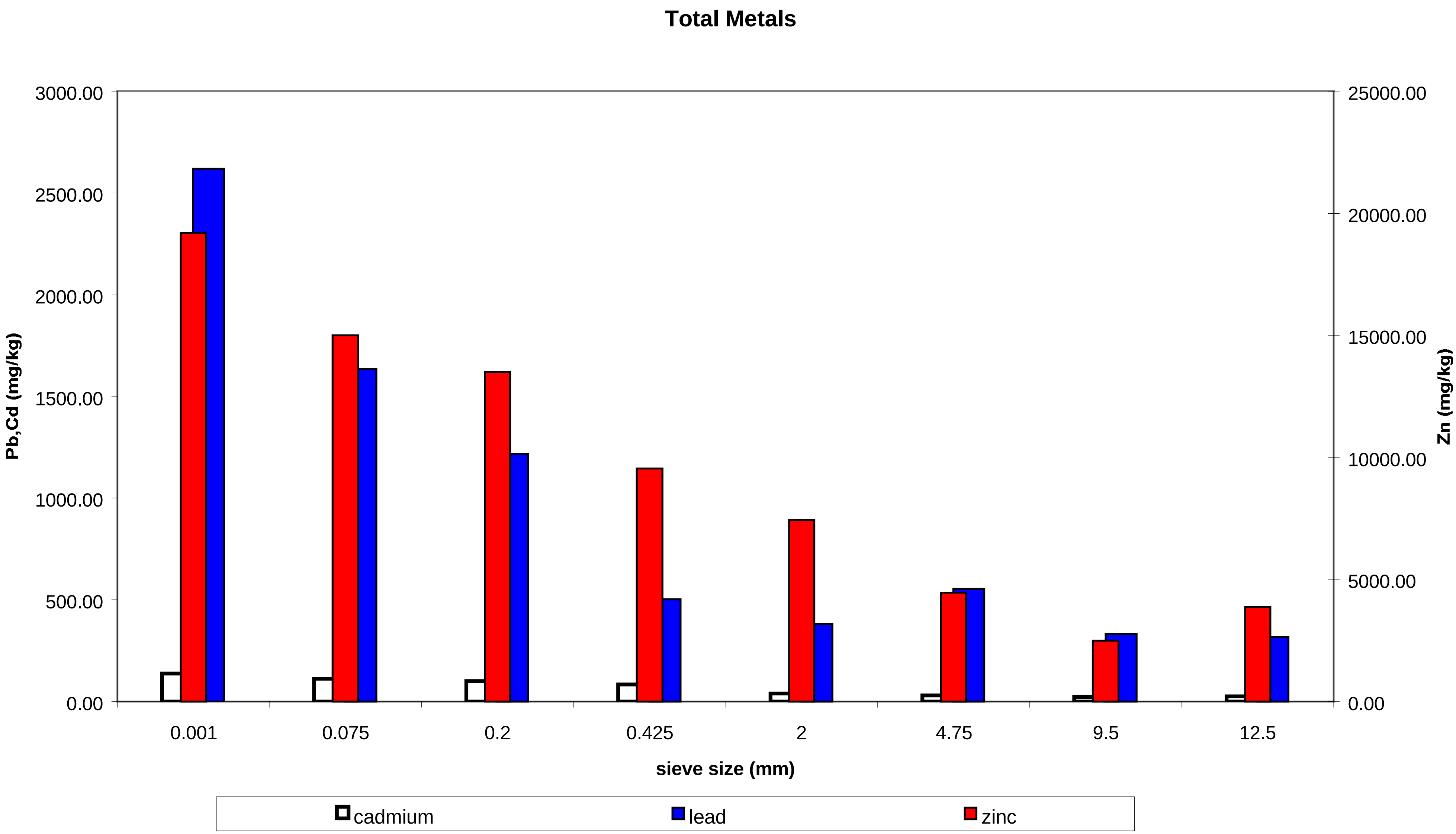

Figure IV-3. Total Metals Concentrations in Size Fractions of Composite Sample #1

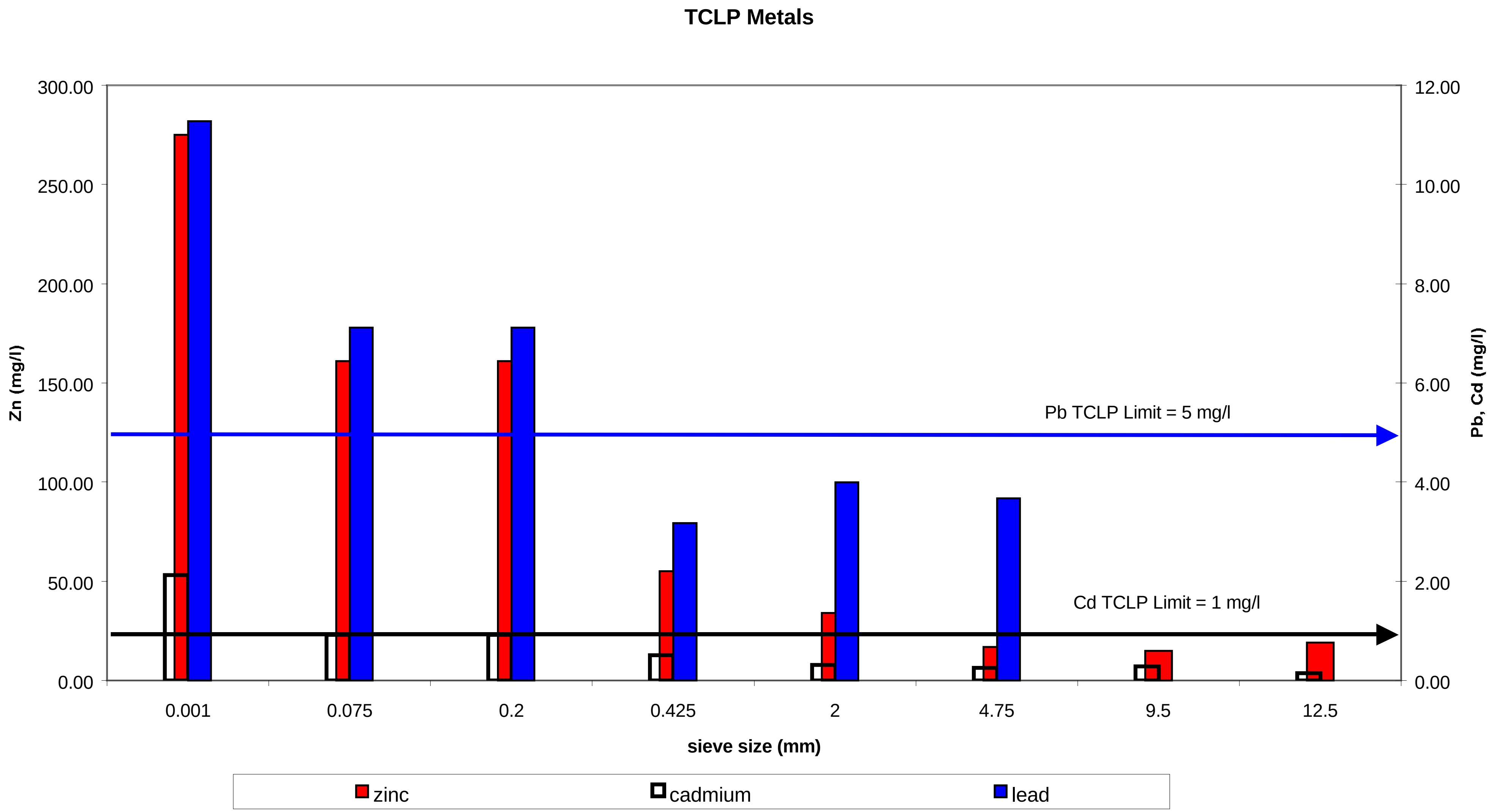

Figure IV-4. TCLP Metals Concentrations in Size Fractions of Composite Sample #1

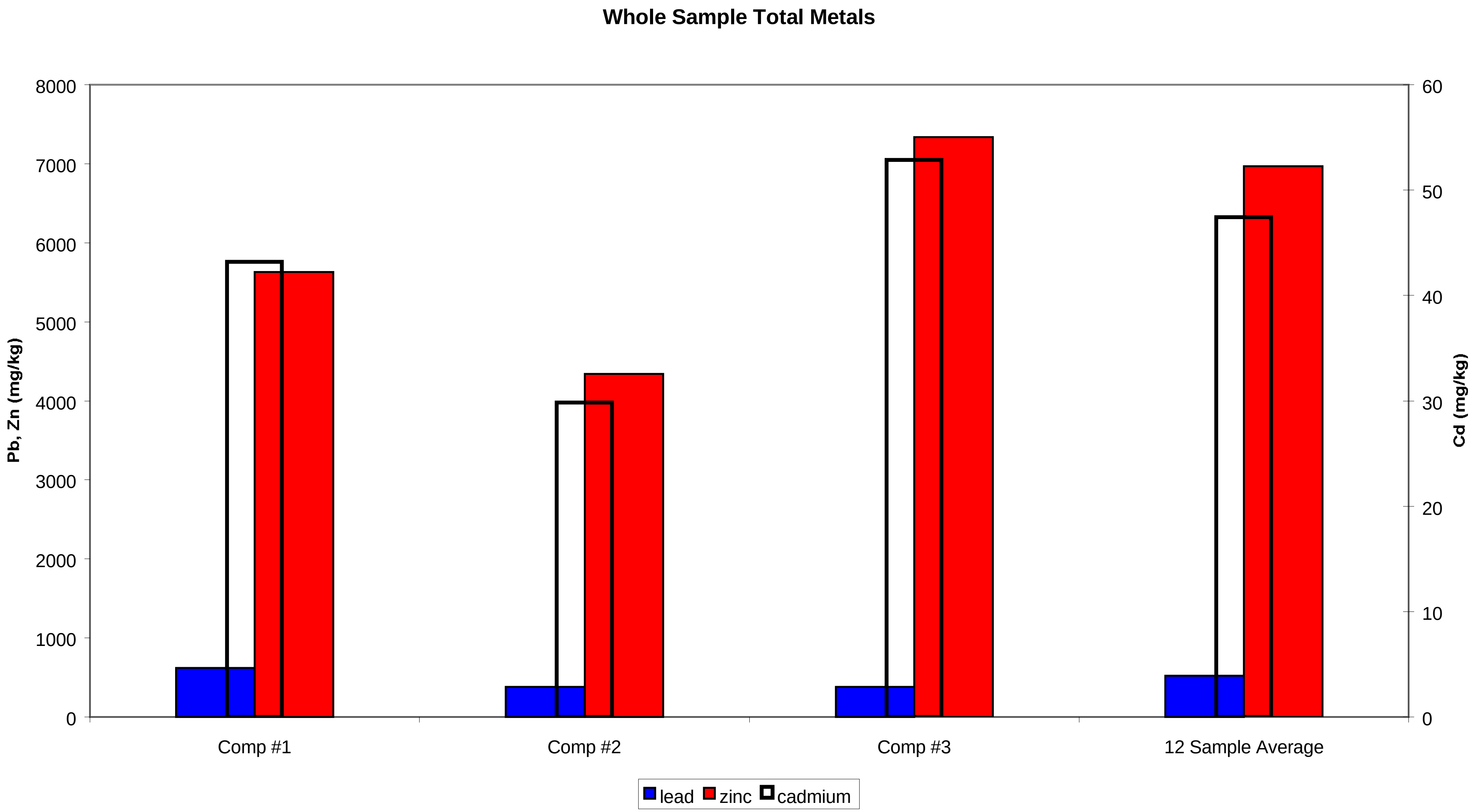

Figure IV-5. Total Metals Concentrations In Whole Samples

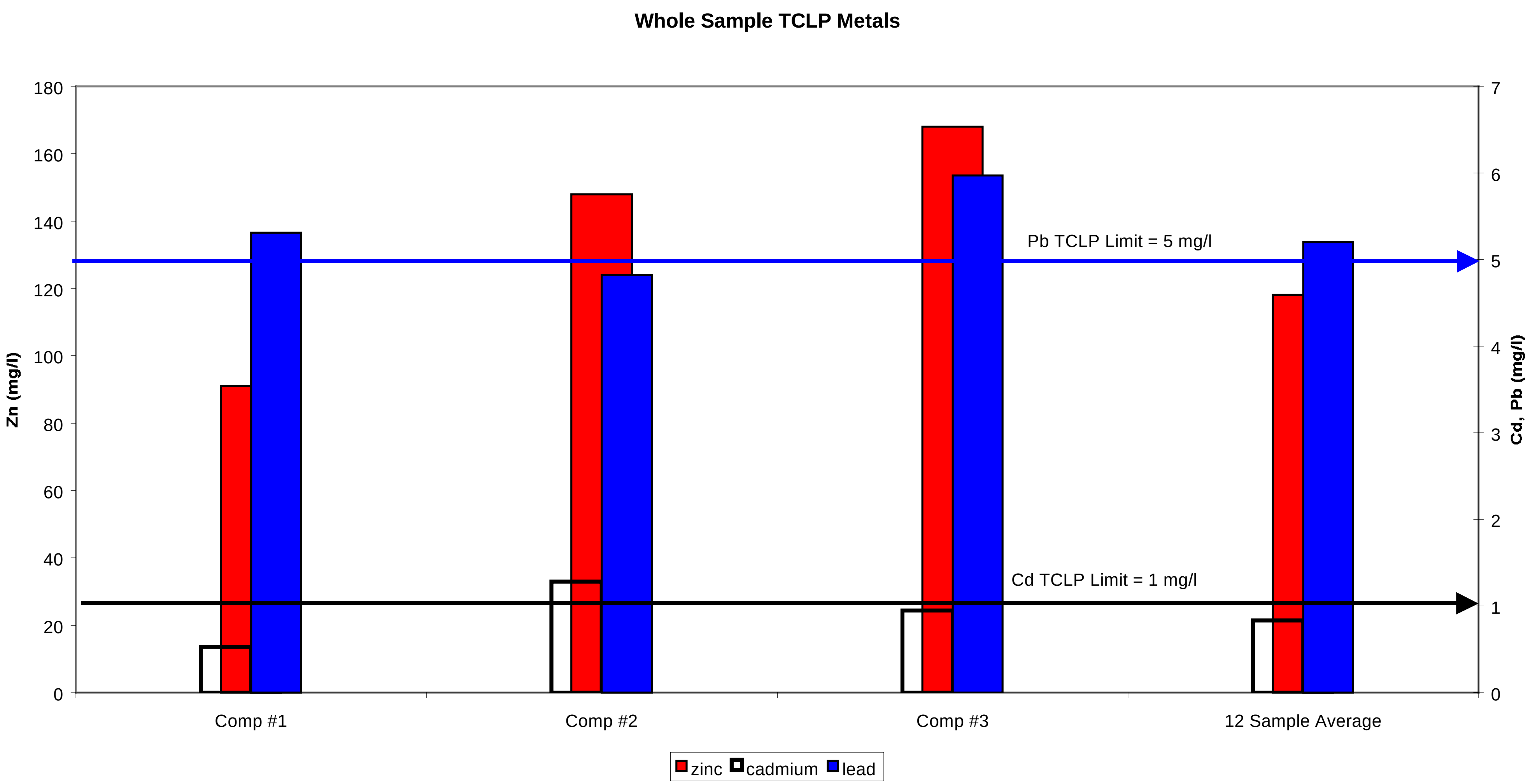

Figure IV-6. TCLP Metals Concentrations in Whole Samples

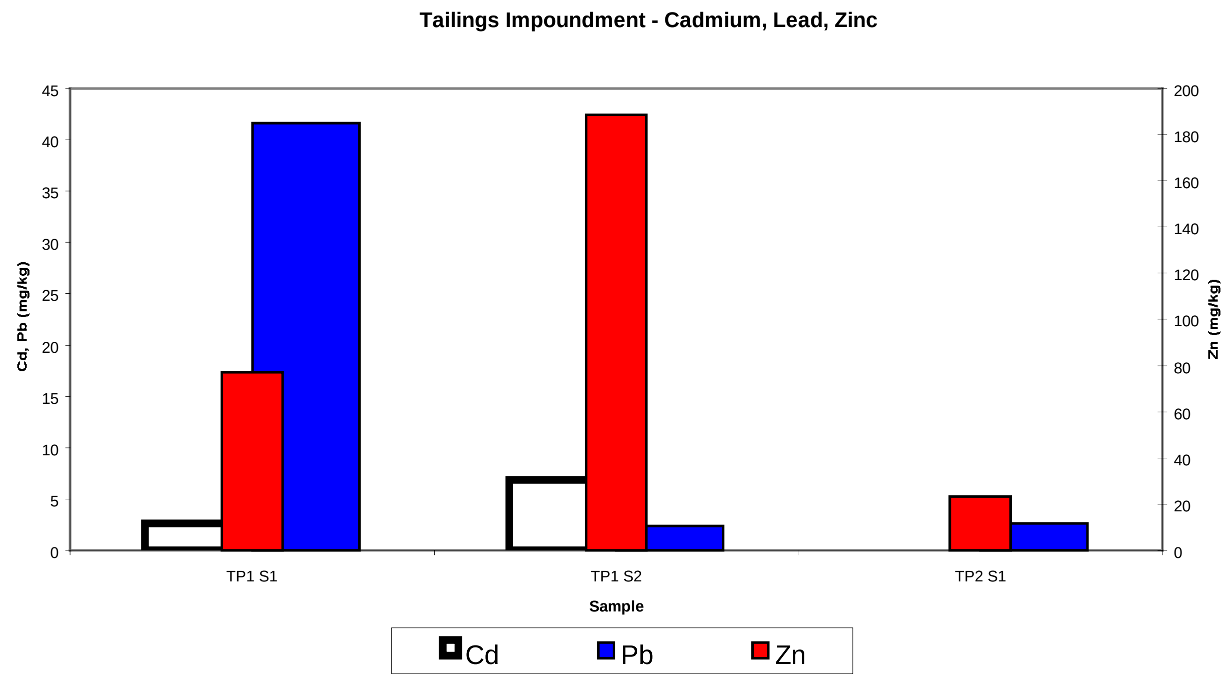

Figure IV-7. TCLP Metals in Tailings Impoundment

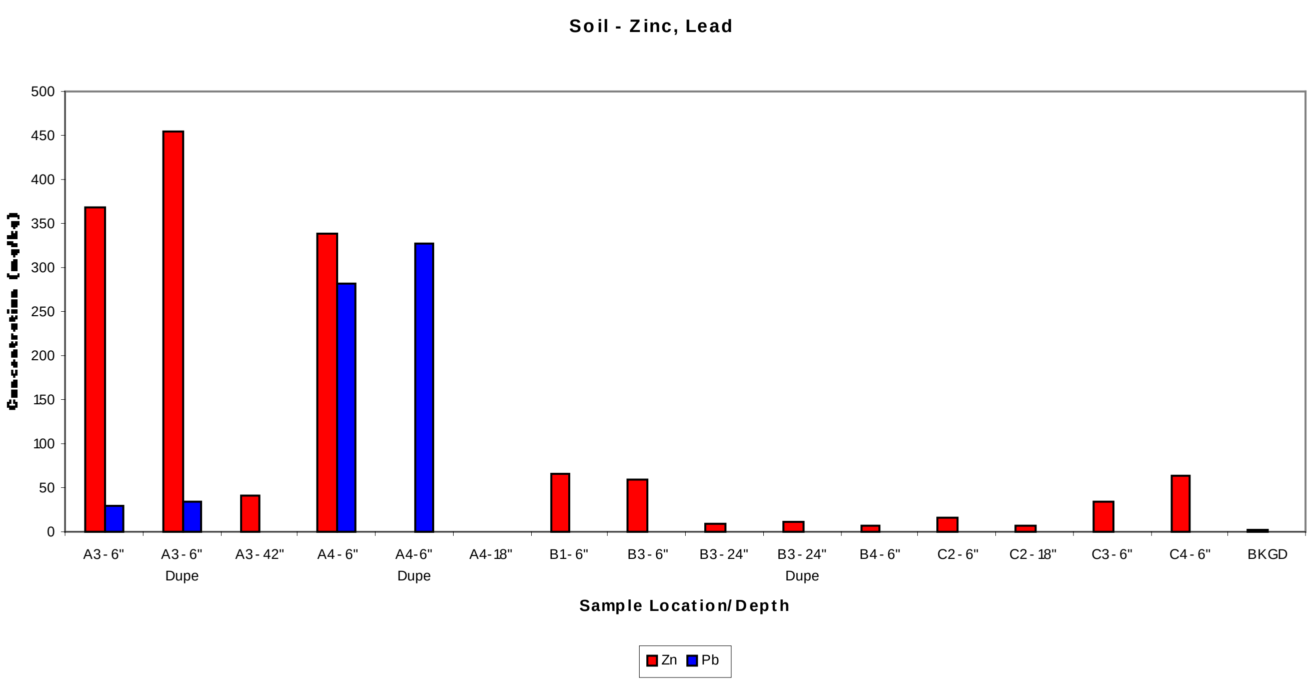

Figure IV-8. Zinc and Lead Concentrations in Soil Samples metals and/or metals-laden chat particles downhill toward Beaver Creek. The decreased slope of the land surface near Beaver Creek reduces the velocity of surface runoff, thus leading to ponding and/or infiltration. The net effect is an accumulation of leachable metals in the soils near Beaver Creek.

It is important to note that none of the metals concentrations in the soil exceed TCLP leachability criteria. Therefore, remediation of the surface soils at the Catholic 40 site is not warranted. However, remediation measures to reduce human exposure, such as revegetation, should be implemented. In addition, measures should be implemented to control off-site migration of the leachable and mobile fractions of the chat material.

Metals Content Trends in Beaver Creek

The concentrations of Pb, Fe, Cd, and Zn at the different sampling locations along Beaver Creek (BC) and at three identified mine discharge (MD) sites are depicted in Figure IV-9. The data represents a one-time sampling collection (12,13 February 2000) during low-flow conditions. Water and sediment samples could not be obtained from MD1, and a sediment sample was not obtained from location BC5.

Two segments along Beaver Creek were analyzed for mass loading to examine the impacts of the mine discharges. The first segment is between BC2 and BC3 in which discharges MD2 and MD3 enter Beaver Creek. The second segment was between BC3 and BC4 in which MD4 enters Beaver Creek. Implicit assumptions used for development of mass loadings were the conservation of mass (volumetric flow) between BC2 and BC3 and a flow input due to groundwater seepage into Beaver Creek. The concentrations of Mn and Fe for each sampling location are depicted in Figure IV-10. The concentrations of Pb, Zn, and Cd for each sampling location are depicted in Figure IV-11.

When comparing BC3 with BC2, the metal loading for Zn showed the greatest increase (ten-fold), whereas Mn, Fe, and Cd increased by three-fold. However, Pb only increased by a factor of 1.2. Water and sediment samples for MD2 and MD3 were taken from a small tributary of Beaver Creek that had been predominantly fed by abandoned boreholes. Comparison of BC4 with BC3 indicates discharge MD4 causes little change in the metal loadings of Beaver Creek except for Pb, which increased by a factor of 1.7. There was a correlation between the water and sediment iron concentrations at each sample location ($r = 0.75$). At the circum neutral pH levels present in Beaver Creek, it is thermodynamically favorable for iron to precipitate out of solution. Zinc, lead, and cadmium remain in solution at circum-neutral pH levels. There are no correlations observed between the water and sediment concentrations for zinc, lead, or cadmium. The elevated levels of these metals in the sediments may be due to chat particles that are present along the creek bed. In addition, Beaver Creek does not have a uniform flow pattern. The sampling program initiated for this study did not take into account the dynamics of the creek.

There are elevated metals concentrations in the water, mine discharge, and sediment samples. Therefore, mine discharge does and has in the past impacted the water quality and aquatic health of the stream. The Criterion Continuous Concentration (CCC) is an estimate of the highest concentration in surface water to which an aquatic community can be exposed indefinitely without resulting in unacceptable effect. The calculated CCC's for Fe, Zn, Cd, and Pb are 1.0000 mg/l, 0.2566 mg/L, 0.0030 mg/L, and 0.0068 mg/L; respectively, based on hardness. There is no CCC for Mn. Therefore, Beaver Creek is impacted by Fe at BC2, 3, 4 and at MD3, 4; by Zn and Cd at all sites downstream of MD1; and by Pb at all sites downstream from MD4.

The metal concentrations in Beaver Creek will have little impact on the water quality of Spring River. At the time of sampling, Beaver Creek was discharging only 1.57 cfs into Spring River that had an approximate flow of 857 cfs. However, long-term discharge could lead to accumulations of metals in the sediments of Spring River. Remediation of Spring River is not

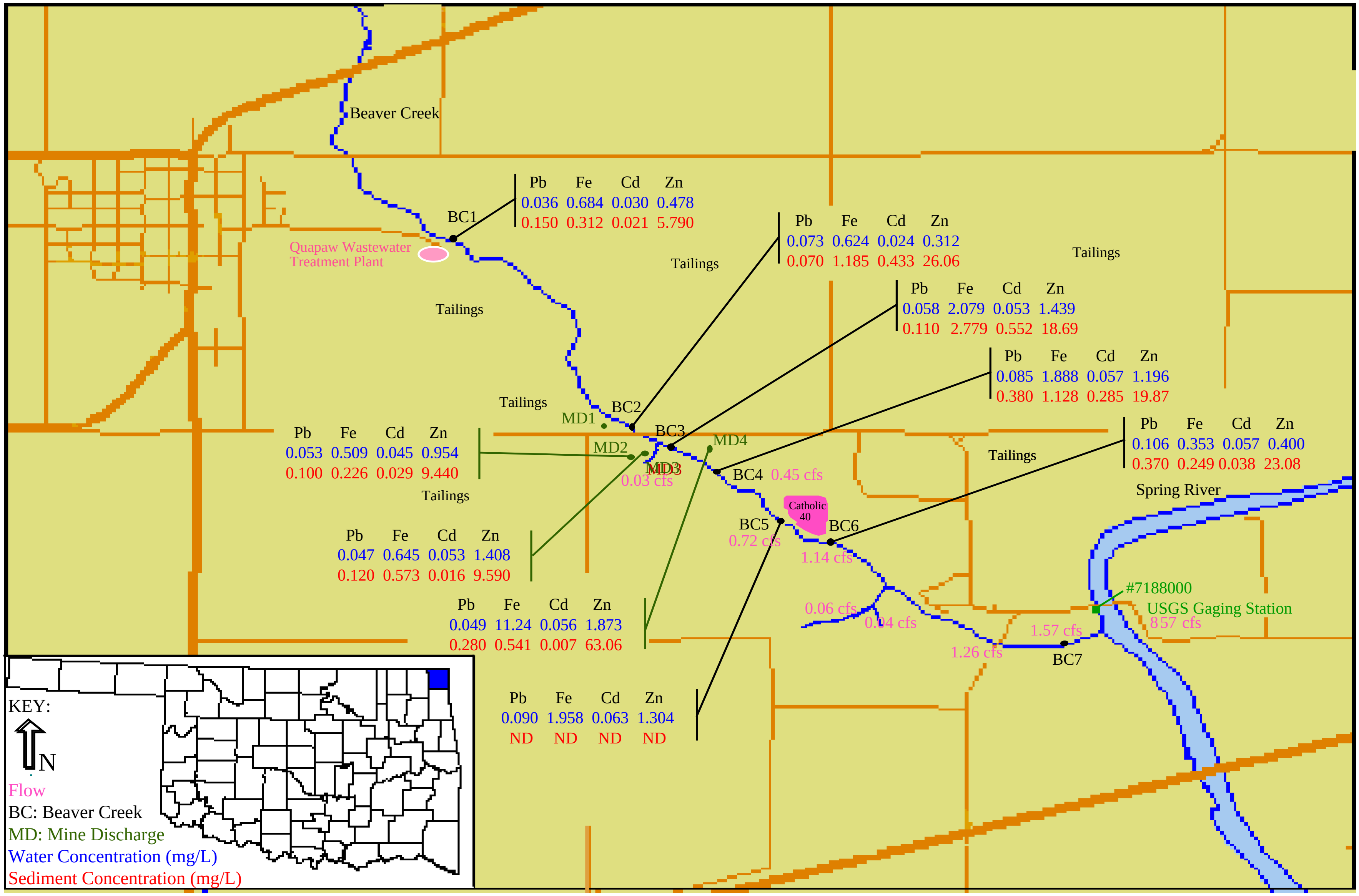

Figure V-9. Sample Locations With Associated Metal Parameters for Both Water and Sediments. The Catholic 40 site is located at SW 1/4 NE 1/4 SEC.6 T.28N, R.23E. Several mine discharges (MD) flow into Beaver Creek (BC) and land use in the area is primarily agricultural.

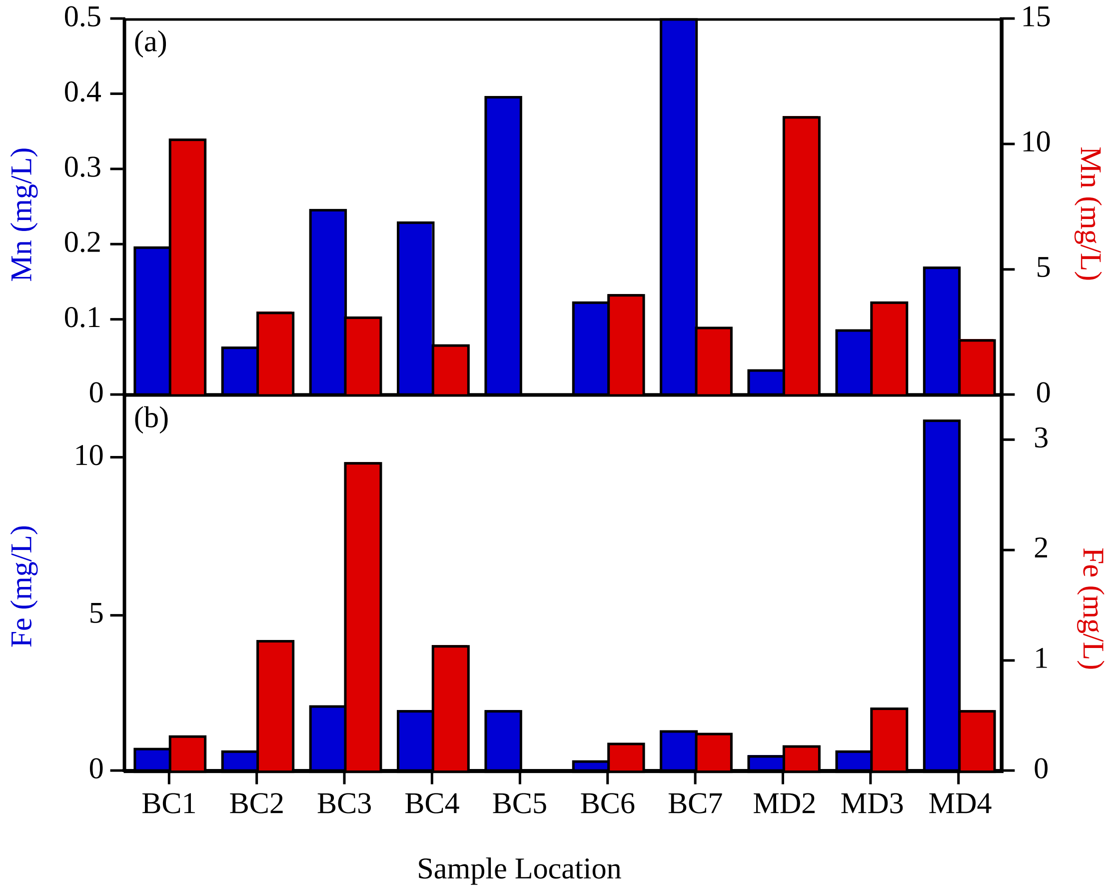

Figure IV-10. Manganese (a) and Iron (b) Concentrations in Beaver Creek. BC is sampling location along Beaver Creek; MD is mine discharge sampling location; ■ is dissolved metal concentration; and ■ is sediment TCLP metal concentration.

feasible; small passive treatment systems for Beaver Creek represent a more economically feasible alternative

Other Water Quality Indicators

In addition to the selected metals, other traditional water quality parameters were used to assess the impacts of mine discharge on Beaver Creek. These parameters include dissolved oxygen (DO), pH, alkalinity, acidity, hardness, and ammonium (Table IV-1). DO levels in natural waters depend on the physical, chemical, and biological activities in the stream, and reflect the productivity of the water body. Plants are primarily responsible for adding oxygen to the water through photosynthesis; oxygen is removed through respiration and the microbial decomposition of dead organic matter. DO is used as an indicator of water quality because at low DO levels aquatic organisms will decrease their activity and many organisms cannot survive at depressed DO levels. DO levels for a healthy stream range from 6 mg/L to 12 mg/L. Sampling site BC1 is located downstream from the Quapaw wastewater outfall, which discharges nutrient-rich, oxygen depleting wastes into the stream. The DO levels in Beaver Creek range from 11.6 to 9.28 mg/L. As expected, the level of DO decreased by a factor of two directly downstream of the wastewater outfall, then gradually increased back to near saturation levels as the water mixed and flowed downstream. At MD4, an upwelling of mine discharge occurs which results in a ten-fold

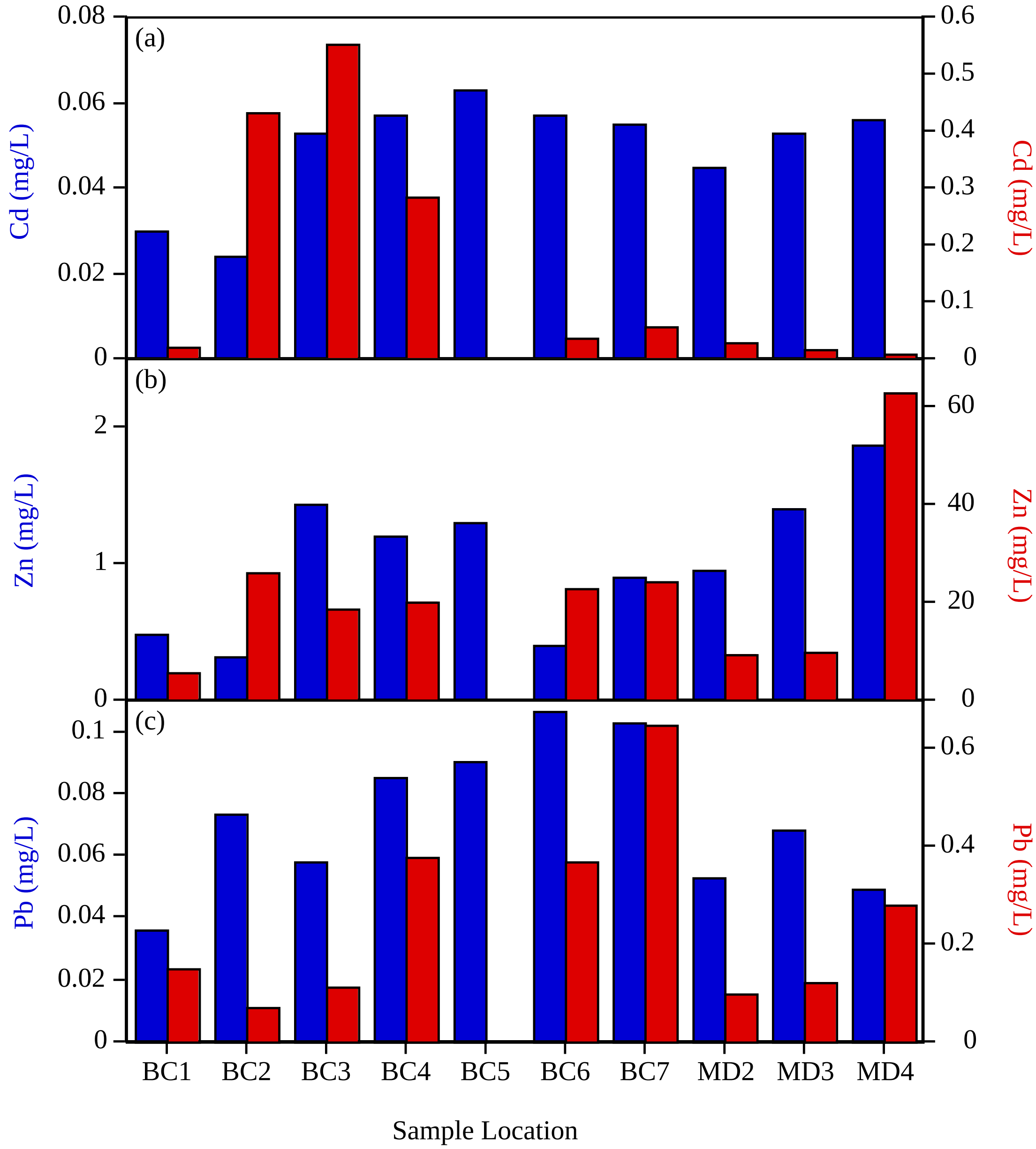

Figure IV-11. Cadmium (a), Zinc (b) and Iron (c) Concentrations in Beaver Creek. BC is sampling location along Beaver Creek; MD is mine discharge sampling location; ■ is dissolved metal concentration; and ■ is sediment TCLP metal concentration.

decrease in DO. This occurs in part because the discharge comes from groundwater, which is not exposed to oxygen. Oxygen that does come into contact with the discharge at the surface results in further oxidization and precipitation of the metals in the discharging water. Because of the low volume of discharge into the stream, the DO level in Beaver Creek was not significantly affected. The DO levels of MD2 and MD3 were within one standard deviation of the mean value.

Table IV-1: Water Quality Parameters for Beaver Creek.

Sample Site	**DO (mg/L)**	**pH**	**Alkalinity (mg/L $CaCO_3$)**	**Acidity (mg/L $CaCO_3$)**	**Hardness (mg/L $CaCO_3$)**	**NH_3 (mg/L)**
BC 1	11.6*	7.75	119*	1.58	214.27	0.35*
BC 2	9.28*	7.23	145	1.26	88.3	0.14*
BC 3	9.82	6.19	154	4.16	308.23	0.13
BC 4	9.81	6.1	154	3.79	252.19	BDL**
BC 5	9.97	7.59	157*	4.22	296.42	0.02*
BC 6	10.42	7.55	153*	0.86	208.58	0.01
BC 7	10.75	7.15	166	3.08	295.30	BDL**
MD 2	9.51	5.52	208	0.97	263.44	0.06*
MD 3	9.7	6.09	200	1.31	283.33	0.01
MD 4	0.22	6.04	200	20.39	251.02	0.04

Average values **BDL= Below Detectable Limits

pH is used as an indicator of water quality because the ability of aquatic organisms to survive decreases when the pH is outside the normal range of 6.0 to 9.0. The pH of Beaver Creek ranged from 6.1 to 7.75, which falls within the acceptable range. Of the mine discharge sites, only MD2 had a pH value below 6; MD3 and MD4 had pH values just above 6. The pH levels in Beaver Creek were impacted in the vicinity of the discharge sites, but then rose to the pre-discharge level at BC5.

Alkalinity is a measure of the capacity to neutralize acid and is primarily a function of carbonate, bicarbonate, and hydroxide content. The alkalinity of Beaver Creek ranges from 119 to 166 mg/L as $CaCO_3$. At the three discharge sites, the alkalinity ranges from 200 to 208 mg/L as $CaCO_3$, which is approximately 1.3 times greater than alkalinity of Beaver Creek. The mine discharges appear to cause only a slight increase in alkalinity in the stream..

Acidity is a measure of the capacity to neutralize bases and is used as an indicator of water quality. Acids contribute to the chemical reaction rates as well as biological processes. Acidity The upstream acidity in Beaver Creek is about 1.5 mg/L as $CaCO_3$, but increases by a factor of three near the mine discharges to a value around 4.0 mg/L as $CaCO_3$. After this initial rise, the acidity stayed about the same for all downstream sites. Only MD3 had a significantly high acidity value of 20.4 mg/L as $CaCO_3$, the other discharges had acidity values closer to 1.5 mg/L as $CaCO_3$. The discharges had a significant impact on the acidity of Beaver Creek.

Hardness is a measurement of the calcium and magnesium ions of the water, which often corresponds with the alkalinity of the water due to dolomite ($CaMg(CO_3)_2$) dissolution processes. The hardness of Beaver Creek ranges from 88.5 to 308.23 mg/L as $CaCO_{3.}$ The discharges do not appear to have a major impact on the hardness levels in Beaver Creek.

Ammonia is mainly produced by decomposition of organic nitrogen-containing compounds and by hydrolysis of urea. As expected, downstream of the wastewater outfall, ammonia levels were elevated. Levels gradually decline from 0.35 mg/L to below detection limits as the water mixes and aquatic plants take up nitrogen nutrients.

The distribution of organisms is used to show the biodiversity of a stream and assess the level of degradation of the stream, as indicated by the presence or absence of species of fish and macroinvertebrates that are intolerant to elevated metal concentrations. The fish community structure indicates an increase in species richness and Shannon's diversity (commonly used index of biodiversity based on relative abundance of different species) downstream (Table IV-2). These

Table IV-2. Habitat Assessment and Bioassessment Scoring for Sample Locations on Beaver Creek.

	Assessment Sites		
	BC4	BC5	BC7
Total Number of Species	2	2	7
Shannon's Diversity	0.45	0.67	1.42
% intolerant species, water quality	50	0	29
% intolerant species, habitat	50	50	43
% omnivore species	50	0	29
% insectivore species	50	50	71
Number of Taxa	11	6	7
Number of Dominant Taxa	6	6	25
% Dominant Taxa	17	30	41
% EPT Taxa	0	0	16
Habitat Score	75	65	99

trends do not appear to be related to habitat quality, but rather are caused by an increase in stream size and migration of fish from Spring River. There is no noticeable trend in the number of fish species that are intolerant to degraded water quality or habitat. Because metal tolerances are unknown and no samples could be taken upstream of the mine discharge, little can be inferred about the effect of the discharge on stream quality from a biological perspective.

The insect samples show an increase in number of Ephemeroptera, Plecoptera, and Trichoptera taxa (EPT) moving downstream. The presence of these three specific species should decrease with decreasing stream health (Table IV-2). There are no clear trends in changes in number of taxa and percent of the total number of individuals made up of the dominant taxon. Downstream of the mine discharge, the number of taxa decreases, while percent of insectivore species in the fish population, number of EPT taxa, and percent of dominant taxa increase. The EPT trend indicates increasing stream health, but the change in dominant taxa numbers indicates decreasing stream health. This could just be due to fluctuations of insectivores in the fish population and the increase in stream size. The data from BC6 was ignored because time constraints led to the collection of samples that are not representative of the community structure at that point.

The laboratory bioassay used a specific species of metal sensitive lettuce seeds to measure any toxic effects from metal contamination. The measured endpoint of the lettuce seed bioassay was root length of new shoots. The results of this experiment indicate decreased growth only at site BC5, the site directly after the discharge, with about the same amount of growth at all the other sites. For every site, both the pure sample and the 50% dilution showed about the same amount of growth; for all but BC5 the 25% dilution and the deionized water blank had less growth. This may be due to the fact that this portion of the stream is just downstream of a wastewater outfall, which contributes nutrients to the water, increasing plant growth.

V. Alternative Selection

Remediation technologies were identified to address three environmental pollution problems: stream water quality, chat contamination and soil contamination. A database of alternative remediation technologies was developed from extensive literature reviews, discussions with experts and best professional judgment. Eight potential technologies were identified for chat, seven technologies were identified for water, and five technologies were identified for soil (Table V-1 to V-3). Selection of the preferred technology for each problem area was based on three independent evaluation criteria: technical feasibility, economic viability, and social/political-acceptance. A composite index model was used to evaluate the alternatives (Canter 1996).

Importance weighting factors were assigned to each criterion as follows: technical feasibility (50%), economical viability (35%), and social/political acceptance (15%). A team scoring mechanism provided an objective procedure for selecting the preferred technologies. Each alternative technology was evaluated relative to each criterion and scored on a scale of 1 to 5 (1 = unacceptable, 2 = poor, 3 = fair, 4 = good, and 5 = excellent) by all team members. The average value was determined for each criterion and the appropriately weighted sums were calculated for each technology to provide the composite index value. The highest scoring technology for each problem area was selected as the preferred alternative. The preferred alternatives identified include passive treatment for water quality improvement, phytoremediation/revegetation for soil remediation, and cold-mix asphalt production for beneficial reuse of chat.

Water Quality

Passive treatment using constructed wetlands was identified as the preferred technology for improving water quality in Beaver Creek. Passive treatment systems rely on natural biogeochemical and ecological processes to ameliorate mine water pollution problems. They are solar-driven, ecologically-engineered ecosystems and therefore require limited energy input. These systems are often the utilized for mine water treatment at abandoned sites because they are relatively inexpensive, require limited operation and maintenance, and provide long-term treatment (Hedin et al. 1994). However, passive treatment systems do require relatively large land areas.

Common passive treatment technologies include aerobic wetlands, anoxic limestone drains, surface-flow compost wetlands, and vertical flow wetlands or SAPS (successive alkalinity producing systems). The types that will be considered for treatment of the mine discharges that flow into Beaver Creek are aerobic wetlands and vertical-flow wetlands.

Aerobic wetlands oxidize metals such as Fe and Mn through oxidation and hydrolysis processes. The rate of oxidation is controlled by the pH of the mine water and the amount of dissolved oxygen available. For acidic conditions ($pH < 4.5$) and low levels of dissolved oxygen, oxidation is controlled mainly by bacteria and can be relatively slow (e.g., days). Under alkaline conditions ($pH > 5.5$) and exposure to the atmosphere, the rate of oxidation is faster (e.g., seconds to minutes; Robb and Robinson, 1995).

When exposed to air, ferrous iron, Fe^{2+}, oxidizes to form ferric iron, Fe^{+3}. The reaction proceeds as follows:

$$Fe^{2+} + \frac{1}{4} O_2 + H^+ \Rightarrow Fe^{+3} + \frac{1}{2} H_2O \qquad \text{(V-1)}$$

Once this reaction takes place, ferric iron can hydrolyze to form a precipitate, iron hydroxide (FeOOH).

$$Fe^{+3} + 2\, H_2O \Rightarrow FeOOH + 3H^+ \qquad \text{(V-2)}$$

Table V-1. Evaluation of Remediation Alternatives for Beaver Creek

Water Quality Improvement Alternative	Technical Feasibility Pros	Cons	Score 0.50
Active treatment	Established, known technology Requires limited area Short water retention times Meet water quality standards	High capital and O&M costs Long term liability Sludge/chemical disposal necessary High energy needs Secondary pollution generated Possible over-treatment	2.80
Reactive barriers	Passive technology Low O&M	Requires substantial hydrogeological info. Long term liability Limited applicability Possible side-effects	2.00
Surface water diversions	Decreases impact on surface water No treatment required Possible use with other options Isolates problem	Past experience failed May change subsurface flow patterns Not a stand-alone option May increase flooding	1.00
Discharge plugging	Eliminates water flow No treatment required	Many variable and unknown locations May transfer problem elsewhere Past experience failed	1.00
Lowering groundwater table	Eliminates water flow No treatment required	High capital and O&M costs Long term and conmtinuous liability Substantial impacts to hydrogeology Subsidence possible Possible unexpected detrimental impacts Impact surface vegetation Large-scale application necessary	1.00
Alkaline injection	Possible use with other options Uses available resource Decreased impact to surface water	Substantial capital and O&M costs Long term liability Substantial impacts to hydrogeology Large-scale application necessary	3.20
Passive treatment	Natural biogeochemical processes No chemicals required Relatively inexpensive Sustainable and long-term solution Stand-alone or with other options low O&M No secondary waste generated May decrease flooding/erosion	Large land area may be required Long water retention times Sludge disposal may be problem Natural pests can effect treatment	4.60

Table V-1. (ontinued)

Water Quality Improvement Alternative	Economics	Score 0.35	Social/Political Acceptance	Score 0.15	Composite Index
Active treatment	High initial capital costs in millions High O&M costs in 100K-millions/yr Monitoring costs substantial	1.60	Not aesthetically pleasing Politically unfavorable costs and liability Social impacts are low	2.00	**2.26**
Reactive barriers	Capital- $300-$900/square foot Monitoring wells needed (@$20/foot) Some O&M costs	4.00	Questionable acceptance Academic interest/future research	4.40	**3.06**
Surface water diversions	Capital costs potentially huge ~$10 Million O&M costs ~$8500/yr	1.60	Politically unfavorable due to past failures Socially unfavorable due to past failures	1.80	**1.33**
Discharge plugging	Capital- $17,000-$42,000/well O&M costs ~$8,000/yr	3.20	Politically unfavorable due to past failures Socially unfavorable due to past failures	2.20	**1.95**
Lowering groundwater table	Very high capital costs for pumps, etc. High monitoring costs Very high O&M (electricity, etc.) ~$ 50 million capital and O&M costs	1.00	Politically unfavorable costs and liability Socially questionable Social liability high Possible health risk (subsidence)	1.00	**1.00**
Alkaline injection	Capital costs ~$10-25 million High O&M costs Chemical costs-$250,000/yr for fly ash	2.40	Potential political liability Socially acceptable	3.00	**2.89**
Passive treatment	Capital ~$20-$150,000/acre Limited O&M costs <$2,000/year Monitoring costs limited	4.80	Aesthetically pleasing Politically acceptable Community involvement high Research interests	4.80	**4.70**

Table V-2. Evaluation of Chat Remediation and Reuse Alternatives

Chat Reuse or Remediation Alternative	Technical Feasibility (50%)		
	Pros	**Cons**	Score
Hot Mix Asphalt	Waste becomes resource Encapsulate potential toxics Use ~80% material Decrease hazard	Current BIA moratorium Possible health hazard during size separation	4.00
Cold Mix Asphalt	Waste becomes resource Encapsulate potential toxics Use ~80% material Decrease hazard	Current BIA moratorium Possible health hazard during size separation	4.50
Concrete	Waste becomes resource Encapsulate potential toxics Use ~80% material Decrease hazard	Current BIA moratorium Possible health hazard during size separation Possible metal leaching	4.00
Engineering Fill	Waste becomes resource Encapsulate potential toxics Use ~80% material Decrease hazard	Current BIA moratorium Possible health hazard during size separation Possible metal leaching	4.00
Reinternment	Perhaps quickest solution Possible decreases hazard	Possible metal leaching Unpredictable consequences Displace mine water Possible health hazard during operation	1.00
Asphalt capping	Decrease hazard Decreased metal leaching	Increased runoff Possible health hazard during operation Loss of land use	1.00
Heap Leaching	Recovers resource from waste	Requires additional info. Possible health hazard during operation	3.00
Recontour/Revegetate	Proven technology Effective against erosion Decreased metal leaching Existing species may be used Possible phytoextraction	Leaves chat on surface May need soil capping Possible waste disposal requirements	3.50

Table V-2. (continued)

Chat reuse or Remediation Alternative	Economics (35%)	Score	Social/Political Acceptance (15%)	Score	Composite Index
Hot Mix Asphalt	Gain $1.10 / yd^3	4.00	Reduces hazard exposure Provides economic benefit Possibly offsets funding	4.50	**4.08**
Cold Mix Asphalt	Gain $9.50 /yd^3	4.00	Reduces hazard exposure Provides economic benefit Possibly offsets funding	5.00	**4.40**
Concrete	Gain &20.25 /yd^3	4.00	Reduces hazard exposure Provides economic benefit Possibly offsets funding	4.50	**4.08**
Engineering Fill	Cost $50.63/yd^3	3.00	Reduces hazard exposure Provides economic benefit Possibly offsets funding	4.50	**3.73**
Reinternment	Cost $5.63 /yd^3	1.00	Reduces hazard exposure Provides NO economic benefit	4.50	**1.53**
Asphalt capping	Cost $62.00 / yd^3	3.00	Possible recreational development	2.50	**1.93**
Heap Leaching	Market value for Zn is about $1000/ton. Market value for Pb is about $500/ton.	3.00	Provides economic benefit Possibly offsets funding	3.50	**3.08**
Recontour/ Revegetate	$60000/ha/30cm for standard addition of nutrients, and maintenance (Cost $3.78 /yd^3) $130000/ha for 60cm soil cap and revegetation (cost $4.09 /yd^3) $61.16/yd^3 for phytextraction.	4.00	Aesthetically pleasing Possible recreational development	4.00	**3.75**

Table V-3. Evaluation of Soil Remediation Alternatives

Soil Remediation and Revegetation Alternative	Technical Feasibility (50%) Pros	Cons	Score
Soil Washing	Commercially available	>50% sand and gravel needed	
	Proven technology for metals of concern	Additives may be problem	
	Modular, quick assembly plants	Off-site disposal of fines	
		Pretreatment for high humic content soils	2.80
Phytoremediation	Solar driven passive remediation	Limited to surface 3 feet	
	Faster than natural attenuation	Long time required	
	Few air and water emissions	Contaminant may enter food chain	
	Generates recyclable metal-rich residue	Regulatory unfamiliarity	
	Minimal environmental disturbance	Requires large surface area	
	Applicable to large areas	Impacted by environmental conditions	
	Reestablishes vegetative cover		
	Suited for metal contamination		5.00
Excavation and Disposal	Removes contaminated material	No treatment	
	Eliminates hazard	Transfers problem to new location	
		High transport costs	1.20
Asphalt Stabilized Base/Engineered Backfill	Stabilizes contaminated soil (non-leaching)	Optimum moisture must be obtained	
	Fast treatment rate		
	w/<30% aggregate, engineered backfill		
	w/>30% aggregate, stabilized base		4.40
Electrokinetic Remediation	Commercially available	Many factors reduce effectiveness	
	In-situ technology	Periodic probe washing necessary	
		High energy requirement (500kw-h/m3)	
		104-124 days to remediate 1 ton samples	2.20
Recontour/Revegetate	Proven technology	Leaves soil in place	
	Effective against erosion	May need soil capping	
	Decreased metal leaching		
	Existing species may be used		
	Possible phytoextraction		5.00

Table V-3. (continued)

Soil Remediation and Revegetation Alternative	**Economics (35%)**	**Score 0.35**	**Social/Political Acceptance (15%)**	**Score**	**Composite Index**
Soil Washing	$136-$226/ton High O & M	2.60	Dust generation, noise, air emissions Potential health hazard Questional performance	1.20	**1.40**
Phytoremediation	Relatively inexpensive $60,000 to $100,000/acre Limited O & M	4.00	(+) High public acceptance Creates park-like aesthetic Provide wildlife habitat	4.80	**4.62**
Excavation and Disposal	$40,000/acre Very expensive	1.80	(+) Removes the waste from the site	3.20	**1.08**
Asphalt Stabilized Base/Engineered Backfill	$30-$45 per ton High O&M	4.00	(+) Provides product	4.00	**4.20**
Electrokinetic Remediation	$50/m3 ~$10/ton/month	3.60	(+) Treats contamination	3.40	**2.87**
Recontour/Revegetate	$0.06/yd2	5.00	Aesthetically pleasing Possible recreational development	5.00	**5.00**

The rate of this reaction depends on the pH of the mine water. The hydrolysis and oxidation reactions will in fact occur at very rapid rates as pH increases. (Hedin, et al., 1994) The net reaction for Fe is shown below.

$$Fe^{2+} + \frac{1}{4} O_2 + 3/2\ H_2O \Rightarrow FeOOH + 2H^+ \qquad \text{(V-3)}$$

These reactions contribute acidity and decrease pH due to the production of H^+ ions. The oxidation and hydrolysis of other metals such as Mn, Pb, Zn, and Cd may also add acidity.

$$Mn^{2+} + \frac{1}{4} O_2 + 3/2\ H_2O \Rightarrow MnOOH + 2H^+ \qquad \text{(V-4)}$$

Due to acidity from metal hydrolysis and from proton acidity, some mine waters have been found to have depressed pH levels < 4.5. Mine waters with pH levels >4.5 may have measurable alkalinity, and thus acid neutralizing capacity. In these waters (like those in Beaver Creek), therefore, the protons produced by metal hydrolysis are neutralized. In the pH range of 5.0-8.0, the principal source of alkalinity in mine waters is bicarbonate ion (HCO_3^-) (Hedin et al., 1994).

The mine waters that discharge into Beaver Creek are net alkaline waters based upon the alkalinity and acidity measurements. Fe and Mn can be removed in the aerobic system through hydrolysis and oxidation. Production of alkalinity is not necessary because the mine waters are net alkaline. The main driving force for successful treatment in an aerobic treatment is oxygen. The design of the aerobic system will include features that can increase the amount of oxygen in the system, such as windmills to enhance aeration. The system will be sized based on empirically-derived Fe removal rates found in Hedin et al. (1994).

Removal of Pb, Zn and Cd in the mine waters discharging to Beaver Creek can be achieved using a vertical-flow wetland system. Successful treatment in vertical-flow wetlands involves bacterial sulfate reduction. Sulfate reduction processes increase pH levels, which further aids in the treatment of mine drainage. Flooding of organic substrates such as spent mushroom compost, sawdust, different manures or mixtures thereof, provide the necessary conditions for this process. Certain bacteria reduce sulfate (SO_4^{2-}) in the mine water, which will produce hydrogen sulfide (H_2S) and bicarbonate (HCO_3^-). The H_2S produced will then form heavy metal sulfides, such as zinc sulfide, which will precipitate.

$$2CH_2O + SO_4^{2-} \Rightarrow H_2S + 2\ HCO_3^- \qquad \text{(V-5)}$$

$$Zn^{2+} + H_2S \Rightarrow ZnS + 2H^+ \qquad \text{(V-6)}$$

The formation of metal sulfides is a net neutral reaction because it results in the production of 2 moles each of bicarbonate and hydrogen ion. However, degassing of H_2S provides a net gain of alkalinity. The rate of removal as sulfide compounds is dependent on pH, solubility product of the metal, and the concentrations of the reactants (Hedin, et al., 1994). The reactions of sulfide with Pb, Cd, and Zn are more likely to occur than the hydrolysis reactions of these metals, in part because the chemical kinetics for such reactions are more favorable. Based on analysis of solubility products, Hedin et al. (1994) found the first metal sulfide that will form is PbS, then ZnS, followed by CdS.

Beaver Creek Passive Treatment System Design

The proposed passive treatment system will consist of three wetland cells (Figure V-1. Cell 1 is a surface flow aerobic wetland designed to remove Fe (Figure V-2). The size of the cell is based on the mass loading of the Fe from the discharge and published Fe removal rates of 20 g $m^{-2}day^{-1}$ (Table 1; Hedin et al., 1994). The required area for cell 1 is 124 m^2 (0.03 acres). However, to prevent drying out of the cell during the summer, a larger area of 0.1 acre is recommended to retain more water. The depth of the cell will be approximately 1 meter to provide for long-term accumulation of FeOOH. A windmill, such as that used in aquaculture processes, will be placed in the cell to increase the rate of aeration, and thus iron oxidation and subsequent hydrolysis. Also, aquatic vegetation will be planted in the cell to produce additional oxygen, act as physical barriers to enhance precipitation and provide wildlife habitat. The water flowing into the cell will be completely gravity fed and the flow between cells will be maintained by head differences. Berms will be constructed on the interior to contain the mine waters. Additional berms on the exterior of the cell will to prevent surface runoff from entering the cell. The exterior berms will be above the 100-year floodplain elevation so that the treatment system will not contribute to, or be affected by, flooding. The slope of the berms will be 2:1 (horizontal to vertical). Discharge from the Cell 1 will flow directly into Cell 2.

Cell 2 is designed as a vertical flow wetland to remove Pb, Cd, and Zn. The size of the wetland is based on Pb, Cd, and Zn removal rates of 0.2, 0.7, and 1 $gm^{-2}day^{-1}$, respectively. The mass loading from the discharge is divided by the removal rate to give an area (Table V-4). In a vertical flow system, the removal rate of Zn is slow compared to Pb and Cd. In order to optimize removal of all three metals, the size of the system was based on Zn removal rates. The required area for this cell is 412 m^2 (0.1 acre).

This cell will be constructed of three layers of media (Figure V-3). The surface layer will consist of 1-1.5 meters of standing water, designed to provide for sufficient hydraulic head to drive the water through to the bottom of the vertical-flow system.Layer two is designed to encourage metal sequestration by means of metal sulfide formation via bacterial sulfate reduction, organic complexation and carbonate formation. Spent mushroom substrate (SMS) will be used as

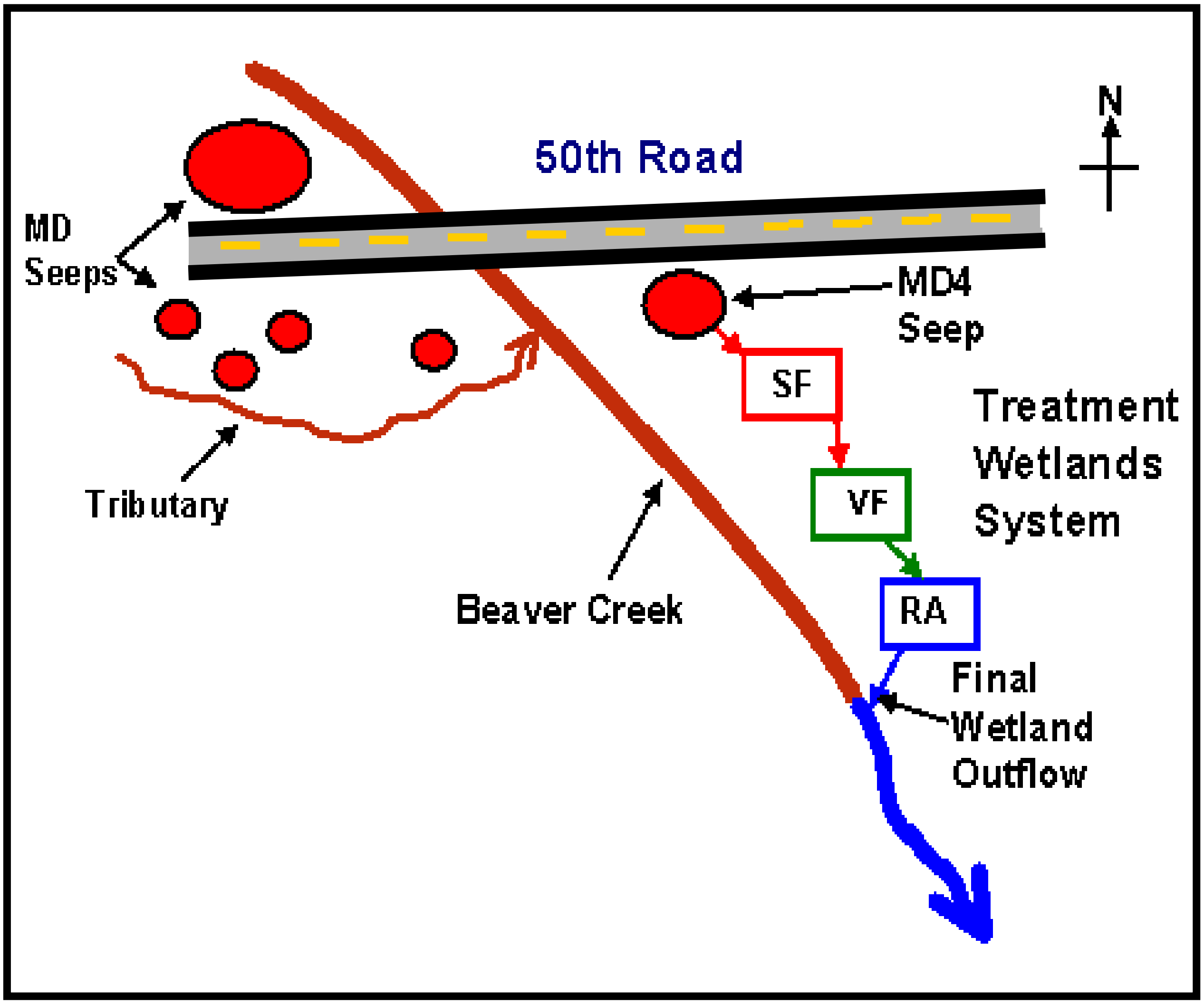

Figure V-1. Schematic Diagram of Passive Treatment System

the organic substrate and will be mixed with limestone (LS) as a means to encourage percolation through the system. SMS is the most common substrate used in mine drainage treatment wetlands in Appalachian coal fields and has been used successfully at a coal mine drainage treatment wetland in Southeastern, OK (Nairn et al., 2000). The ratio of SMS to LS will be 2:1 by volume. SMS can be obtained locally from J&M Farms in Miami, OK and limestone can be obtained from nearby quarries.

Layer three serves as a drainage layer consisting of limestone to act as a permeable layer to transmit the water through underdrain pipes to the Cell 3. Berms will be designed in the same manner as Cell 1with slopes of 2:1.

Cell #3 (Figure V-4) is a surface flow aerobic wetland designed to aid in the reaeration of the water to remove hydrogen sulfide (H_2S) gas produced in Cell 2. The size of this wetland is based on an oxygen transfer rate of 4.5 mg L^{-1}at 20 ^oC (Table V-4). The recommended area for cell 3 is 444 m^2 (0.1 acre). The berms for Cell 3 are designed in the same manner as Cell 1, with slopes of 2:1. The main difference between Cell 1 and Cell 3 is that Cell 3 will utilize aquatic vegetation beds to increase the rate of oxygen transfer in lieu of the mechanical windmill system. The effluent from Cell 3 will be discharged to Beaver Creek.

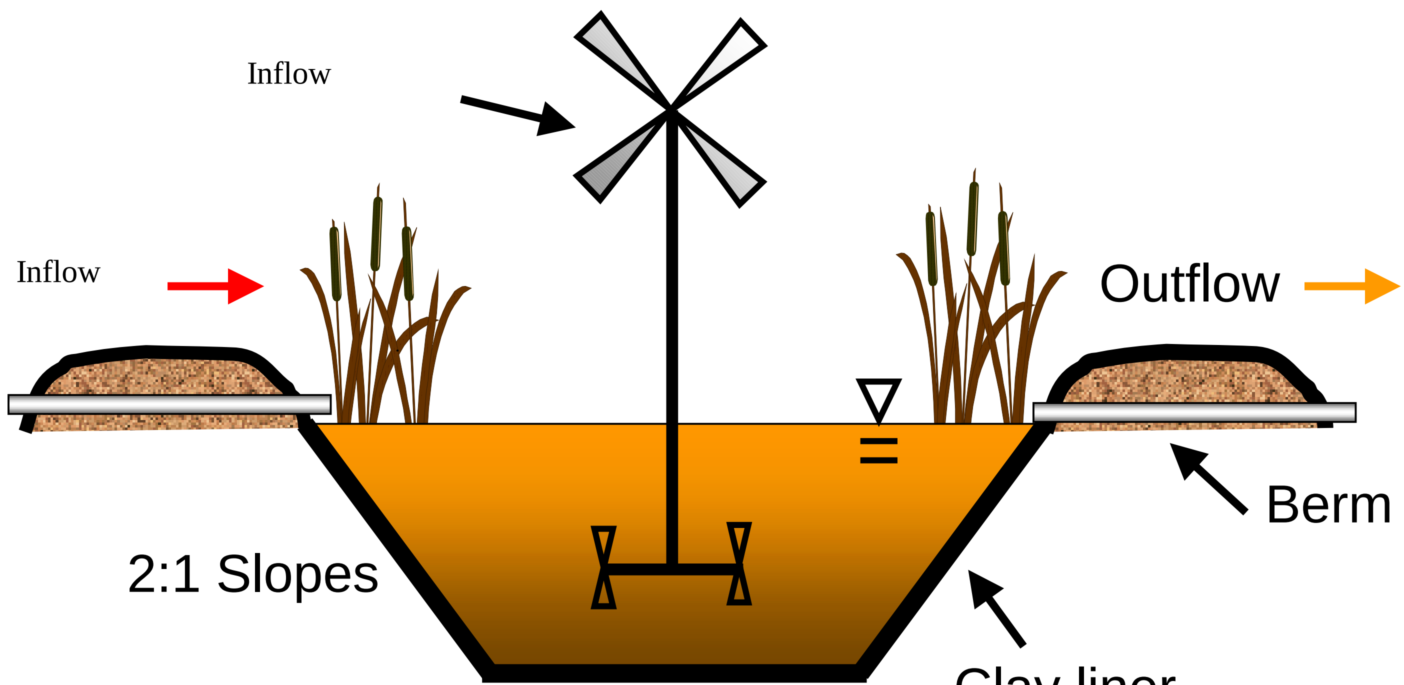

Figure V-2. Surface Flow Aerobic Wetland

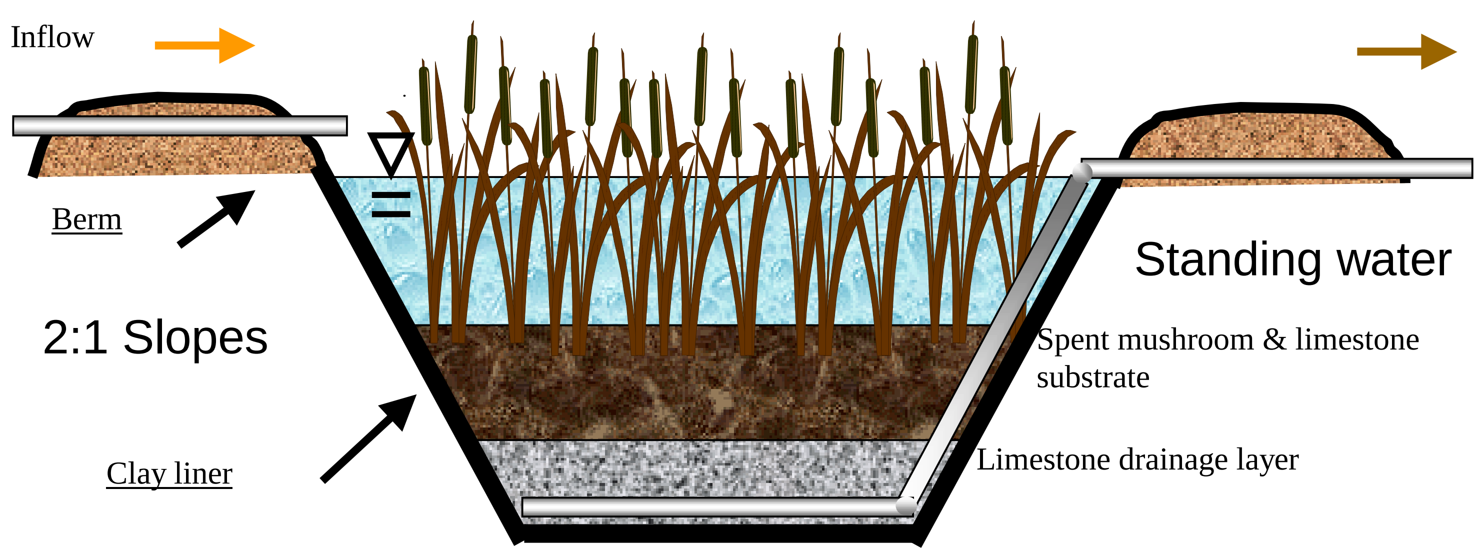

Figure V-3. Vertical Flow Wetland

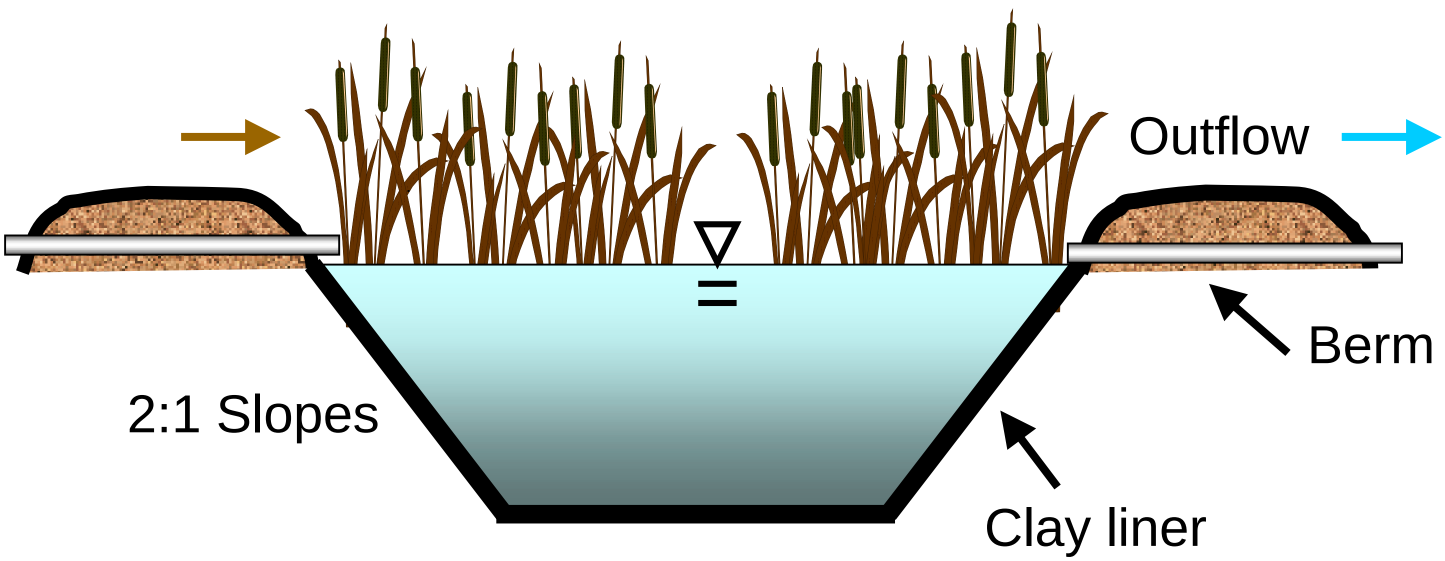

Figure V-4. Surface Flow Aerobic Wetland

Table V-4: Design Parameters for Sizing Passive Treatment Cells

Parameter	Cell	Mass Loading (g day^{-1})	Sizing Rate (g m^{-2} day^{-1})	Required Area* (m^2)	Required Area* (Acres)
Iron	1	2475	20	124	0.03
Zinc	2	412	1.0	412	0.1
Cadmium	2	12	0.7	18	---
Lead	2	10	0.2	54	---
Oxygen	3	2000	4.5	444	0.1

***Areas were calculated for Fe and Zn removal in Cells 1 and 2, respectively (assuming simultaneous removal of Cd and Pb), and for oxygen addition in Cell 3.**

The employment of a passive system for the treatment of mine discharges can be an inexpensive and effective alternative. Passive systems such as surface flow aerobic wetlands and vertical-flow wetlands are currently being used for mine drainage treatment and have proven to be a very efficient in treating metal-rich waters (Skousen, 1998; Nairn et al, 2000; and Hedin etal., 1994). However, in order to successfully treat the discharge water that flows into Beaver Creek, discharge measurements and water quality data must be collected for a period of at least one water-year. This information is essential in determining the seasonal variations in the mine upwellings that impact Beaver Creek. By treating most of these discharges, the water quality of Beaver Creek will improve substantially. However, it may not feasible to treat all of the mine discharges that impact the creek because some of impacts occur due to upwellings in the streambed.

With proper design and maintenance, the proposed treatment systems will continue to work for a long period of time. Passive treatment can be used as a long-term solution for many types of mine drainage and at a much lower cost than traditional active treatment (Skousen, et al., 1998). Additional technical considerations for designing a treatment wetland are other characteristics of the water being treated, performance capabilities, design, operation and maintenance costs, discharge rates, and environmental factors (Kadlec and Knight, 1996). Over the lifetime of the proposed systems, monitoring must be conducted to determine system

performance. The design principles used here may also be applied to areas in the Tar Creek watershed, such as the high volume discharges near Commerce, OK.
The cost estimate for constructing wetlands treatment systems is outlined in Table V-5. Preliminary cost estimates were developed for the system designed to treat discharge from MD4 as discussed above. However, in order to effectively mitigate the water quality problems in the Beaver Creek watershed upstream of the Catholic 40, all six mine drainage discharge sites will have to be addressed (Figure V-1). The figures in Table V-2 reflect total costs for constructing wetland treatment systems to treat all six mine drainage discharges.

Table V-5. Cost Estimate for Constructed Wetlands Treatment Systems

CATEGORY	ITEM	QUANTITY	UNIT COST	COST	TOTALS
Capital Costs	Windmill	1	$20,000 ea	$20,000	
	Substrate materials	5000 lbs	4/lb	$200,000	
	Piping & control structures		$20,000	20,000	
	Land acquisition	5 acres	$10,000/acre	$10,000	
Labor	Excavation and installation	5 acres	$100,000	$100,000	
Subtotal					$350,000.00
Maintenance	10 years	10 years	$1,200/yr	$12,000	$12,000.00
TOTAL					$362,000.00

Chat

The remediation alternative for addressing the chat materials is a series of integrated processes that will ultimately allow for beneficial use of the chat in an environmentally sound manner. The on-site chat materials will first be excavated and stockpiled in engineered windrows. These engineered stockpiles will be oriented parallel to the predominant wind direction to minimize wind erosion and control offsite migration of the fine (i.e., respirable) particles. The windrows will be contoured to control runoff, revegetated to minimize erosion, and contain interior leachate collection systems (see Figure V-5). All surface runoff and leachate collected will be directed to an asphalt lined detention basin. The fluids collected in the detention basin will be used to irrigate the vegetative cover of the windrows on an as needed basis.

After stabilizing the engineered windrows and establishing a vegetative cover, the materials within the windrows can be size separated to produce commercial grade aggregate. Chat particles will be separated into the hazardous (<0.425 mm) and non-hazardous (>0.425mm) size fractions. It is envisioned that initially the hazardous small size fraction will not be utilized for commercial purposes. These materials will simply be placed back into stockpiles and re-vegetated. Technologies for economically extracting the metals contained in these materials are not currently available. If ongoing research does not lead to development of viable extraction technologies in the future, these materials could ultimately require disposal in a secured landfill.

The commercial grade aggregate extracted from the engineered windrows does not represent a health threat and could be safely used in a variety of beneficial products. Some of the beneficial use products investigated for this project are concrete, asphalt, and engineered fill material. It was assumed that all of the processed aggregate could be used on-site to manufacture asphalt.

Chat Products

Samples of the chat material from the Catholic 40 site were used in formulating mix designs for concrete, asphalt, and engineered fill. Mix designs were developed using test specimens from chat composite sample #1. Each of the various mix designs was tested for engineering properties (e.g., compressive strength, etc.). Specimens from the optimal mix design for each product were then submitted for analysis of total and TCLP metals.

Figure V-6 shows the total metals content of the chat material before (composite sample #1) and after incorporation into mixes for asphalt and concrete. It is interesting to note that the asphalt mix formulation is dramatically lower in total zinc concentration than the native material or the concrete sample, even though the same chat materials was used for all three samples. It appears that the hot-mix encapsulation process has affected the zinc content of the chat material. More testing is needed to verify this phenomenon.

Figure V-7 shows the TCLP metals in the chat material and in the asphalt and concrete product. It is readily apparent that encapsulation in asphalt or concrete binds up the heavy metals within the chat. Both of the product test specimens passed the TCLP leachability criteria for heavy metals.

It is important to note that the test specimens depicted in Figures V-6 and V-7 contained whole samples from composite #1, i.e., the chat was not size separated prior to being incorporated into the mix. This information indicates that the chat is safe for use in engineered materials such as concrete and asphalt. However, it is important to note that processing of the chat material for use in engineered products will dramatically increase the potential for mobilizing the hazardous size fraction, both through air entrainment and leaching. Proper safety precautions, including the use of personal protective equipment and periodic health screening will need to be utilized at all facilities handling the chat material.

The cost estimate for the chat remediation and reuse activities is depicted in Table V-6. Cost estimates are provided for each of the three major phases of chat remediation and reuse (i.e., engineered stockpiles, aggregate production, asphalt manufacturing). The overall cost for total remediation and reuse of the chat materials on the Catholic 40 is approximately $30 per cubic yard. It is important to note that the total cost figures in Table V-6 do not include any revenues produced from the sale of aggregate and/or asphalt. These revenues could partially offset the cost of remediation.

Soils

The selected remediation technologies for addressing the elevated zinc (Zn), cadmium (Cd), and lead (Pb) concentrations in the soils at the Catholic 40 are re-vegetation and phytoremediation. Re-vegetation measures will be integrated into the overall plan for addressing the chat materials (i.e., re-contouring, engineered piles, leachate and runoff control). Re-contouring and re-vegetating the surface materials of the Catholic 40 will control dust, stabilize erodible slopes, and increase the aesthetic value of the area.

Phytoremediation is a technology that uses plants to extract toxic compounds from contaminated soil. Certain plants have the ability to tolerate high concentrations of heavy metals in their plant tissue. A plant that grows in the presence of heavy metals can often accumulate up to 5% of its biomass in metals. This technology is suited for those sites having soil contamination within 3 meters of the soil surface (Schnoor et al., 1995). Hence, phytoremediation can simply be incorporated into the revegetation measures. Table V-7 includes the cost estimate for re-vegetating the soils at the Catholic 40.

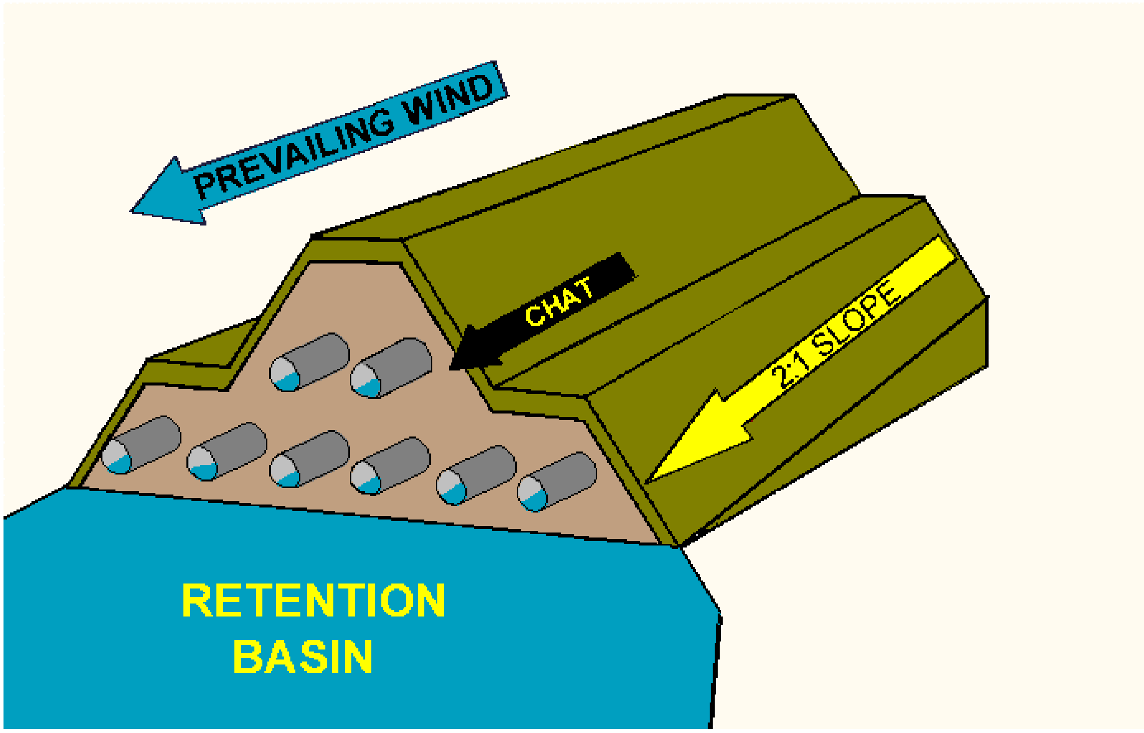

Figure V-5. Engineered Chat Stockpile and Retention Basin

Cost and Revenue Estimates

The overall cost and revenue estimates for remediation activities at the Catholic 40 site is depicted in Table V-8. The initial cost to implement the remediation and reuse technologies described above is approximately $2.3 million. Annual maintenance costs are estimated to be around $5000.

The costs for remediating the Catholic 40 site could be partially offset by revenues generated from the sale of commercial grade aggregate and/or asphalt. It is projected that the chat materials on the Catholic 40 site could produce over 70,000 tons of commercial grade aggregate. Assuming that two tons of cold mix asphalt can be produced from each ton of aggregate yields a total asphalt production of approximately 140,000 tons. Current market prices for asphalt materials are on the order of $25/ton, which results in total revenues of $3.5 million.

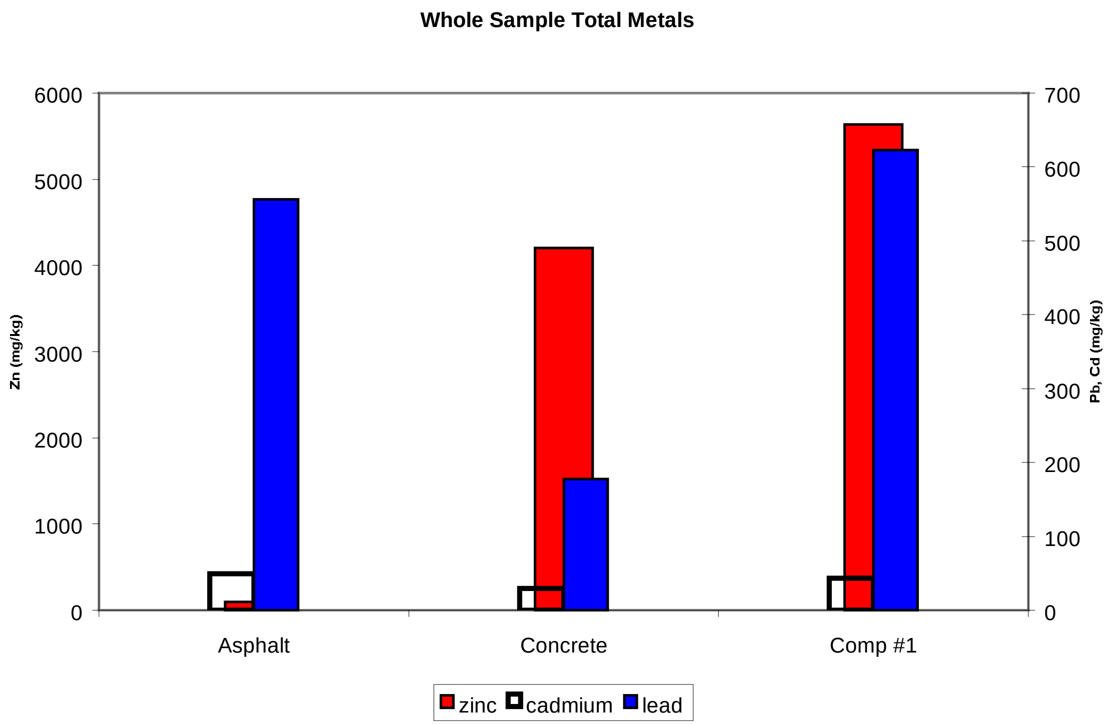

Figure V-6. Total Metals in Chat Products

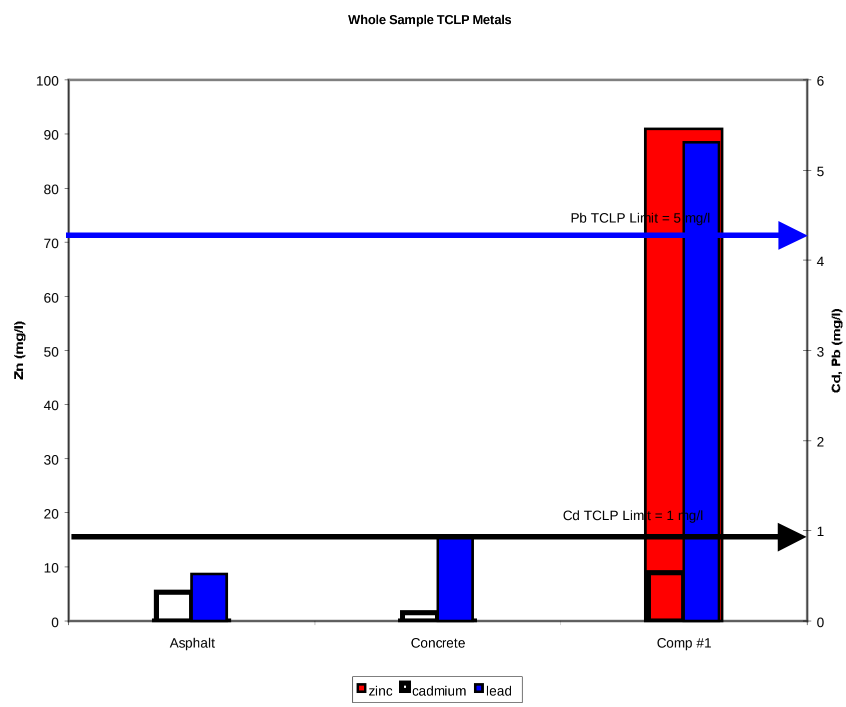

Figure V-7. TCLP Metals in Chat Products

Table V-6. Cost Estimate for Remediation and Reuse of Chat on the Catholic 40

CATEGORY	ITEM	QUANTITY	UNIT COST	COST	TOTALS
Moving chat material into engineered stockpiles	Excavate and transport on-site to stockpiles	65,000 cy	$1.60/cy	$104,000	
	Re-vegetate using hydromulch with solar-powered irrigation		$.15	$9,750	
Construct asphalt lined runoff retention basin	300' x 300' x 8" thick asphalt liner; asphalt @13 ft^3/ ton = 4500 tons	4500 tons	$20.00/ton	$9,000	
Chat Subtotal					$122,750.00
Produce commercial grade aggregate	Size separate aggregate from stockpiles	65,000 cy	$2.50/cy	$162,500	
Aggregate Subtotal					$162,500.00
Manufacture asphalt	Process on-site aggregate	72,000 tons	$22.50/ton	$1,620,000	
Asphalt Subtotal					$1,620,000.00
Maintenance	10 years	120 months	$200/mo.	$24,000	$24,000.00
TOTAL					$1,929,250.00
AVERAGE REMEDIATION COST ($/cy)					$29.68

Table V-7. Cost Estimate for Soil Revegetation at the Catholic 40

CATEGORY	ITEM	QUANTITY	UNIT COST	COST	TOTALS
Capital and Labor	Re-contouring and grading	10 acres	$1000/acre	$10,000	
	Revegetate	10 acres	$300/acre	$3000	
Subtotal					$13,000.00
Maintenance	10 years	10 years	$1,200/yr	$12,000	$12,000
TOTAL					$25,000.00

Table V-8. Total Costs for Remediation and Reuse Activities at the Catholic 40 Site

COST CATEGORY	COMPONENT	COSTS	TOTALS
Capital and Labor	Stockpile chat materials	$122,750	
	Aggregate production	$162,500	
	Manufacture asphalt	$1,620,000	
	Construct wetlands systems	$350,000	
	Soil remediation/revegetation	$13,000	
TOTAL CAPITAL COSTS			$2,268,250.00
Annual Maintenance	Chat remediation	$2400/yr	
	Wetlands systems	$1200/yr	
	Soil revegetation	$1200/yr	
TOTAL ANNUAL COSTS			$4,800.00

References

Adgate, J. L., R. D. Willis, T. J. Buckley, J. C. Chow, J.G. Watson, G. G. Rhodes, and P. Lioy, "Chemical Mass Balance Source Apportionment of Lead in House Dust", Environmental Science and Technology, Vol. 32, No. 1, 1998, pp. 7.

Aggus, L.R., L.E. Vogele, W.C. Rainwater and D.I. Morais. 1983. "Effects of acid mine drainage from Tar Creek on fishes and macroinvertebrates in Grand Lake, Oklahoma", National Reservoir Research Council, U.S. Fish and Wildlife Service, Fayetteville, AR. 100 pp.

American Public Health Association, American Water Works Association, and Water Environmental Federation, Standard Methods for the Examination of Water and Wastewater, 19th ed., 1995.

Canter, L.W., Environmental Impact Assessment, 2nd ed., McGraw-Hill: 1996.

Carroll, S.A., P.A. O'Day and M. Piechowski, 1998, "Rock-water interactions controlling zinc, cadmium and lead concentrations in surface waters and sediments, U.S. Tri-State Mining District. 2. Geochemical Interpretation", Environmental Science and Technology , 32:956-965.

Centers for Disease Control, "Preventing lead poisoning in young children", A Statement by the Centers for Disease Control, Atlanta, GA: Centers for Disease Control, 1985 (CDC Report Number 99-2230).

Community Health Action & Monitoring Program, "Final Report: CHAMP Program – Ottawa County, Oklahoma Towns of Picher, Cardin, and Quapaw", July 1996 – June 1997", 1997.

Friberg, L., Nordberg, G.F., Kessler, E. and Vouk, V.B. (eds.), Handbook of the Toxicology of Metals, 2nd ed. Vols I, II, Amsterdam: Elsevier Science Publishers B.V., 1996.

Gibson, D. J., "Plant Communities and the Potential for Ecotypic Differentiation on Lead and Zinc Mine Spoils in Northeastern Oklahoma", M.S. Thesis, University of Oklahoma, Norman, OK, U.S. 1981a.

Gibson, D., "The Natural Revegetation of Lead/Zinc Mine Spoil in Northeastern Oklahoma", M.S. Thesis, University of Oklahoma, Norman, OK, U.S. 1981b.

Gosselin, R.E., Smith, R.P., Hodge, H.C., Clinical Toxicology of Commercial Products. 5th ed. Baltimore: Williams and Wilkins, 1994.

Hedin, R. S., Nairn, R.W., Kleinmann, R.L.P., Passive Treatment of Coal Mine Drainage, United States Department of the Interior, Bureau of Mines, 1994.

Kadlec, R. H. and Knight, R. L., Treatment Wetlands. Lewis Publishers: New York, 1996.

Luza, K.V., “A study of stability problems and hazard evaluation of the Oklahoma portion of the Tri-State Mining Area”, U.S. Bureau of Mines Mining Research Contract Report J0100133, 1983, 147 pp.

McKnight. E.T. and R.P. Fischer, “Geology and ore deposits of the Picher field, Oklahoma and Kansas”, U.S. Geological Survey Professional Paper 588, 1970, 165 pp.

Nairn, R.W., Mercer, M.N., Lipe, S.A., “Alkalinity Generation and Metals Retention in Vertical-Flow Treatment Wetlands”, Draft Submitted for Publication to ASSMR proceedings, 2000.

Perkin-Elmer Corporation, Atomic Absorption Spectroscopy Analytical Methods, 1996, pp. 300.

Reed, E.W., S.L. Schoff, and C.C. Branson, “Ground-water resources of Ottawa County, Oklahoma”, Oklahoma Geological Survey Bulletin 72, 1955, 203 pp.

Robb, G. A., and Robinson, J. D. F., “Acid drainage from mines”, The Geographical Journal, Vol. 161, No. 1, 1995, pp. 47-55.

Robbins, S.L., Cotran, R.S. and V. Koumar, Pathological Basis for Disease, WB Saunders, Philedalphia, 1989, pp. 490-550.

Schnoor, J.L., Licht, L.A., McCutcheon, S.C., Wolfe, N.L., and Carreira, L.H., “Phytoremediation of Organic and Nutrient Contaminants”, Environmental Science and Technology, Vol. 29, No. 7, 1995, pp. 318a-323a.

Skousen, J., Rose, A., Geidel, G., Foreman, J., Evans, R., Hellier, W., and members of the Avoidance and Remediation Working Group of the Acid Drainage Technology Initiative, Handbook of Technologies for Avoidance and Remediation of Acid Mine Drainage. The National Mine Land Reclamation Center: Morgantown, WV. 1998.

Spruill, T. B., “Assessment of Water Resources in Lead-Zinc Mined Areas in Cherokee County, Kansas and Adjacent Areas”, United States Geological Survey Water-Supply Paper 2268, United States Government Printing Office, WA, 1987.

Tulsa Tribune, “Zinc Field Figures Recalled”, October 19, 1976.

USEPA, “Health Assessment Document: Cadmium”, EPA-600/8-81-023, 1981, pp. 1-11.

USEPA, “Methods for the Chemical Analysis of Water and Wastes”, EPA/440/4-90/003, 1983a, Environmental Monitoring and Support Laboratory, Cincinnati, OH.

USEPA,“NPL Site Narrative at Listing Tar Creek (Ottawa County), Oklahoma”, U.S. EPA, Office of Emergency and Remedial Response, 1983b, 3 pp.

U.S. Environmental Protection Agency, ”Tar Creek Superfund Site Fact Sheet”, U.S. EPA, Office of Emergency and Remedial Response, 1997a.

U.S. Environmental Protection Agency, “Record of Decision, Residential Areas Operable Unit 2, Tar Creek Superfund Site, Ottawa County, Oklahoma”, U.S. EPA, Region VI, Dallas, TX, 1997b 59 pp.

U.S. Environmental Protection Agency, "EPA National Priorities List Narrative: Tar Creek (Ottawa County), OK", U.S. EPA, Office of Emergency and Remedial Response, 1999, 3 pp.

Weidman, S., Williams, C.F., and Anderson, C.O., "Miami-Picher Zinc-Lead District", University of Oklahoma Press, Norman, OK, 1932.