Stream Recovery through Managed Biogeochemical Redox Coupling in Ecologically Engineered Passive Treatment Systems: A Natural Infrastructure Approach

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Abstract

Two full-scale mine water passive treatment systems (PTS) were installed in the Tar Creek (Kansas-Oklahoma, USA) watershed of the historic Tri-State Mining District, each including multiple process units designed for specific biogeochemical functions. Both systems produce net alkaline effluents containing metals concentrations meeting in-stream water quality criteria and collectively retain 71000 kg Fe, 3100 kg Zn, 84 kg Pb, 9 kg Cd, and 25 kg As annually. The first order receiving stream demonstrated substantial water quality improvement and ecological recovery, with documented increases in both fish species richness and abundance, as well as the return of other fauna.

Keywords: Nature-based Solutions, Ecosystem Restoration, Water Quality Improvement

Introduction

Ecological engineering, defined by Mitsch and Jorgensen (2004) as "the design of sustainable ecosystems that integrate human society with its natural environment for the benefit of both", has been an established academic discipline since the 1960s (e.g., Odum 1962, 1971). However, in recent years the related terms natural infrastructure and nature-based solutions have become common in both the technical literature and popular press (e.g., Chung *et al* 2021, Cohen-Shacham *et al*. 2016). Although developed on parallel yet separate tracks from these broader areas of inquiry (e.g., Hedin *et al*. 1994, Skousen *et al*. 2017), mine water passive treatment is a representative application of ecological engineering and arguably the ultimate application of natural infrastructure (infrastructure that uses, restores, or emulates natural ecological processes created by nature or human design (Title 23 US Code 2012)) and nature-based solutions (actions to protect, sustainably manage, and restore natural and modified ecosystems that address societal challenges effectively and adaptively, simultaneously benefiting people and nature (IUCN 2023)).

In this study, long-term evaluations of several mine water discharges, two full-scale mine water passive treatment systems (PTS), and a common receiving stream were conducted in the Tar Creek Superfund Site, part of the historic and now derelict Tri-State Lead-Zinc Mining District, USA. Chemical and hydrological characterization of the discharges began in 2004, multi-process unit PTS were installed in 2008 and 2017, and chemical, hydrological, and ecological assessments (e.g., fish community analyses) of the stream have continued since 2004. Individual PTS process units were designed to promote specific biogeochemical mechanisms to address a suite of ecotoxic metals. Multidisciplinary assessments of the PTS and receiving stream provide insight into the success of these ecological engineering technologies.

Methods

The study site includes an unnamed receiving stream (first-order tributary to Tar Creek) and two full scale PTS (Figure 1). The Mayer Ranch (2008) and Southeast Commerce (2017) PTS include ten and four process units, respectively, alternating between promotion of oxidative (e.g., oxidation and hydrolysis) and reductive (e.g., sulfate reduction) mechanisms. Design, construction, and performance data are summarized in Nairn *et al*. (2010, 2020), Oxenford and Nairn (2010), and Labar and Nairn (2018). Monthly to quarterly water quality, volumetric discharge, and fish community data have been generated since 2004. Water quality efforts include a full suite of physicochemical parameters (pH, dissolved oxygen, specific conductance, oxidation-reduction potential (ORP), total alkalinity, turbidity), anions (SO_4^{2-}, Cl^-, PO_4^{3-}, NO_2^-, NO_3^-) and total and dissolved (<0.45 mm) metals and metalloids (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Se, Si, and Zn). University of Oklahoma Center for Restoration of Ecosystems and Watersheds (CREW) standard operating procedures follow US Environmental Protection Agency (USEPA) and US Geological Survey (USGS) methods for all field and laboratory water analyses and include approved quality assurance and quality control practices. Standardized stream fish collections included taking ten seine (3.17 mm mesh, 1.22 m deep, 2.44 m long) hauls per site, including as many microhabitats as possible.

Results

Both PTS have demonstrated effective removal of total and dissolved trace metals. Table 1 summarizes flow-weighted influent and effluent data for selected water quality constituents for Mayer Ranch PTS from November 2008 to December 2022 and for Southeast Commerce PTS from February 2017 to December 2022. Overall changes in total and dissolved Fe, Zn, Cd, and As concentrations are greater than 90% and effective removal of Ni (84-91%) and Pb (62-91%) are also demonstrated. Changes in concentrations of biogeochemically conservative ions (Mg, K, Na, and Cl^-) are less than 5% at Mayer Ranch and less than 18% at Southeast Commerce, indicating promotion of targeted redox-mediated passive treatment

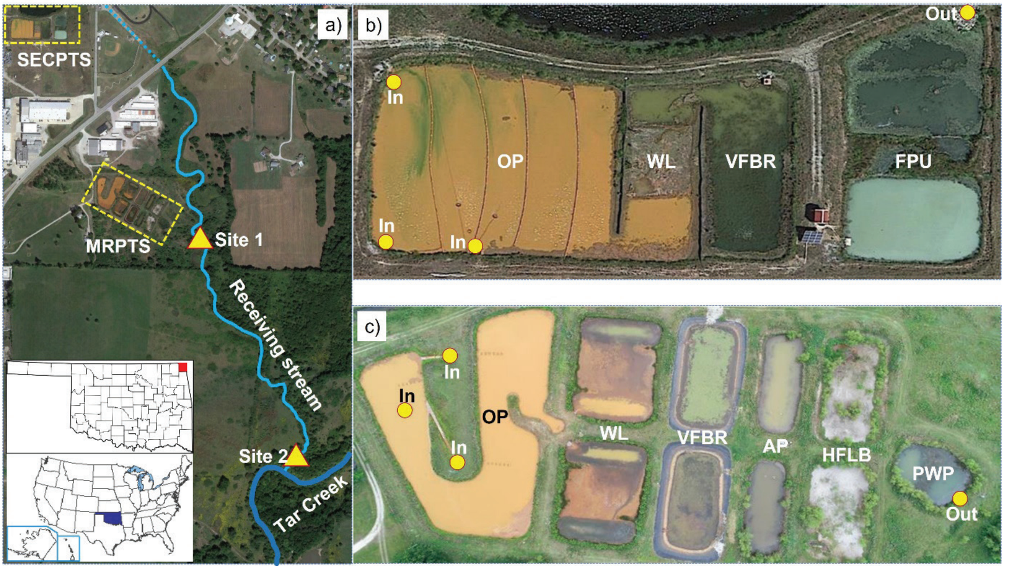

Figure 1 Study sites showing ***a)*** *location of two PTS, receiving stream, confluence with Tar Creek, and in-stream sampling locations; inset maps show location of Oklahoma in the US and Ottawa County in Oklahoma;* ***b)*** *Southeast Commerce PTS including inflows and outflow and (from L to R) oxidation pond with baffle curtains (OP), surface flow wetland (WL), vertical flow bioreactor (VFBR) and final polishing unit (FPU);* ***c)*** *Mayer Ranch PTS including inflows and outflow and (from L to R) oxidation pond (OP), parallel trains of surface flow wetlands (WL), vertical flow bioreactors (VFBR), reaeration ponds (AP), horizontal flow limestone beds (HFLB), and a polishing wetland/pond (PWP). Study site image from Google Earth (2021) and PTS images collected by OU CREW small Unoccupied Aerial Vehicle (sUAS).*

mechanisms and limited effects of dilution or evapotranspiration. Nominal volumetric discharge rates were 420 and 600 L/min at Mayer Ranch and Southeast Commerce PTS, respectively.

Figures 2 and 3 demonstrate the role of designed redox manipulations on water quality in these nature-based solutions. Elevated iron concentrations at Mayer Ranch and Southeast Commerce PTS are removed through oxidation, hydrolysis, precipitation, and settling in the OP and WL process units (Oxenford and Nairn 2011); As concentrations are also decreased via sorption to precipitated iron oxyhydroxide solids. Conversely, elevated Zn concentrations, although decreased by sorptive process in oxidative units, are effectively addressed through reductive biogeochemical means in the VFBR process units (LaBar and Nairn 2018). Other trace metals (Cd, Co, Fe, Ni, and Pb) are retained in the sulfide fraction in VFBR substrates, as

Table 1 *Summarized influent and effluent data for two PTS (median ± standard error (sample size > practical quantitation limit or PQL)). Data for three influent discharges at Mayer Ranch were flow-weighted; at Southeast Commerce, data for one representative influent discharge are presented.*

	Mayer Ranch PTS		Southeast Commerce PTS	
	Influent	**Effluent**	**Influent**	**Effluent**
pH	5.99±0.02(62)	7.06±0.02(61)	5.94±0.02(40)	6.83±0.04(69)
ORP (mV)	-41±13(52)	72±20(53)	-49±24(32)	35.30±15(58)
Alk. (mg/L)	385±3.78(62)	182±5.61(60)	396±2.75(38)	121±5.24(69)
T. Fe (mg/L)	160±2.56(62)	0.33±0.05(61)	140±2.43(38)	1.08±0.14(69)
D. Fe (mg/L)	156±2.58(47)	0.08±0.08(46)	136±3.36(38)	0.21±0.11(68)
T. Zn (mg/L)	6.91±0.14(62)	0.14±0.10(60)	6.54±0.08(38)	0.07±0.13(66)
D. Zn (mg/L)	6.48±0.15(47)	0.05±0.12(47)	6.41±0.08(38)	0.05±0.13(65)
T. Cd (mg/L)	15.16±0.83(61)	1.01±0.15(8)	19.45±0.86(37)	1.08±0.09(16)
D. Cd (mg/L)	15.04±0.98(47)	1.14±0.50(6)	17.67±0.75(37)	1.06±0.41(12)
T. Pb (mg/L)	77.64±10.09(62)	29.63±2.05(18)	279±9.19(38)	24.38±0.71(52)
D. Pb (mg/L)	86.93±12.94(46)	26.29±2.01(19)	254±8.48(38)	24.03±0.70(44)
T. As (mg/L)	61.23±1.62(61)	<PQL(0)	87.22±2.07(37)	<PQL(0)
D. As (mg/L)	64.10±13(45)	<PQL(0)	84.34±28(37)	<PQL(0)
T. Ni (mg/L)	0.81±0.01(62)	0.12±0.03(59)	0.71±0.01(38)	0.07±0.03(67)
D. Ni (mg/L)	0.78±0.01(47)	0.12±0.04(46)	0.70±0.01(38)	0.07±0.03(66)
T. Ca (mg/L)	698±5.69(62)	702±10.76(61)	660±6.10(38)	616±7.14(69)
D. Ca (mg/L)	694±6.56(47)	687±10.62(47)	659±5.74(38)	617±6.80(69)
T. Mg (mg/L)	175±3.05(62)	175±3.62(61)	149±2.37(38)	131±2.07(69)
D. Mg (mg/L)	170±2.44(47)	168±3.00(47)	150±2.45(38)	131±1.94(69)
T. K (mg/L)	24.25±0.26(62)	23.08±0.78(61)	22.13±0.21(38)	20.43±0.39(69)
D. K (mg/L)	23.73±0.30(47)	23.27±1.02(47)	22.33±0.23(38)	20.33±0.39(69)
T. Na (mg/L)	95.29±1.67(62)	95.45±2.09(61)	87.99±1.55(38)	84.11±1.64(69)
D. Na (mg/L)	93.83±1.69(47)	95.71±1.93(47)	90.44±1.62(38)	85.78±1.59(69)
SO_4^{2-} (mg/L)	2193±28(60)	2078±62(59)	2070±52(38)	1822±28(69)
Cl^- (mg/L)	31.65±0.49(35)	32.09±0.72(34)	29.25±0.58(26)	24.05±0.86(27)

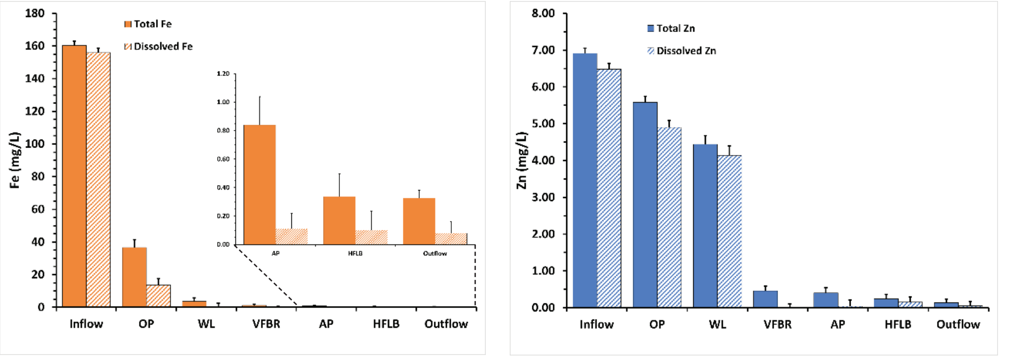

Figure 2 *Changes in iron and zinc concentration with flow through the Mayer Ranch PTS. Iron concentrations decrease to <3 mg/L by oxidative processes in OP and WL units and to <0.5 mg/L in final outflow. Zinc concentrations decrease to <0.5 mg/L by reductive process in the VFBR units and to <0.1 mg/L in the final outflow.*

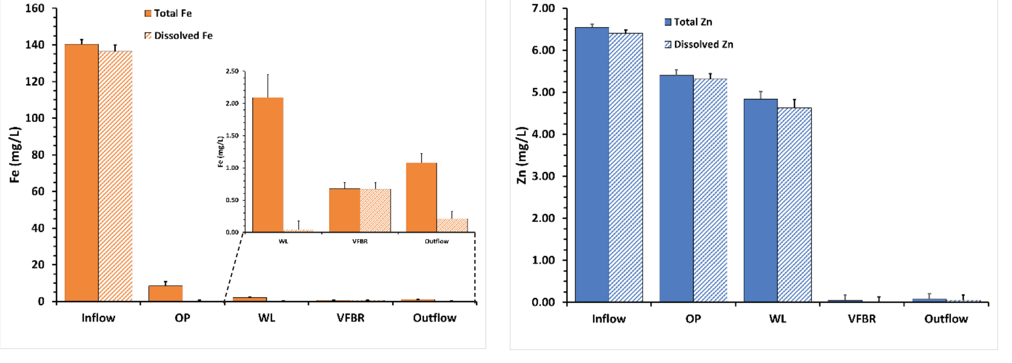

Figure 3 *Changes in iron and zinc concentration with flow through the Southeast Commerce PTS. Total and dissolved iron concentrations decrease to ≈2 and <0.05 mg/L by oxidative processes in OP and WL units. Zinc concentrations decrease to <0.05 mg/L by reductive process in the VFBR units.*

confirmed by acid volatile sulfide/extracted metals, scanning electron microscopy, and x-ray diffraction analyses.

Water quality in the receiving stream was noticeably influenced by biogeochemical changes in PTS effluents resulting from installation of targeted natural infrastructure. The Southeast Commerce PTS effluent enters the receiving stream near its headwaters, while the Mayer Ranch PTS effluent enters approximately 1000 m downstream. Data for two downstream locations are presented in Figure 4. Sites 1 and 2 are approximately 25 and 1000 m, respectively, downstream of the Mayer Ranch PTS effluent confluence with the receiving stream.

Fish communities exhibited demonstrative effects of in-stream water quality improvement. Fish species richness at Sites 1 and 2 increased from 6 to 13 and 7 to 17 species, respectively, after installation of the two PTS as nature-based solutions and is comparable to local unimpacted reference streams. In this small first order tributary, fish assemblages were dominated by small-bodied minnows and centrarchids, including western mosquitofish (*Gambusia affinis*), bluegill sunfish (*Lepomis macrochirus*), green sunfish (*Lepomis cyanellus*), and largemouth bass (*Micropterus salmoides*), although populations of darters, catfish, shiners, shad, suckers, and stonerollers were also noted.

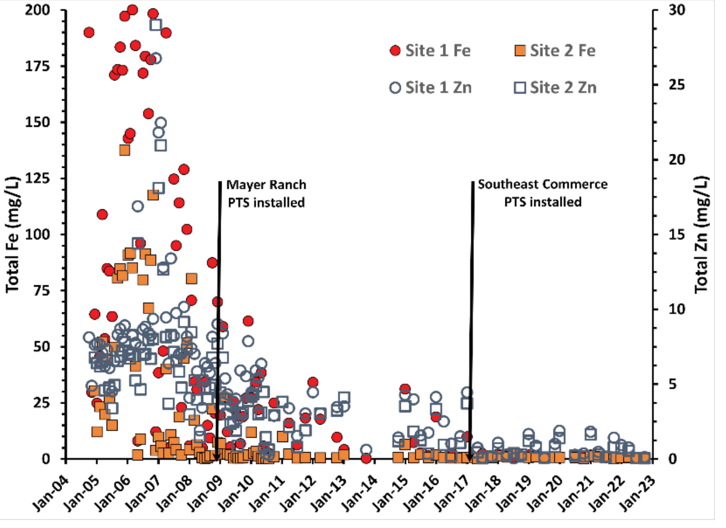

Figure 4 *In-stream total iron and zinc concentrations from October 2004 through December 2022 at two receiving stream locations. Site 1 is approximately 25 m from the Mayer Ranch PTS effluent and 1025 m from the Southeast Commerce PTS effluent. Site 2 is approximately 1000 m from the Mayer Ranch PTS effluent and 2000 m from the Southeast Commerce PTS effluent. The Mayer Ranch and Southeast Commerce PTS began operations in November 2008 and February 2017, respectively. Although dramatically decreased after PTS installation, in-stream concentrations remain slightly elevated due to legacy mining effects including in-stream tailings deposits.*

Since no in-stream habitat was restored, the reestablishment of robust fish communities indicates changes due to water quality improvements. In addition, based on field research activities in this watershed since 1998, robust and active North American beaver (*Castor canadensis*) populations were initially noted in 2013 (after installation the Mayer Ranch PTS in 2008), followed by North American river otter (*Lontra canadensis*) populations in 2022 (after both PTS were operational).

In-stream water quality changes due to mine water passive treatment decreased the magnitude of aquatic ecotoxicity due to trace metals. Toxicity of select trace metals is affected by water hardness. Increased hardness decreases bioavailability and, therefore, resulting ecotoxicity. In-stream hardness-adjusted aquatic life criteria for several metals have been developed by USEPA through the National Recommended Water Quality Criteria process (USEPA 2023). Calculations for the Criterion Maximum Concentration (CMC, representing acute toxicity) and Criterion Continuous Concentration (CCC, representing chronic toxicity) have been empirically derived. The CMC and CCC represent the greatest in-stream concentrations of a toxicant to which organisms can be exposed for a brief period of time (CMC) and for an indefinite period of time (CCC) without causing an adverse effect. For acute toxicity, the equation takes the form of:

$$CMC_{dissolved} = e^{(mA \times [\ln(hardness)] + bA)} \times CF$$

where mA and bA are known metals-specific constants and CF is a freshwater correction factor. The calculation for $CCC_{dissolved}$ takes an identical form where mA and bA are replaced by metals-specific mC, bC, and CF values. Acute and chronic criteria for Cd, Pb, and Zn are hardness dependent. An acute criterion for Fe does not exist and the chronic Fe criterion is constant (1000 mg/L). The PTS dramatically decreased metals concentrations, but calculations of hardness-adjustments aquatic life criteria are critical for evaluation of acceptable in-stream concentrations.

Examining the acute and chronic criteria for median in-stream metals concentrations demonstrates the effect of the passive treatment on receiving stream ecotoxicity (Table 2). Prior to installation of any nature-based solutions (October 2004 to December 2008, N = 49-51), only the acute criterion for Cd and the acute and chronic criteria for Pb were met at Sites 1 and 2. Zn concentrations were 4 to 5 times the respective criteria, while Fe concentrations exceeded the criterion by 20 to 84 times. After installation of the Mayer Ranch PTS in 2008 but prior to the installation of Southeast Commerce PTS in 2017 (January 2009 to January 2017, N = 37-38), acute and chronic criteria for Cd and Pb were met at both sites, and the Fe criterion was met at Site 2. Zn concentrations were 2 to 3 times the respective criteria, while Fe concentrations at Site 1 exceeded the criterion by 17 times. After installation and operation of both PTS (February 2017 to December 2022, N = 22), acute and chronic criteria for Cd, Pb, Zn and Fe were met at both sites, although in-stream concentrations remain elevated above expected background values due to legacy mining effects, including in-stream tailings deposition.

Conclusions

Water quality impairment due to unabated artesian discharges of trace-metals contaminated mine waters was documented in a first-order tributary to Tar Creek, in the abandoned Tri-State Lead-Zinc Mining District of Ottawa County, Oklahoma, USA, from 2004 to 2008. A natural infrastructure approach, based on design, installation, and operation of specific passive treatment process units promoting targeted redox-specific trace metals retention mechanisms, resulted in improvement in mine water and in-stream water quality and the restoration of in-stream ecological communities. The Mayer Ranch

Table 2 *Median in-stream Cd, Pb, Zn and Fe concentrations compared to hardness-adjusted acute and chronic aquatic life criteria for three periods of time: prior to passive treatment (2004-2008), after installation and operation of the Mayer Ranch PTS (2009-2017), and after installation and operation of both the Mayer Ranch and Southeast Commerce PTS (2017-2022). Bolded values demonstrate that in-stream metals concentrations meet the appropriate aquatic life criteria.*

	Site 1			Site 2		
	In-stream Concentration (mg/L)	**Acute criteria (mg/L)**	**Chronic criteria (mg/L)**	**In-stream Concentration (mg/L)**	**Acute criteria (mg/L)**	**Chronic criteria (mg/L)**
2004-2008	*Hardness = 2150 mg/L*			*Hardness = 2155 mg/L*		
Cd	12.41	**31.23**	7.13	8.41	**31.31**	7.14
Pb	38.92	**1395**	**54.37**	28.81	**1399**	**54.53**
Zn	7718	1577	1590	6688	1580	1593
Fe	83674	---	1000	19808		1000
2009-2017	*Hardness = 1994 mg/L*			*Hardness = 2028 mg/L*		
Cd	5.18	**29.01**	**6.71**	2.64	**29.50**	**6.81**
Pb	26.09	**1268**	**49.40**	32.94	**1295**	**50.47**
Zn	3494	1479	1492	2998	1501	1513
Fe	16842	---	1000	713	---	**1000**
2017-2022	*Hardness = 1376 mg/L*			*Hardness = 1500 mg/L*		
Cd	1.04	**20.18**	**4.99**	1.12	**21.96**	**5.35**
Pb	20.67	**790**	**30.80**	21.77	**882**	**34.38**
Zn	418	**1080**	**1089**	335	**1162**	**1172**
Fe	748	---	**1000**	606	---	**1000**

PTS annually retains approximately 36500 kg Fe, 1550 kg Zn, 20 kg Pb, and 3.3 kg Cd, and the Southeast Commerce PTS annually retains approximately 34700 kg Fe, 1575 kg Zn, 64 kg Pb, and 5 kg Cd. The prohibition of historic mass loading of trace metals into the stream resulted in increases in fish community species richness and documented return of aquatic mammals. Nature-based solutions like passive treatment provide effective and low maintenance options promoting recovery of ecosystem services in the receiving stream.

Acknowledgements

The authors thank many previous OU CREW members who contributed to this research and are especially indebted to William J. Matthews and Edie-Marsh-Matthews, who led initial fish community studies, and several private landowners, who provided access and cooperation. Major funding was provided by US Environmental Protection Agency (104(b)(3)X7-97682001), US Geological Survey (04HQAG0131), Oklahoma Department of Environmental Quality and Secretary of Energy and Environment (PO2929019163 and Q015081) and Grand River Dam Authority (100052 and A15-240).

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