STREAM WATER QUALITY IMPROVEMENTS AFTER INSTALLATION OF A PASSIVE TREATMENT SYSTEM[1]

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Abstract: Perennial borehole discharges have flowed unabated from abandoned lead-zinc mines in the Tri-State Mining District for 30 years and considerably degraded the physical, chemical, and biological integrity of a first-order tributary to Tar Creek in Ottawa County in northeastern Oklahoma. Water quality has been monitored at the discharges and the receiving tributary monthly since fall 2004. Construction of a large multi-cell passive treatment system was completed in late 2008. Prior to construction of the treatment system, metals loads immediately downstream from the confluence of the discharges and tributary were 163 kg Fe/d, 20 kg Zn/d, 52 g Cd/d, and 106 g Pb/d. In the first year of operation, the passive treatment system has been successful at removing Cd, Pb, and As to below detection limits and Fe and Zn to <1 mg/L. These changes have resulted in substantial decreases in in-stream loading to 23 kg Fe/d, 6 kg Zn/d, 12 g Cd/d, and Pb to below detection limits. Mining influences, upstream of this confluence, continue to degrade water quality. However, the passive treatment system has resulted in significant decreases in metal mass loadings.

Additional Key Words: metal mining, acid mine drainage, natural treatment systems, stream restoration

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Introduction

Mine drainage from abandoned hard-rock mines continues to pose substantial ecological and human health risks (USEPA, 2004; Limerick et al, 2005). The Tar Creek Superfund Site, part of the Tri-State Mining District in Ottawa County of northeastern Oklahoma, is one of the most challenging hard-rock abandoned mine reclamation sites in the United States due to the extensive areal extent and considerable volume of contaminated ground and surface water (Nairn et al, 2001). Mine drainage from abandoned Pb-Zn mines (both artesian flows and waste pile runoff) has resulted in physical, chemical, and biological degradation of Tar Creek through direct inputs to the stream itself as well as through discharge into tributaries that flow into the stream.

Mine drainage in the Tar Creek Superfund Site is characterized by elevated concentrations of metals (particularly Fe, Zn, Pb, and Cd), mineral acidity, and sulfate. Due to the carbonate nature of the host rock, the discharges also contain elevated concentrations of alkalinity (as $CaCO_3$), which buffers the mineral acidity and results in net alkaline waters with circum-neutral pH. Despite the fact that substantially lower contaminant concentrations were documented after 20+ years of discharge (e.g. DeHay et al, 2003; Coffey and Nairn, 2003), Fe, Zn, and Cd concentrations are still above National Recommended Water Quality Criteria for maintenance of aquatic communities (USEPA, 2002). Substantial decreases in native macroinvertebrate and fish populations have been documented over the past 30 years (Aggus et al, 1983; Iverson, 2003). In addition, changes in reproductive responses have been discovered in the pollution-tolerant fish, *Gambusia affinis* (Franssen, 2009).

Considering the large scale and complexity of contamination sources, solutions to the water quality issues in this area have remained elusive. 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), not excluding those in the Tar Creek Superfund Site. Based upon conclusions from the Tar Creek Superfund Task Force, passive treatment was identified as the most promising remediation technology for these waters (Nairn et al, 2001). This paper describes the observed changes in contaminant concentrations and mass loadings in a first-order tributary and Tar Creek after receiving discharge from the first passive treatment system in the mining district.

Methods

Site Background

The first site targeted for passive treatment implementation in the Tar Creek Superfund Site is located in southeast Commerce, OK. Abandoned borehole discharges flowed unabated for 30 years, causing physical, chemical, and biological degradation to an unnamed first-order tributary to Tar Creek. These discharges represent approximately 20% of the mass loading from artesian discharges in the Tar Creek watershed. Additional mining influences upstream of these discharges also impact water quality. An initial demonstration project began in mid-2005 to design, construct, and monitor a passive treatment system to remediate the discharges, lessening their impact on the receiving tributary. Passive treatment system results are reported by Nairn et al. (2010).

Sampling sites on the tributary were identified when the initial monitoring effort began in October 2004. These sites include three sites on the tributary as well as one site directly downstream of the confluence of the tributary and Tar Creek (RTC). The first site on the tributary is located upstream of the confluence with the targeted mine discharges (UTU), the second is located directly downstream of the confluence with the discharges (UTD), and the third is located further downstream before the tributary meets Tar Creek (RUT). All four sites as well as the mine drainage discharges are shown in Fig. 1.

Sampling and Analysis

Two mine discharges (SA and SB) have been sampled monthly since October 2004. A third discharge (SD) was discovered during construction of the passive treatment system and has been sampled monthly since January 2009. Monthly monitoring of the unnamed tributary has been conducted since October 2004. Temperature, pH, dissolved oxygen (DO), oxidation-reduction potential, total dissolved solids, conductivity, and specific conductance 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 sulfuric acid using a Hach digital titrator (Method 8203) and via a Hach 2100P Turbidimeter, respectively. Volumetric discharge rates were determined either with a SonTek FlowTracker Handheld Acoustic Doppler Velocimeter or 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 HNO_3 to pH <1 for total metals analyses and a second sample was stored on ice at ≤4°C for anions analyses. Samples were then transported to the Center for Restoration of Ecosystems and Watersheds (CREW) laboratories at the University of Oklahoma for analyses.

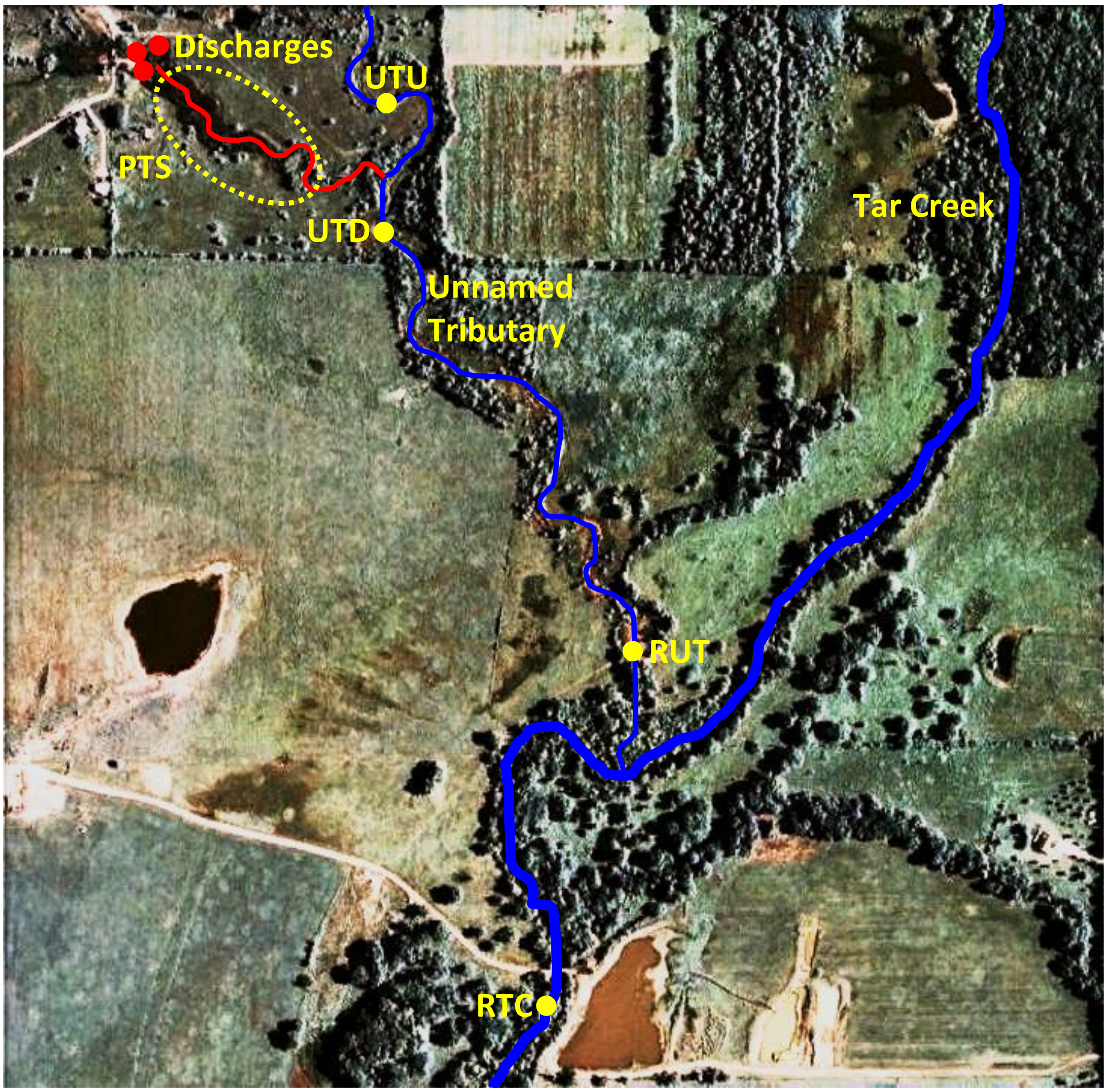

Figure 1. Aerial photograph of three mine drainage discharges, approximate outline of passive treatment system, and sampling locations on Unnamed Tributary and Tar Creek. Base aerial photograph (GoogleEarth 2010) taken June 2006, prior to passive treatment system implementation

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 15 analytes (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, Zn). Samples retained for anions 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-}, SO_4^{2-}).

Results and Discussion

Prior to construction of the passive treatment system, discharge from the abandoned boreholes had a significant impact on the water quality of the unnamed tributary. The Mann-Whitney test was used to compare median concentrations and loadings at UTU to median concentrations and loadings (prior to installation of the passive treatment system) at UTD. The results indicated the discharges (which entered the tributary between these two sites) caused a significant ($p<0.05$) increase in concentrations and loadings of Fe, Zn, Cd, and Pb at UTD. Although concentrations of Fe, Zn, and Pb decreased by the time the water reached RUT (Table 1), the changes were not great enough to significantly improve water quality.

Table 1. Selected median water quality data from discharges and streams from October 2004 until December 2008.

		UTU	SA	SB	UTD	RUT	RTC
pH	**(s.u.)**	6.62	6.01	5.97	6.15	6.34	6.77
DO	**(mg/L)**	6.85	1.17	1.04	4.57	4.85	7.27
Alkalinity	**(mg/L as $CaCO_3$)**	122	402	371	234	138	90
Fe	**(mg/L)**	4.2	171	178	71	20	2.74
Zn	**(mg/L)**	7.32	8.34	8.15	7.72	6.69	3.48
Cd	**(mg/L)**	0.01	0.02	0.02	0.01	0.01	0.004
Pb	**(mg/L)**	0.03	0.07	0.07	0.04	0.03	BDL
Mn	**(mg/L)**	3.51	1.47	1.51	1.82	1.95	0.78
As	**(mg/L)**	0.02	0.06	0.06	0.04	0.03	BDL
Ni	**(mg/L)**	0.29	0.94	0.94	0.54	0.54	0.11
SO_4^{-2}	**(mg/L)**	1147	2209	2264	1508	1618	782
Disharge	**(L/m)**	960	109	281	1922	5340	33726

Implementation of the passive treatment system resulted in significant improvements in the mine discharge water quality. Cd, Pb, and As were removed to below detection limits (0.64 µg/L, 19.48 µg/L, and 22.34 µg/L, respectively) and Fe and Zn decreased to <1 mg/L. Contaminant loading in the unnamed tributary due to the mine discharges targeted for treatment has been decreased to negligible amounts. In addition, the system effluent no longer exceeds the National Recommended Water Quality Criteria for any of the metals of concern. A more thorough explanation of these improvements is reported in Nairn et al. (2010).

Water quality in the tributary upstream of the three mine discharges continues to be impacted by mining and non-mining influences and has not changed significantly since the passive treatment system became operational. However, water quality downstream of the discharges has shown considerable improvement. Mann-Whitney medians comparisons have indicated that concentrations of the primary metals of concern (Fe, Cd, Pb, and Zn) as well as Ni have decreased significantly ($p<0.05$) as a result of the passive treatment system. By the time the water flows to the next sampling point (RUT), Fe concentrations have decreased further, as well as other metals known to be removed via sorption processes with Fe precipitates (specifically Cd, Zn, and Ni). Although the tributary has shown marked water quality improvement since the treatment system became operational, concentrations of metals in Tar Creek itself have not decreased significantly in that time. This fact is due to the vast extent of the contamination across the upstream portions of the Tar Creek watershed and the multitude of mine discharges and surface impacts on the stream. Summary data for all four sampling locations are shown in Table 2.

In-stream Fe and Zn concentrations have shown the most noticeable improvement since water began flowing through the passive treatment system. Figures 2 and 3 illustrate the changes in mean total Fe and Zn concentrations in the tributary and Tar Creek before and after implementation of the passive treatment system. Concentrations at UTU were averaged over the entire sampling period as there was no significant difference in the concentrations before and after the treatment system became operational. Iron concentrations decreased ~75% at UTD and ~87% at RUT. Zn concentrations decreased ~47% at UTD and ~57% at RUT. However, by the time the combined waters reached RTC, the impacts of removing these metals is negligible due to the much larger watershed, higher flow, and upstream metals load of Tar Creek.

Table 2. Selected mean water quality data from unnamed tributary and Tar Creek collected after implementation of passive treatment system

		UTU	UTD	RUT	RTC
pH	**(s.u.)**	6.62	6.50	6.78	6.93
DO	**(mg/L)**	6.85	5.60	7.58	8.38
Alkalinity	**(mg/L as $CaCO_3$)**	122	192	138	98
Fe	**(mg/L)**	4.2	20	1.67	2.44
Zn	**(mg/L)**	7.32	4.01	3.00	3.43
Cd	**(mg/L)**	0.01	0.01	0.003	0.003
Pb	**(mg/L)**	0.03	BDL	BDL	BDL
Mn	**(mg/L)**	3.51	3.28	2.11	0.82
As	**(mg/L)**	0.02	BDL	BDL	BDL
Ni	**(mg/L)**	0.29	0.25	0.19	0.08
SO_4^{-2}	**(mg/L)**	1147	1793	1485	838
Discharge	**(L/m)**	960	1053	1291	31958

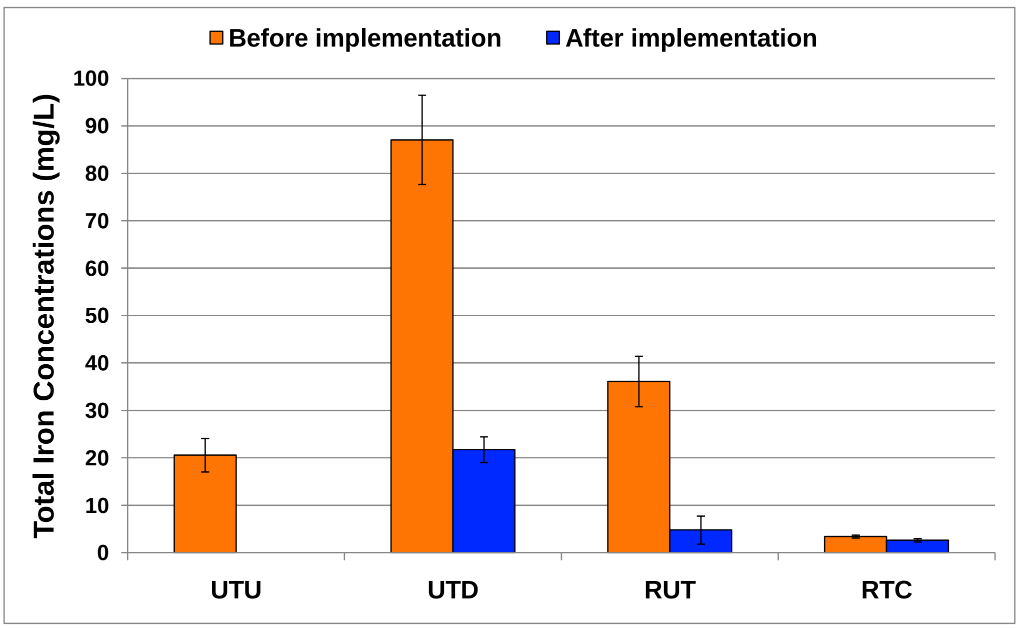

Figure 2. Mean total iron concentrations in the receiving streams before and after implementation of the passive treatment system. Error bars represent ± one standard error.

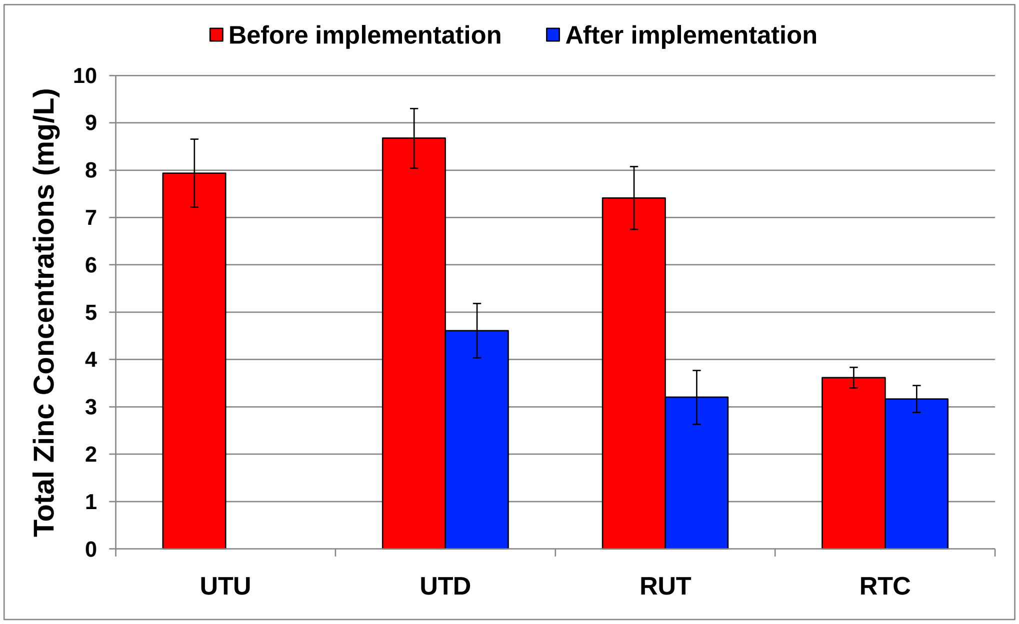

Figure 3. Mean total zinc concentrations in the receiving streams before and after implementation of the passive treatment system. Error bars represent ± one standard error.

Prior to construction of the passive treatment system, mean metals loads immediately downstream of the confluence of the discharges and tributary (UTD) were 163 kg Fe/d, 20 kg Zn/d, 52 g Cd/d, and 106 g Pb/d. Following passive treatment, the mean metals loads in the same location have decreased to 23 kg Fe/d, 6 kg Zn/d, and 12 g Cd/d, with Pb concentrations below detection limits. This amounts to an 85%, 68%, and 76% reduction in Fe, Zn, and Cd loads, respectively, due to the passive treatment system. Similar decreases were seen at RUT.

Although significant decreases in metals concentrations were not seen at RTC, there has been a substantial decrease in metals loads since operation of the passive treatment system began. Iron loads have decreased ~6%, Zn ~31%, and Cd ~37%. Whether these reductions are due to removal of the metals from the three treated discharges or are a result of natural attenuation or seasonal variability within Tar Creek requires further study.

Although effluent of the passive treatment system does not exceed the National Recommended Water Quality Criteria, concentrations of some metals in the unnamed tributary itself continue to exceed criteria. Water downstream of the system effluent (UTD) exceeds the

Criterion Continuous Concentration (CCC) for Cd and Zn as well as the Criteria Maximum Concentration (CMC) for Zn. These criteria are also exceeded further downstream at RUT and RTC.

Conclusions

The unnamed tributary continues to be impacted by mining influences within its watershed and continues to contribute metals loads to Tar Creek. However, the impacts from the three mine discharges have been significantly reduced as a result of the passive treatment system. In addition to measured improvements in water quality, visual inspections have revealed a much clearer stream, with less Fe precipitates. Future evaluation at the site will include vegetation and wildlife inspections to determine that the stream is indeed recovering to a valuable aquatic habitat.

Substantial metal loading from artesian discharges and waste pile runoff continues untreated within the Tar Creek Superfund Site. Although operation of the first passive treatment system in the Superfund Site has not significantly decreased metals concentrations in Tar Creek itself, it has had a significant impact on metals concentrations and loads in the receiving first-order tributary. Operation of the system has demonstrated that it is not only possible to treat these mine discharges effectively, but also that doing so will improve water quality in the streams directly receiving the discharges.

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