

Toward Sustainability of Passive Treatment in Legacy Mining Watersheds: Operational Performance and System Maintenance

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Abstract

For 40 years, passive treatment systems (PTS) have been preferred options at many abandoned sites, in part due to presumptions of continuous water quality improvement performance and limited operation and maintenance commitments. However, documentation to support these presumptions is typically lacking. Long-term regular performance evaluation (12 years) was conducted for a large, multi-process unit PTS receiving artesian-flowing lead-zinc mine waters ($\approx 1000 \text{ m}^3/\text{day}$) at the Tar Creek Superfund Site, Tri-State Mining District, USA. Since 2008, the Mayer Ranch PTS has consistently retained $>95\%$ of targeted metal mass. Regular, periodic, and rehabilitative maintenance commitments were also documented.

Keywords: passive treatment, oxidation ponds, vertical flow bioreactors, operation and maintenance

Introduction

Metals-contaminated waters from derelict mining operations may degrade surface waters for decades to centuries (e.g. Younger et al. 2002). For almost 40 years, passive treatment systems (PTS) have been preferred options at many abandoned sites, in part due to presumptions of continuous water quality improvement performance with limited operation and maintenance commitments. Since initial evaluations of water quality improvement in natural wetland ecosystems in the late 1970s and early 1980s (Huntsman et al. 1978, Weider and Lang 1982), hundreds of PTS have been constructed worldwide to address coal and metal mining influenced waters (e.g. Rose 2010, Skousen et al. 2017). These ecologically engineered ecosystems rely on the managed promotion of naturally occurring geochemical, microbiological, and ecological mechanisms in designed process units, including ponds, wetlands, bioreactors, geochemical reactors and similar systems (Hedin et al. 1994, Younger et al. 2002, Watzlaf et al. 2004, Nairn et al. 2010). Compared to active treatment systems, which typically

rely on non-renewable energy inputs, regular additions of alkaline chemicals, and substantial labor and maintenance efforts for effective treatment, PTS rely on hydraulic head differences, extended hydrologic residence times, and provision of appropriate biogeochemical conditions in specific process units. In some cases, solar and wind power may be used to operate compressors or blowers for effective aeration.

In one of the first comprehensive analyses of PTS, Hedin et al. (1994) examined the water quality improvement performance of 13 systems built between 1987 and 1992 in the northern Appalachian coal fields of the eastern United States. These authors developed what have now become widely accepted empirically derived area-adjusted mass removal rates to aid in PTS design. Hedin et al. (1994) found that the net alkaline or net acidic nature of source water quality is the primary driver of passive treatment process unit selection. In terms of long-term performance, the authors suggested the lifetime of aerobic systems receiving net alkaline mine water, which accumulate passively precipitated iron oxide

sludges, is limited by available freeboard. For organic substrate-based systems receiving net acidic mine waters, lifetime is controlled by relationships between available CaCO_3 content and rates of bacterial sulfate reduction in the substrate. For designs current at that time, aerobic system lifetimes were estimated at 25-50 years, and organic substrate-based system lifetimes were estimated at 11 years. Furthermore, evolution of source waters through time (e.g., decreasing contaminant concentrations as reactive surfaces are exhausted, passivated, or otherwise rendered non-contributing) made these estimated lifetimes technically feasible and economically reasonable. Also noted by Hedin et al. (1994) were operation and maintenance concerns, including dike stability and pest infestations.

Skousen et al. (2017) provided a recent review of PTS, with an emphasis on systems in the Appalachian coal fields. Based on experience with hundreds of systems constructed during a period of more than 30 years, Skousen et al. (2017) discussed operation and performance of predominantly biological (e.g. aerobic and anaerobic wetlands, bioreactors) and geochemical (e.g. anoxic limestone drains, leach beds) systems. They noted similar design criteria as Hedin et al. (1994) and recognized proper process unit selection and sizing as critical to water quality improvement success. Although these authors failed to provide detailed insight into long-term performance, they emphasized the need for maintenance in all PTS.

However, despite decades of operation, detailed documentation to support continuous long-term water quality improvement performance and to examine operation and maintenance commitments is lacking for most systems. In this study, long-term regular performance evaluation (4 to 12 times per year for 12 years) was conducted for a large, multi-process unit, PTS receiving artesian-flowing lead-zinc mine waters (design flow of $\approx 1000 \text{ m}^3/\text{day}$) at the Tar Creek Superfund Site, part of the historic and now abandoned Tri-State Mining District, USA. In addition, periodic maintenance activities were documented, including

regular (marginally labor-intensive, quarterly to annually), periodic (requiring greater labor efforts, every two to three years) and rehabilitative (requiring substantial labor and equipment commitments, once per decade) maintenance.

Methods

The Mayer Ranch PTS (MRPTS, Figure 1) consists of 10 process units: an initial oxidation pond (OP), followed by parallel trains of surface flow wetlands (SFW), vertical flow bioreactors (VFBR), re-aeration ponds (ReAP), and horizontal flow limestone beds (HFLB), and a single polishing pond/wetland (PPW). The system receives three artesian borehole discharges (SA, SB, and SD) of net alkaline, metals-contaminated mine water from flooded underground workings that have been flowing unabated since 1979.

The University of Oklahoma (OU) Center for Restoration of Ecosystems and Watersheds (CREW) began periodic water quality and quantity data collection in 1998, with regular monthly sampling from 2004 to 2010, and quarterly (four times per year) sampling since 2010. MRPTS has been in effectively continuous operation since November 2008. Details on design, construction, and initial water quality improvement performance may be found in Nairn et al. (2010); details on specific process unit biogeochemical performance may be found in Oxenford and Nairn (2010), LaBar and Nairn (2018), and Nairn et al. (2018).

Regular data collection efforts included volumetric flow rates, physical parameters (pH, dissolved oxygen, temperature, specific conductance, oxidation-reduction potential, alkalinity, turbidity), sulfate, and a full suite of total and dissolved ($<0.45 \mu\text{m}$) metals (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Si, and Zn). OU CREW standard operating procedures follow US Environmental Protection Agency (USEPA) or US Geological Survey (USGS) methods for all analyses and include approved quality assurance/quality control protocols. During each field visit, any operation and maintenance activities were documented.

Results

Since regular monitoring began in 2004, source water concentrations of metals of concern have demonstrated steady and regular decreases. Figure 2 illustrates statistically significant ($p < 0.05$) decreases for total Zn concentrations for the three artesian discharges. Fe and Cd concentrations demonstrated similar changes, but Pb concentrations showed a recent anomalous increase in source waters, from $68 \pm 1.38 \mu\text{g/L}$ (2004 – 2017) to $235 \pm 18 \mu\text{g/L}$ (2018 – 2020). As previously hypothesized by Hedin et al. (1994), the evolution of source mine water chemical composition over time, coupled with decades-long design lifetimes, make PTS especially applicable to abandoned mine waters. Assuming no change in the slope of the decreases, MRPTS source zinc concentrations are predicted to be $< 0.01 \text{ mg/L}$ at some point between 2028 and 2036.

Table 1 summarizes MRPTS influent and effluent water quality data from 2008 to 2020. The system consistently increased pH and decreased concentrations of total and dissolved (dissolved data not presented) Fe, Zn, Ni, Pb, Cd, As and SO_4^{2-} . Concentrations of conservative base cations (e.g. Na) remained effectively unchanged with flow

through MRPTS, indicating minimal effects of dilution or evapotranspiration but considerable influences of designed biogeochemical mechanisms.

Figure 3 plots selected constituents for the system influents and effluents of each process unit as the ratio of measured value divided by maximum value (C/C_{max}). Iron was effectively retained via oxidation,

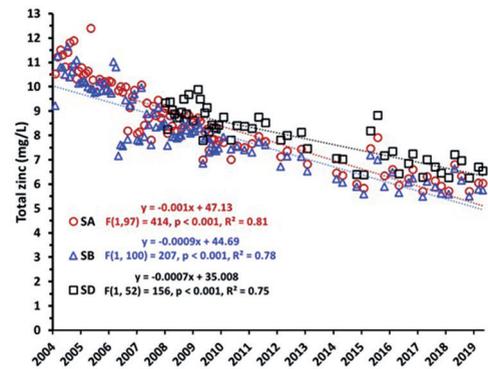


Figure 2 Total zinc concentrations versus time in three abandoned borehole artesian discharges that flow into MRPTS showing statistically significant decreases ($p < 0.001$) over time. Sample sizes (n) are 99, 102 and 54 for discharges SA, SB, and SD, respectively.

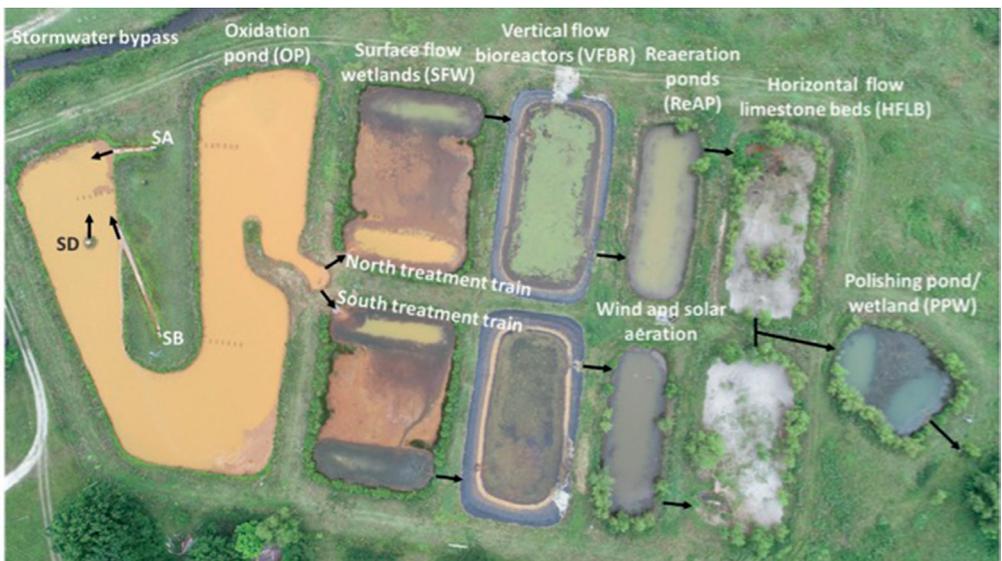


Figure 1 Aerial image of the Mayer Ranch passive treatment system in June 2018 showing three artesian discharges, ten distinct process units, and water flow paths (black arrows). Image obtained via small Unmanned Aerial System after rehabilitative maintenance operations had been completed.

Table 1 Selected water quality data (median ± standard error) for MRPTS, representing 102 influent and 51 effluent sampling events. Effluent lead and cadmium concentrations exceeded practical quantitation limits (PQLs) for only 10 and 6 events, respectively.

| | Influent | Effluent |
|-------------------|-----------|-----------|
| pH | 5.95±0.01 | 7.03±0.03 |
| Alkalinity (mg/L) | 393±3.66 | 177±6.55 |
| Fe (mg/L) | 182±2.03 | 0.33±0.06 |
| Zn (mg/L) | 7.95±0.16 | 0.14±0.12 |
| Ni (mg/L) | 0.91±0.01 | 0.08±0.03 |
| Pb (µg/L) | 69±4.73 | 30±3.26 |
| Cd (µg/L) | 16±0.61 | 1.01±0.19 |
| As (µg/L) | 62±1.14 | <PQL |
| Co (µg/L) | 60±2.93 | 5.13±2.44 |
| Sulfate (mg/L) | 2182±35 | 2096±73 |
| Na (mg/L) | 95±1.08 | 97±2.41 |

hydrolysis, precipitation and settling in the OP and SFW. Iron mass removal rates in the OP were 21±2.8 g Fe m⁻² day⁻¹, mirroring the 20 g m⁻² day⁻¹ design criteria for net alkaline waters from Hedin et al. (1994). In 2014, in situ estimates of wet iron sludge depths ranged from 41 to 116 cm in the OP (design depth ≈ 152 cm) and from 7 to 45 cm in the SFW (design depth ≈ 60 cm). Percent crystallinity increased with depth, with amorphous ferrihydrite in surface samples and evidence of goethite crystallization in deeper samples. Arsenic and other trace metals were also retained through sorptive processes in the oxidative units.

Concentrations of Zn, Cd, Pb, and other trace metals were decreased due to oxidative, reductive and sorptive processes in multiple process units. Sequential extractions of VFBR organic substrates indicated that most of the Cd, Co, Fe, Ni, Pb, and Zn were retained in the refractory organic/sulfide fraction (LaBar and Nairn 2018). These results were confirmed for Cd, Fe, Pb, and Zn through subsequent acid volatile sulfide/simultaneously extracted metals (AVS/SEM) analyses. Framboidal pyrite and zinc sulfide colloidal aggregates were identified in these substrates via scanning electron microscopy.

Since 2008, MRPTS has consistently retained >95% of targeted metal mass, including approximately 37000 kg Fe, 1700 kg Zn, 185 kg Ni, 96 kg Mn, 15 kg Pb, 13 kg As, 11 kg Cot, and 3 kg Cd on an annual basis,

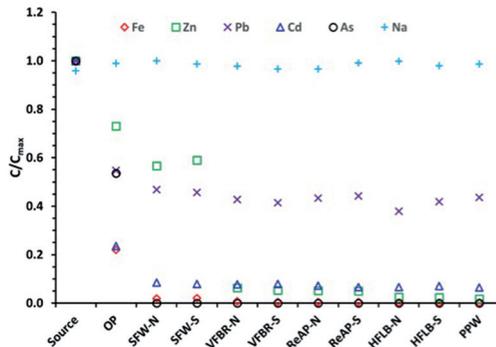


Figure 3 Selected metal concentrations with flow through MRPTS process units, plotted as median value for each location divided by system maximum median value. Plotted Pb concentrations for all locations other than Source (n=98) and OP (n=38) represent only the <3% of 459 location-date pairs where [Pb]>PQL.

with mass differences of calcium, magnesium, sodium and potassium of <5%. Effluent waters met receiving stream ambient water quality criteria and have led to reestablishment of viable and diverse fish communities and aquatic mammal populations without any active in-stream restoration.

Regular (quarterly to annually) system maintenance included monitoring of process unit water surface elevations, removal of debris (typically aquatic vegetation) from flow structures, and exclusion of aquatic mammals (e.g. muskrats, Ondatra zibethica and beavers, Castor canadensis). Water surface elevations were determined continuously by a network of pressure transducers and were critically important in determining maintenance needs (Figure 4). Periodic maintenance (every 2 – 3 years) included removal of woody vegetation (e.g. willows, Salix nigra and cottonwoods, Populus deltoides) and monitoring of solids accumulations. It is estimated that regular and periodic maintenance required approximately 300 person-hours per year.

Rehabilitative maintenance efforts were conducted twice in the first decade of operational life. By early 2017, both VFBRs exhibited evidence of hydrologic and hydraulic failure. Water throughput rates decreased dramatically, resulting in water surface elevation increases and subsequent effects on upstream process units and breaching of protective dikes (Figure 4).

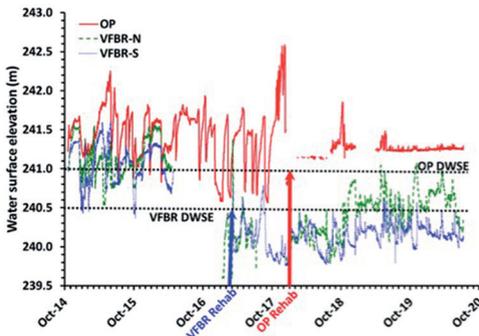


Figure 4 Water surface elevations for MRPTS OP and VFBR process units for six years. DWSE refers to design water surface elevations. Rehabilitative maintenance events indicated by vertical arrows.

These process units were dewatered and the existing organic substrate (45% spent mushroom substrate, 45% wood chips and 10% manufactured sand) was mixed with a small excavator. Despite areas with considerably degraded substrate, the original hydraulic conductivity was restored (Table 2) through these efforts.

In addition, the original buried piping structure between the OP and parallel SFW periodically exhibited substantial water throughput issues over several years. Although calculated head losses were approximately 5 cm in the piping system, measured water level differences in these units were as much as 70 cm (Figure 4), likely due to decreases in cross-sectional areas of the pipes. Repeated attempts to clean the pipes via a flexible auger (plumbers snake) and water jet flushing proved ineffective. It was hypothesized that an air lock periodically formed in the piping system. Therefore, the outflow structure of the OP was replaced with a 3-m wide open water outlet channel feeding two inlet weir structures that connected to the parallel SFW (Figure 1). The existing piping system remained in place to provide maintenance redundancy. Each rehabilitative maintenance effort required approximately two weeks of system down time and rental of small earth moving equipment.

All maintenance work was completed by OU CREW personnel. Other than removal of woody vegetation every 2-3 years, no vegetation harvesting has been required. After 12 years of continuous operation, no iron

Table 2 VFBR hydraulic conductivity (K) values pre-construction, after eight years of continuous operation and after rehabilitative efforts (which have been maintained for more than three years).

| Year | Hydraulic conductivity measurement | Vertical K (m/day) | |
|-------|--|--------------------|--------|
| | | VFBR-N | VFBR-S |
| 2008* | Laboratory falling head | 4.77 | 4.77 |
| 2016 | Laboratory falling head | 0.51 | 0.43 |
| 2016 | Field falling head | 0.13 | 0.19 |
| 2017 | Field falling head (post-rehabilitation) | 4.50 | 4.50 |

*Pre-construction

oxyhydroxide sludge removal from the OP or replacement of organic media in the VFBRs has been necessary, although accumulations and changes are regularly tracked. Notably, all rehabilitative maintenance efforts were driven by hydraulic failures and not by biogeochemical, microbiological, or ecological concerns.

Conclusions

Properly designed and sized PTS may provide water quality improvement performance for many years if adequate maintenance is completed. Design lifetimes are typically estimated at 20 years but may be extended if proper monitoring and maintenance are conducted. In this study, a 12-year old PTS receiving iron-rich lead-zinc mine waters was evaluated. Consistent long-term water quality improvement and ecological recovery of the receiving stream were documented. Maintenance efforts, including vegetation removal, nuisance aquatic mammal control, and two substantial rehabilitative efforts, were documented. VFBR organic substrates were stirred and buried piping systems were replaced. Properly designed, constructed, and maintained passive treatment systems are viable technologies for addressing legacy watershed pollution.

Acknowledgments

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