

INITIAL EVALUATION OF A LARGE MULTI-CELL PASSIVE TREATMENT SYSTEM FOR NET-ALKALINE FERRUGINOUS LEAD-ZINC MINE WATERS¹

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Abstract: Artesian discharges of net-alkaline, ferruginous waters from abandoned underground lead-zinc mines cause considerable surface water degradation at the Tar Creek Superfund Site, part of the historic Tri-State Mining District of Oklahoma, Kansas and Missouri. At the study site, perennial borehole discharges have flowed unabated for almost 30 years and considerably degraded the physical, chemical, and biological integrity of a first-order tributary to Tar Creek. Based on a comprehensive water quality and quantity characterization study, a large multi-cell passive treatment system was designed to receive approximately 1000 L/minute of mine water flowing from these abandoned boreholes (pH 5.95±0.06, total alkalinity 393±18 mg/L CaCO₃, total acidity 364±19 mg/L CaCO₃, Fe 192±10 mg/L, Zn 11±0.7 mg/L, Cd 17±4 ug/L, Pb 60±13 ug/L and As 64±6 ug/L). The passive treatment system (~ 2 ha total surface area) includes an initial oxidation pond followed by parallel treatment trains consisting of aerobic wetlands, vertical flow bioreactors, re-aeration ponds, and horizontal-flow limestone beds. Waters from the parallel trains are recombined in a polishing wetland prior to final discharge. In the first year of operation, mean final effluent waters had pH >7, were net alkaline and contained < 1 mg/L total Fe and < 0.1 mg/L total Zn, and had concentrations of Cd, Pb and As below detectable limits. The treatment system is successfully removing nearly 107 kg Fe/d, 5 kg Zn/d, 42 g Pb/d, 11 g Cd/d and 38 g As/d and is addressing approximately 20% of the contaminant mass loading from artesian mine pool discharges in the Tar Creek watershed.

Additional key words: hard rock mining, metal mining, acid mine drainage, natural treatment systems

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Introduction

Abandoned hard-rock mine sites pose considerable ecological and human health risks (USEPA 2004; Limerick et al. 2005) and ground and surface water contamination is often a major concern at these locations. Contaminated mine drainage is characterized by elevated concentrations of metals (Fe, Zn, Cd, Pb, Cu, Ni, Mn, Al, etc.), acidity, and sulfate (e.g., Younger et al. 2002). Relatively laborious and cost-intensive active treatment technologies are not viable options for most abandoned mines (e.g., Younger et al. 2002; Watzlaf et al. 2004). However, passive treatment technologies relying on natural biogeochemical, physical, and microbiological processes may provide viable, relatively low-cost and more sustainable alternatives to traditional technologies. This paper describes the initial evaluation of an innovative passive treatment system designed to treat abandoned ferruginous Pb-Zn mine waters at the Tar Creek Superfund Site, part of the historic Tri-State Mining District. The multi-cell system is the first application of any full-scale mine water treatment at this Superfund site and in the Mining District (Fig. 1).

Significant quantities of Pb and Zn were produced from the Tri-State Mining District from the 1890s through the 1960s. By the early 1970s when mining ceased, almost two million tons of Pb and nine million tons of Zn had been produced (McKnight and Fischer 1970). Due to extensive degradation of land and water resources and resulting risks to human and ecological health, the Tar Creek Superfund Site (representing the Picher Mining Field and the Oklahoma portion of the Mining District) was proposed for the Comprehensive Environmental Response, Compensation and Liability Act (Superfund) National Priorities List in 1981 and received final listing in 1983 (USEPA 2010a).

During mining, large capacity dewatering operations pumped approximately $50,000 \text{ m}^3 \text{ d}^{-1}$ of water from the mines (Reed et al. 1955). Upon decline and cessation of mining, groundwater began to accumulate in the mine voids. By late 1979, metal-rich waters began to discharge via artesian pressure into Tar Creek and its tributaries. The first documented discharges of mine drainage were at a location near southeast Commerce, OK (Oklahoma Water Resources Board 1983) and were subsequently identified for passive treatment implementation (Nairn et al. 2009). These discharges, containing elevated Fe, Zn, Cd, Pb and As concentrations, represent about one-fifth of the contaminant mass loading from artesian discharges in the watershed.

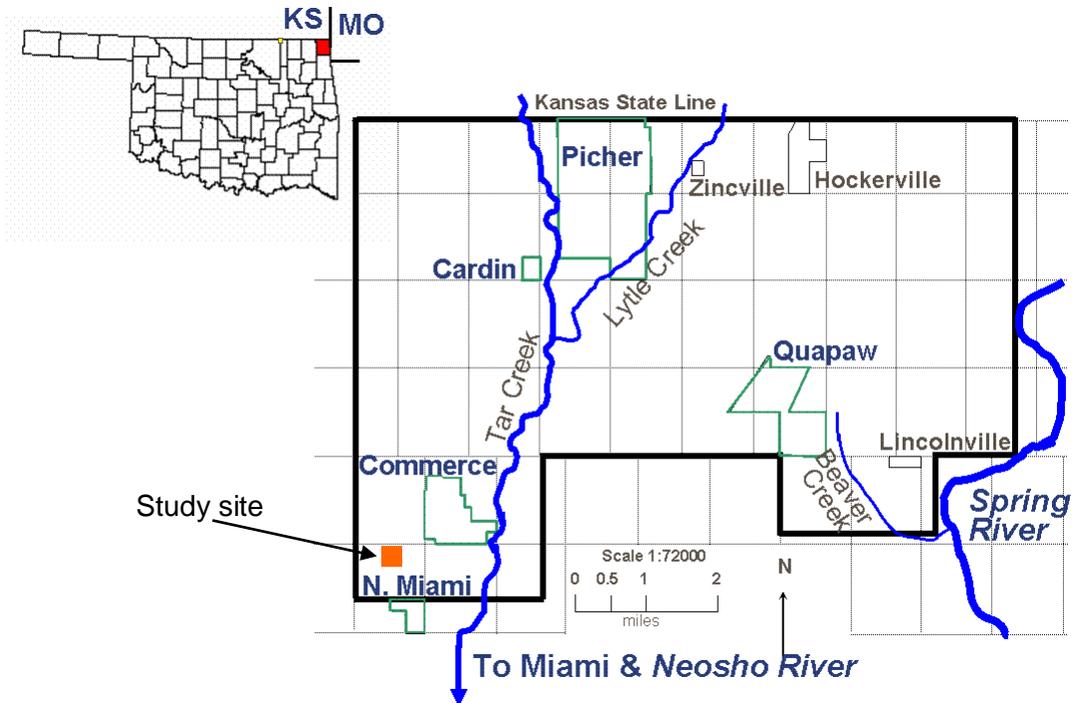


Figure 1. Schematic diagram of the Tar Creek Superfund Site, OK showing location of study site; inset state map of Oklahoma shows location of Ottawa County.

Methods

Study Site

Periodic water quality and quantity data collection efforts at the study site began in 1998, with regular monthly sampling beginning in 2004 and continuing to the present. This area of the Tar Creek Superfund Site has a limited amount of waste rock and tailings impacts but substantial influence from artesian mine drainage discharges. The targeted discharges have circum-neutral pH (5.96 ± 0.06), total alkalinity of 405 ± 13 mg/L as CaCO_3 and combined flow rates of up to 1000 L/minute. Metals and sulfate concentrations are elevated above expected levels (Table 1).

Design and construction of the passive treatment system was reported by Nairn et al. (2009) and is summarized in Fig. 2 and Table 2. The system consists of ten distinct process units including two parallel trains. Waters from three discharges (SA, SB, and SD) flow into an initial oxidation pond (1), followed by parallel surface-flow aerobic wetlands/ponds (2N and 2S), vertical-flow bioreactors (3N and 3S), re-aeration ponds (4N and 4S), horizontal-flow limestone beds (5N and 5S), and are recombined in a single polishing pond/wetland (6). Each process unit is designed to carry out specific functions as described in Table 2 (Nairn et al, 2009).

Table 1. Summary total metals and sulfate concentration data for mine drainage discharges SA, SB and SD (as shown in Fig. 2) from monthly monitoring 2004-2009. Data are presented in mg/L as mean \pm standard error (number of analyses).

	SA	SB	SD
Al	0.302 \pm 0.083 (54)	0.346 \pm 0.086 (56)	0.177 \pm 0.044 (11)
As	0.067 \pm 0.003 (55)	0.064 \pm 0.001 (57)	0.063 \pm 0.002 (11)
Ca	731 \pm 5.91 (55)	725 \pm 6.50 (57)	737 \pm 9.02 (11)
Cd	0.016 \pm 0.0008 (55)	0.015 \pm 0.0007 (57)	0.018 \pm 0.002 (11)
Co	0.060 \pm 0.005 (52)	0.058 \pm 0.005 (54)	0.080 \pm 0.009 (9)
Cr	0.002 \pm 0.0003 (37)	0.002 \pm 0.0003 (35)	0.002 \pm 0.0001 (6)
Cu	0.004 \pm 0.0006 (53)	0.004 \pm 0.0005 (54)	0.002 \pm 0.0002 (10)
Fe	187 \pm 2.05 (55)	189 \pm 1.45 (57)	184 \pm 2.98 (11)
K	25.6 \pm 0.302 (32)	26.4 \pm 0.329 (31)	25.8 \pm 0.270 (11)
Li	0.384 \pm 0.016 (3)	0.381 \pm 0.017 (3)	0.375 \pm 0.020 (2)
Mg	197 \pm 1.49 (55)	196 \pm 1.36 (57)	202 \pm 3.16 (11)
Mn	1.56 \pm 0.012 (55)	1.60 \pm 0.015 (57)	1.73 \pm 0.061 (11)
Na	95.6 \pm 0.788 (55)	93.9 \pm 0.697 (57)	96.6 \pm 1.612 (11)
Ni	0.936 \pm 0.008 (55)	0.935 \pm 0.008 (57)	0.966 \pm 0.016 (11)
Pb	0.059 \pm 0.002 (54)	0.065 \pm 0.002 (57)	0.070 \pm 0.003 (11)
Zn	9.67 \pm 0.160 (55)	9.23 \pm 0.154 (57)	9.04 \pm 0.123 (11)
SO ₄	2209 \pm 87 (12)	2264 \pm 147 (12)	2343 \pm 317 (11)



Figure 2. Oblique aerial photograph of passive treatment system taken February 4, 2009 showing mine drainage discharges and individual process unit designations.

Table 2. Summary of process units, primary targeted water quality parameters and design function for the passive treatment system.

Process unit	Targeted parameter	Function
Oxidation pond	Fe	<ul style="list-style-type: none"> • Oxidation, hydrolysis and settling of iron oxyhydroxide solids • Trace metal sorption
Surface-flow wetlands/ponds	Fe	<ul style="list-style-type: none"> • Solids settling
Vertical-flow bioreactors	Zn, Pb, and Cd	<ul style="list-style-type: none"> • Retention of trace metal sulfides via reducing mechanisms
Re-aeration ponds	Oxygen demand and odor	<ul style="list-style-type: none"> • Wind- and solar-powered re-aeration • Stripping oxygen demand and H₂S • Adding O₂
Horizontal-flow limestone beds	Zn, Mn and hardness	<ul style="list-style-type: none"> • Final polishing of Zn as ZnCO₃ • Final polishing of Mn as MnO₂ • Adding hardness to offset bioavailability of any remaining trace metals
Polishing pond/wetland	Residual solids	<ul style="list-style-type: none"> • Solids settling • Photosynthetic oxygenation • Ecological buffering

Water Sampling and Analysis

Water first entered the system in December 2008 and monthly monitoring at all process unit influent and effluent locations began in January 2009. Temperature, pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), total dissolved solids, conductivity, and specific conductance (SC) were determined *in situ* with a YSI 600QS multiparameter datasonde and YSI 650MDS display. Total alkalinity and turbidity were measured immediately after sample collection via titration with appropriate normality H₂SO₄ acid using a Hach digital titrator (Method 8203) and via a Hach 2100P Turbidimeter, respectively. Volumetric discharge rates were determined with a calibrated bucket and stopwatch.

Samples were collected in 250-mL HDPE bottles for each sample location-event pair. One sample was preserved with trace metal grade HNO₃ to pH <1 for total metals analyses and a second sample was stored on ice at ≤4°C for anions analyses. On select occasions, additional

samples were collected for dissolved metals analyses via filtering (0.45 μm) before acidification. Samples were transported to the Center for Restoration of Ecosystems and Watersheds (CREW) laboratories at the University of Oklahoma for analyses.

Preserved samples for metals analyses were first nitric acid digested in a CEM MARSXpress Digestion System following EPA Method 3015 (USEPA 2006). Digested samples were then analyzed with a Varian Vista-PRO simultaneous axial Inductively Coupled Plasma-Optical Emission Spectrometer following EPA Method 6010b (USEPA 2006) for 16 analytes (Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb and Zn). Samples retained for anion analysis were filtered through 0.2 μm nitrocellulose filters and analyzed with a Metrohm ion chromatograph following EPA Method 300.1 (USEPA 1993) for seven analytes (Br^- , Cl^- , F^- , NO_2^- , NO_3^- , PO_4^{3-} , and SO_4^{2-}).

Results and Discussion

System Performance

In the first ten months of operation, the passive treatment system performed as designed from a water quality perspective (Table 3). The net alkaline nature of the mine waters was maintained throughout the system as target metals were removed from solution. Due in part to degassing of elevated CO_2 concentrations in the artesian discharges, pH increased from less than 6 to >7 at final discharge. Coupled oxidative and reductive processes lead to fluctuating DO and ORP values throughout the system and a demonstrated seasonality as the rates of biological processes varied. The remaining discussion focuses on constituents of interest.

Iron retention. During this initial period of performance, flow-weighted mean total Fe concentrations decreased from 177 ± 2.33 mg/L to 0.57 ± 0.21 mg/L at the final outflow (Table 3, Fig. 3). The great majority of total iron removal occurred in the initial oxidation pond and parallel surface-flow aerobic wetlands/ponds, with mean removal rates of 21 ± 2.8 g $\text{m}^{-2}\text{d}^{-1}$ and 3.7 ± 3.4 g $\text{m}^{-2}\text{d}^{-1}$, with the latter rate being load-limited.

The initial oxidation pond was designed specifically for iron oxidation, hydrolysis, precipitation, and settling; Oxenford et al. (2010) report specifically on Fe removal dynamics in this process unit. A statistically significant relationship between area-adjusted iron removal rate and effluent water temperature did exist for this process unit ($r = -0.83$, $p < 0.01$; Fig. 4) indicating greater removal under colder conditions as reported by Hedin (2008).

The parallel surface-flow aerobic wetlands/ponds were designed for iron oxide solids retention and include influent and effluent deep water areas with an interior shallow wetland shelf. Although planted, vegetation establishment on this wetland shelf was limited in this first growing season (<10% coverage), perhaps inhibiting solids retention.

Table 3. Selected mean water quality data from artesian discharges and process unit effluents. All data are mg/L except pH (standard units) and alkalinity (mg/L as CaCO₃). BDL = below detection limits.

		pH	DO	Alk.	Fe	Zn	Cd	Pb	Mn	As	Ni	SO ₄ ⁻²
Discharges	SA	6.01	1.17	402	171	8.34	0.015	0.065	1.47	0.062	0.94	2209
	SB	5.97	1.04	371	178	8.15	0.016	0.069	1.51	0.064	0.94	2264
	SD	5.99	1.27	386	181	9.00	0.015	0.070	1.62	0.061	0.96	2343
Cell 1		6.10	3.83	161	30	6.71	0.003	0.029	1.48	BDL	0.87	2173
Cell 2	N	6.51	7.94	135	4.4	5.76	BDL	BDL	1.50	BDL	0.81	2199
	S	6.40	7.00	131	4.4	5.97	BDL	BDL	1.58	BDL	0.82	2216
Cell 3	N	6.85	0.35	262	1.3	0.24	BDL	BDL	1.36	BDL	0.045	2311
	S	6.84	0.28	242	1.1	0.28	BDL	BDL	1.35	BDL	0.042	2091
Cell 4	N	7.20	3.86	236	0.87	0.16	BDL	BDL	1.38	BDL	0.035	2076
	S	7.10	3.51	232	0.92	0.23	BDL	BDL	1.44	BDL	0.042	2099
Cell 5	N	6.98	0.65	229	0.57	0.087	BDL	BDL	1.28	BDL	0.033	2064
	S	6.95	0.42	227	0.63	0.109	BDL	BDL	1.40	BDL	0.033	2195
Cell 6		7.11	2.65	224	0.57	0.096	BDL	BDL	1.38	BDL	0.035	2057

Zinc retention. Flow-weighted mean total Zn concentrations decreased from 8.29 ± 0.08 mg/L to 0.10 ± 0.04 mg/L for the entire system (Fig. 5). Zinc was targeted for retention via several mechanisms in individual process units of the treatment system, including sorption (Cell 1), ZnS precipitation (Cells 3N and 3S), and ZnCO₃ formation (Cells 5N and 5S). Over the course of initial operation, Zn was removed in all of these cells. In the initial oxidation pond, Zn concentrations decreased to 6.71 ± 0.37 mg/L, representing an area-adjusted removal rate of 0.28 ± 0.05 g m⁻²d⁻¹. Retention likely occurred through co-precipitation and sorption to iron oxyhydroxide precipitates. The tendency of these processes to occur at circum-neutral pH is well documented (Edwards and Benjamin 1989; Dzombak and Morel 1990; Benjamin and Sletten 1996; Carroll et al. 1998).

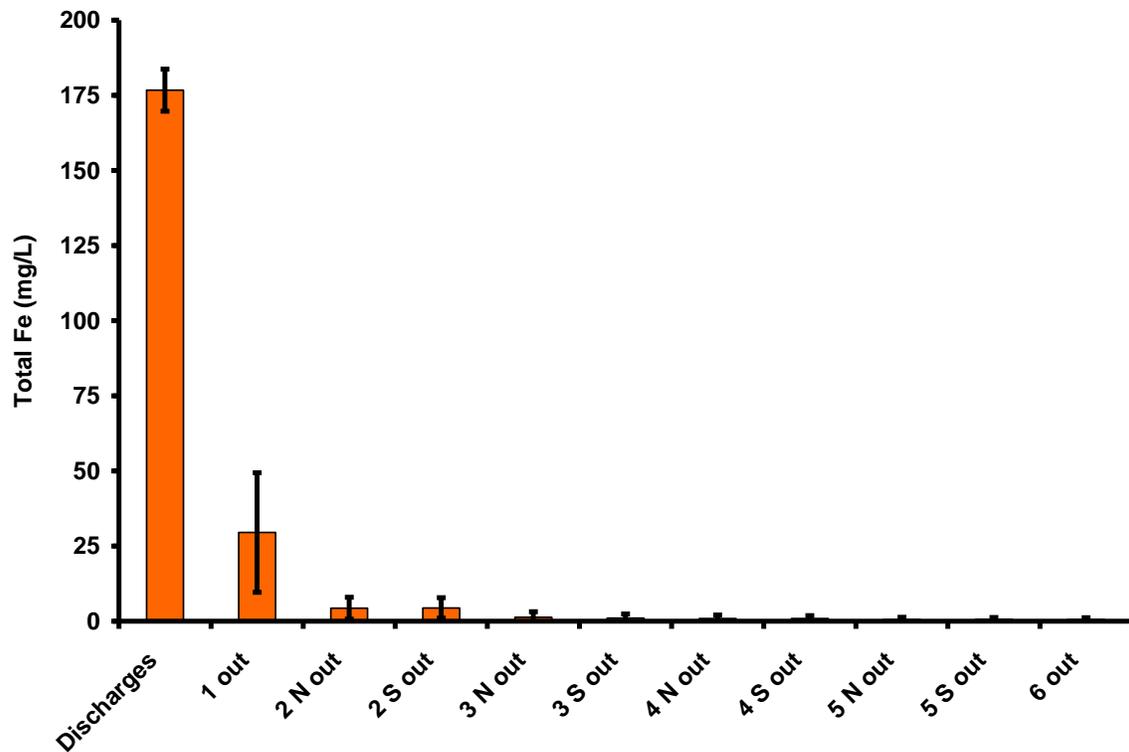


Figure 3. Mean total iron concentrations for artesian discharges and process unit effluents; error bars represent \pm one standard deviation.

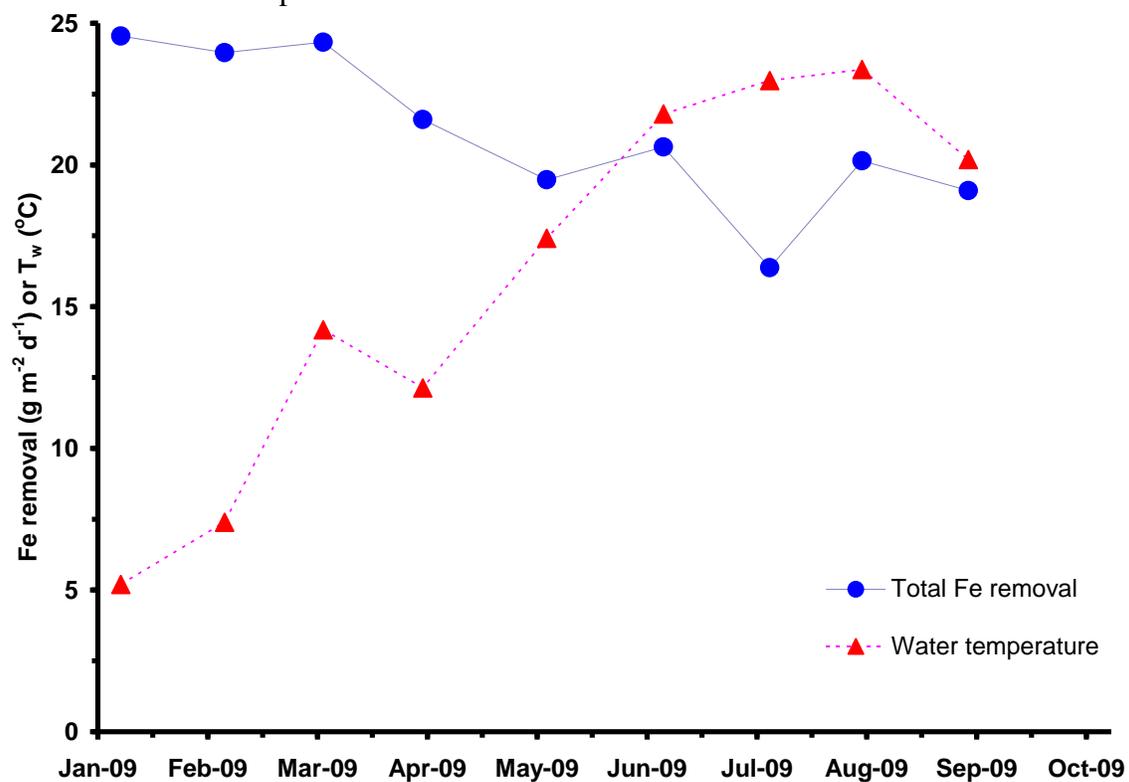


Figure 4. Total iron removal rate and effluent water temperature for initial oxidation pond cell 1.

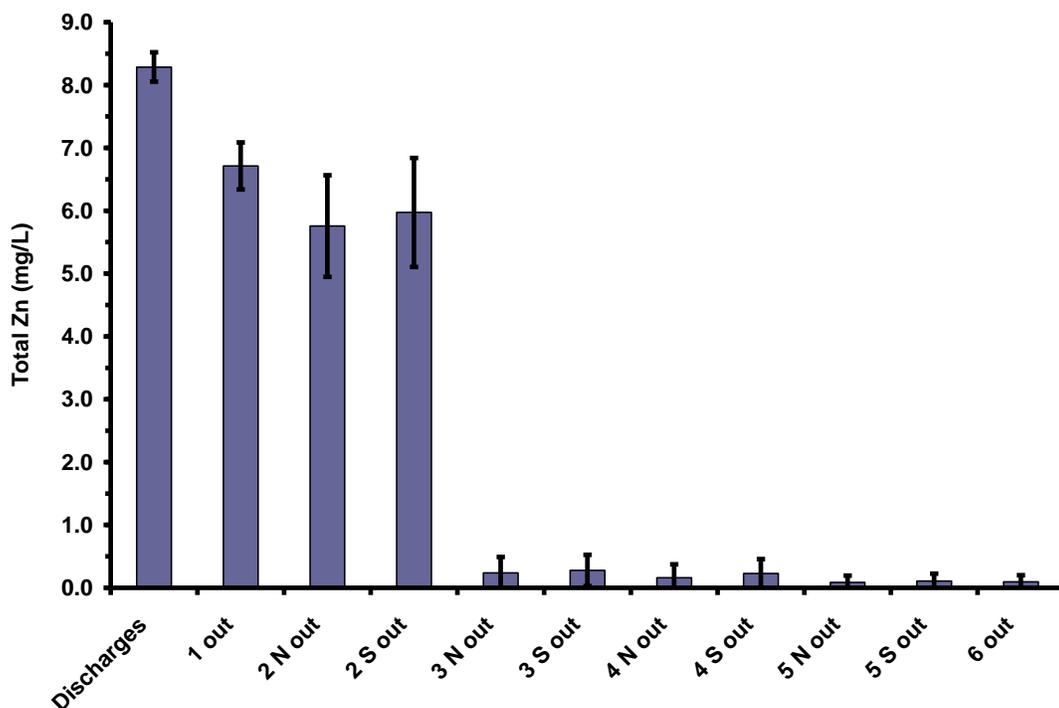


Figure 5. Mean total zinc concentrations for artesian discharges and process unit effluents; error bars represent \pm one standard deviation.

In the vertical-flow bioreactors, Zn concentrations decreased from 5.76 ± 0.81 mg/L to 0.24 ± 0.25 mg/L in Cell 3N and from 5.97 ± 0.87 mg/L to 0.28 ± 0.25 mg/L in Cell 3S. These cells were designed specifically to remove Zn and other trace metals through reductive mechanisms, converting free Zn and SO_4^{2-} to ZnS. Removal rates were much higher in these cells than in cell 1 (1.46 ± 0.27 and 1.45 ± 0.21 g $\text{m}^{-2}\text{d}^{-1}$ in cells 3N and 3S, respectively). Biological sulfate reduction in vertical-flow bioreactors is well-documented as a metal removal mechanism (e.g., Jong and Perry 2006; Neculita et al. 2007) and was the primary Zn retention processes for this passive treatment system.

In the horizontal-flow limestone beds, Zn concentrations decreased from 0.16 ± 0.21 mg/L to 0.09 ± 0.11 mg/L in Cell 5N and from 0.23 ± 0.23 mg/L to 0.11 ± 0.12 mg/L in Cell 5S. Relatively low influent Zn concentrations resulted in load-limited removal rates of 0.03 ± 0.04 and 0.02 ± 0.02 g $\text{m}^{-2}\text{d}^{-1}$ for cells 5N and 5S, respectively. These cells were designed to remove Zn through mechanisms specific to proper pE-pH conditions (Cravotta and Trahan 1999; Nuttall and Younger 2000). Although pE values (converted from field ORP readings) were typically within the needed range for amorphous ZnCO_3 and ZnO formation (-0.1 to $+0.9$ v), pH values

were 6.95-7.20, below the needed pH values of 7.5-8.2.

Trace Metals. Other metals of specific interest in these waters were Cd, Pb, and As. All three were removed to below detection limits (0.64, 19.5 and 22 $\mu\text{g/L}$, respectively) before the outflow of the second process units, presumably through sorptive processes. Although the vertical-flow bioreactors were designed to remove Cd and Pb as well as Zn, Cd and Pb rarely remained in measureable concentrations at this stage of the treatment system. On two instances (January and August 2009), Cd was detected in the inflow to the vertical-flow bioreactors at a concentration of approximately 1 $\mu\text{g/L}$, but was removed through reductive processes occurring within the cells.

The other trace metal found in significant concentrations in these waters was Ni. A small percentage (<10%) of Ni was removed through co-precipitation and sorption in Cell 1. However, the majority of Ni (~95%) was removed via reductive mechanisms in the vertical-flow bioreactors. The concentration decreased from $0.81 \pm 0.03 \text{ mg/L}$ to $0.05 \pm 0.04 \text{ mg/L}$ in Cell 3N and from $0.82 \pm 0.04 \text{ mg/L}$ to $0.04 \pm 0.03 \text{ mg/L}$ in Cell 3S. Ni concentrations did not decrease significantly in the remainder of the system, with final system effluent concentrations of $0.035 \pm 0.01 \text{ mg/L}$.

Sulfate. Flow-weighted mean SO_4^{2-} concentrations were elevated in the discharges ($2239 \pm 26 \text{ mg/L}$) and decreased to $2047 \pm 72 \text{ mg/L}$ in the final outflow. Sulfate concentration changes in the vertical-flow bioreactors, although demonstrating a great deal of temporal variability, provided mean calculated sulfate reduction rates of 0.53 and 0.40 $\text{mol m}^{-3}\text{d}^{-1}$ for cells 3N and 3S, respectively. These values are slightly greater than reported values for field-scale systems of approximately 0.3 $\text{mol m}^{-3}\text{d}^{-1}$ as reported earlier (e.g., Dvorak et al. 1992; Neculita et al. 2007) but were not unexpected during this initial operational period.

Overall Water Quality Changes. The passive treatment system described in this paper demonstrated that the quality of these artesian hard-rock mine discharges may be effectively addressed through an appropriate combination of ecologically engineered process units (Table 4). Final effluent concentrations of Cd, Pb and As were below detection limits and percentage decreases for Fe, Zn and Ni in the entire system were 99.7, 98.8 and 96.3%, respectively. Conservative ion (e.g., Mg and Li) concentration changes were between 0.3 and 1.2% indicating that design-targeted biogeochemical mechanisms affected contaminant

concentrations and dilution played little if any role.

Table 4. Summary total metals and sulfate concentration data for flow-weighted influent and final system effluent. Data are presented in mg/L as mean \pm standard error; n = 3-9 depending on analyte. BDL = below detection limits.

	Influent	Final effluent
Al	0.094 \pm 0.009	0.071 \pm 0.030
As	0.063 \pm 0.002	BDL
Ca	742 \pm 9.0	740 \pm 22.3
Cd	0.016 \pm 0.002	BDL
Co	0.066 \pm 0.008	0.007 \pm 0.0004
Cr	0.001 \pm 0.0002	0.002 \pm 0.0006
Cu	0.002 \pm 0.0003	0.003 \pm 0.0003
Fe	177 \pm 2.33	0.57 \pm 0.207
K	26.0 \pm 0.286	31.1 \pm 4.82
Li	0.366 \pm 0.010	0.365 \pm 0.018
Mg	200 \pm 2.53	198 \pm 7.49
Mn	1.51 \pm 0.016	1.38 \pm 0.197
Na	94.9 \pm 1.63	96.6 \pm 4.23
Ni	0.945 \pm 0.015	0.035 \pm 0.007
Pb	0.068 \pm 0.003	BDL
Zn	8.29 \pm 0.078	0.096 \pm 0.037
SO ₄	2239 \pm 26	2047 \pm 72

Conclusions

The discharges addressed by the passive treatment system represent approximately 20% of the contaminant mass loading from artesian mine drainage discharges in the Tar Creek Watershed. The stream and its tributaries receive additional contaminant mass loading from other artesian discharges, waste pile and pond runoff, and other sources. It is obvious that considerable efforts would be required to satisfactorily address mining-related water quality deterioration in this watershed. In 1994, approximately 15 years after the first discharges began to flow, the State of Oklahoma concluded that “the impacts to Tar Creek... are because of irreversible man-made conditions” and furthermore U.S. EPA “concur with the State’s conclusion that the surface water conditions are irreversible” (USEPA 1994). However, appropriately designed passive treatment systems appear to be capable of treating these waters effectively and evaluation of future watershed-scale applications is warranted.

From the bioavailability and ecotoxicity perspectives, the untreated artesian discharges exceeded the hardness-adjusted U.S. EPA Criterion Continuous Concentrations (CCC) for Cd,

Fe, Ni, and Zn and the Criterion Maximum Concentration (CMC) for Zn (USEPA 2010b). In general, as hardness increases the toxicity of the metal decreases. Despite the fact that there was no significant increase in hardness values in the system, the system effluent no longer exceeds any of these criteria. LaBar et al. (2010) report on stream water quality changes related to operation of this passive treatment system.

Future research at this site will focus on development of a detailed mechanistic understanding of passive biogeochemical processes leading to water quality changes. Research infrastructure has been installed to examine sedimentation rates in the initial oxidation pond, pore water chemical composition in the vertical-flow bioreactors, oxygenation kinetics in the re-aeration cells and dissolution/precipitation dynamics in the horizontal-flow limestone beds. Ancillary ecological benefits provided in the passive treatment system itself and in the receiving waters will be examined, as well as public educational opportunities.

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