

*Aerating Off the Grid:
Advancing Passive Treatment with Solar and Wind Power*



Final Report

Cooperative Agreement S11AC20000
Applied Science Program
Office of Surface Mining, Reclamation and Enforcement

Submitted to:
Office of Surface Mining, Reclamation and
Enforcement
Mid-Continent Region
Program Support Division
Program and Technology Support Branch
501 Belle Street
Suite 216
Alton, IL 62002
Phone: 618-463-6463 x5113 or x5114

Submitted by:
Robert W. Nairn, PhD
Center for Restoration of Ecosystems and
Watersheds
University of Oklahoma
202 West Boyd Street
Room 334
Norman, OK 73019
Phone: (405) 325-5911

Table of Contents

	Page
<i>Executive Summary</i>	3
1.0 Introduction	4
<i>1.1 Iron retention via aerobic mechanisms in oxidation ponds</i>	5
<i>1.2 Re-aeration of vertical flow bioreactor effluents in re-aeration ponds</i>	7
<i>1.3 Water column re-aeration using renewable energy sources</i>	8
2.0 Project Description	9
<i>2.1 Purpose, goal and objectives</i>	9
<i>2.2 Project tasks</i>	10
<i>2.3 Experimental and analytical procedures</i>	11
3.0 Study Sites	12
<i>3.1 Mine #6 passive treatment system (Arkansas)</i>	12
<i>3.2 Rock Island #7 passive treatment system (Oklahoma)</i>	14
<i>3.3 Mayer Ranch passive treatment system (Oklahoma)</i>	17
4.0 Results and Discussion	19
<i>4.1 Overall system water quality performance</i>	19
<i>4.1.1 Mine #6 passive treatment system</i>	19
<i>4.1.2 Rock Island #7 passive treatment system</i>	22
<i>4.1.3 Mayer Ranch passive treatment system</i>	38
<i>4.2 Hydraulic performance</i>	52
<i>4.2.2 Rock Island #7 passive treatment system tracer studies</i>	56
<i>4.2.3 Mayer Ranch passive treatment system tracer studies</i>	61
<i>4.2.4 Spatial water quality</i>	65
5.0 Conclusions	68
6.0 Personnel Summary	70
7.0 Resulting Presentations and Publications	71
8.0 Literature Cited	71
Appendices	75

Executive Summary

Methods to enhance aerobic passive treatment are necessary to decrease passive treatment system size and thus reduce construction and maintenance costs. Effective methods would be both economically attractive and environmentally necessary. For this project, it was hypothesized that relatively simple, renewable energy-driven re-aeration devices requiring limited operation and maintenance would effectively enhance aerobic passive treatment processes by re-oxygenating and mixing the water column, thus positively affecting iron (Fe) oxidation and retention rates and/or sulfide (S^{-2}) and biochemical oxygen demand (BOD) removal. The efficacy of two different re-aeration devices (wind- and solar-powered) were evaluated specifically as to their effect on mine water quality improvement, oxygen demanding substance removal and hydraulic performance. Through a combination of water quality and quantity analyses (both temporal inflow/outflow and in situ spatial studies) and tracer studies (to determine retention times and other characteristics), the effects of these enhancements on treatment performance was evaluated.

Solar- and wind-driven re-aeration devices demonstrated a considerable positive influence on retention of traditional mine drainage constituents of concern, e.g. metals. At all study sites, effluent metal concentrations were significantly lower than influent concentrations and apparent rates of metal retention were similar to expected values. Solar- and wind-driven re-aeration devices also had a demonstrable effect on dissolved oxygen concentrations, oxygen percent saturation and oxidation-reduction potential values. Concentrations of oxygen demanding substances (BOD and total sulfide) in vertical flow bioreactor effluents were effectively decreased by subsequent solar- and wind- driven re-aeration in downstream ponds. Although concentrations varied widely over time, overall decreases were documented. Re-aeration had considerable influence on the hydraulic characteristics of passive treatment system process units. Re-aeration resulted in considerable differences in hydraulic retention time, number of reactors in series, dispersion number and index of short-circuiting

Overall, off the grid aeration shows promise as a passive treatment tool. Enhanced removal of nuisance constituents like sulfide produced by vertical flow bioreactors shows potential for further application. The influence of these devices on iron oxidation removal rates warrants further study at a suite of sites with appropriate flow and system conditions. Further inquiry into hydraulic performance is also warranted, as the relationship between specific hydraulic characteristics and water quality improvement performance are evaluated.

1.0 Introduction

The environmental impacts of untreated mine waters are well-documented (e.g., Younger et al. 2002). These waters often contain elevated concentrations of dissolved metals (especially Fe, Mn, Al, and sometimes Pb, Zn, Cd, Cu, Ni, etc.), sulfate and acidity. Whether net alkaline or net acidic, elevated metal concentrations in mine waters can be ecologically devastating to receiving waters and effective treatment is necessary for watershed recovery. At abandoned sites, water quality degradation may last for decades or longer without treatment.

Traditional mine drainage active treatment technologies rely on additions of highly alkaline chemicals (e.g., NaOH, Ca(OH)₂, CaO) to facilitate metal oxidation, hydrolysis and precipitation under controlled pH conditions. These relatively laborious and cost-intensive operations require regular maintenance and active manipulation and therefore are not viable options for most abandoned mines (e.g., Younger et al. 2002, Watzlaf et al. 2004). Passive treatment technologies, i.e., those that rely on natural biogeochemical and microbiological processes to ameliorate mine drainage problems, provide a viable treatment alternative to costly and laborious active treatment technologies. Passive systems require less operational and maintenance labor and have lower initial costs but require larger land areas than traditional chemical treatment systems. These low-maintenance and relatively inexpensive natural systems are often the only viable option for abandoned mine drainage treatment (e.g., Hedin et al. 1994, Watzlaf et al. 2004; Nairn et al. 2010).

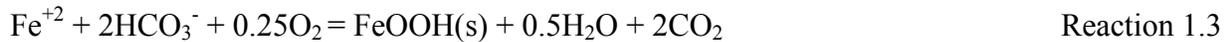
Hundreds of passive treatment systems have been constructed to address abandoned mine water quality problems. In some cases, system performance has been less than adequate due to lack of understanding of site-specific water quality or quantity characteristics, required treatment mechanisms or the limited maintenance necessary to sustain performance, all of which may result in poor performance. The overall goal of this project was to advance the treatment effectiveness of abandoned mine drainage passive treatment systems by examining, understanding and improving aeration in both oxidation and re-aeration ponds. Although common passive treatment process units, these aerobic ponds often require large land areas to effectively remove iron, the principal contaminant addressed via oxidation, hydrolysis and settling mechanisms, or to re-aerate waters after passage through anaerobic conditions in vertical flow bioreactors. Therefore, methods to enhance aerobic treatment are necessary to decrease passive treatment system size and thus reduce construction and maintenance costs. This study examined the role of off the grid aeration technologies (wind- and solar-powered aeration) in enhancing overall passive treatment system performance. Two common passive treatment system process units were targeted: oxidation ponds (for iron retention) and re-aeration ponds (to aerate waters after vertical flow bioreactors).

1.1 Iron retention via aerobic mechanisms in oxidation ponds

The dominant physicochemical treatment processes in oxidation ponds are iron oxidation, hydrolysis, precipitation and settling. Therefore, they are only applicable to the successful treatment of net alkaline mine drainages (whether due to natural bicarbonate concentrations or alkalinity produced in anoxic limestone drains or similar technologies) as substantial proton acidity is the result of these reactions (Hedin et al. 1994; Watzlaf et al. 2004). These processes are represented in reactions 1.1 and 1.2, where reduced ferrous iron (Fe^{+2} or Fe(II)) is oxidized to ferric iron (Fe^{+3} or Fe(III)), which readily hydrolyzes to form solid ferric oxyhydroxide and produce proton acidity under net alkaline conditions.



The overall reaction for iron oxidation and hydrolysis with subsequent neutralization of proton acidity by bicarbonate alkalinity results in reaction 1.3.



Numerous studies have long-identified ferrous iron oxidation (reaction 1.1) as the rate limiting step (e.g., Schnaitman et al 1969, Singer and Stumm 1970) in this reaction scheme. Despite the wealth of literature on the role of acidophilic bacteria in iron oxidation in natural waters, under net alkaline, circum-neutral pH conditions, abiotic iron oxidation is the prevailing process (e.g., Kirby et al. 1999, Athay et al. 2001). Stumm and Morgan (1996) discussed limitations on the oxidation of dissolved iron forms (Fe^{+2} , $FeOH^+$, $Fe(OH)_2$) as well as sorbed Fe(II). According to Dempsey et al. (2001), oxidation of $Fe(OH)_2$ dominates at $pH > 5$. This homogenous oxidation of dissolved $Fe(OH)_2$ may be described by the following rate equation (equation 1.1).

$$rate_{\text{homogenous}} = \frac{k_1[Fe^{+2}][O_2]}{\{H^+\}^2} \quad \text{Equation 1.1}$$

where the rate constant includes the formation constant for $Fe(OH)_2$ (after Dempsey et al. 2001). Sung and Morgan (1980) identified ferric oxyhydroxide as a catalyst for abiotic oxidation of Fe(II). The oxidation of sorbed Fe(II) is described as heterogeneous and may be described by the following rate equation at $pH > 5$ (equation 1.2 after Dempsey et al. 2001):

$$rate_{\text{heterogenous}} = \frac{k_2[Fe(III)][Fe^{+2}][O_2]}{\{H^+\}} \quad \text{Equation 1.2}$$

The overall rate at $\text{pH} > 5$ is therefore the sum of the homogenous and heterogeneous reactions. Furthermore, Park and Dempsey (2005) found that rates of Fe(II) oxidation were proportional to dissolved oxygen concentrations and both dissolved and sorbed Fe(II) up to a given surface density.

Iron oxidation has been determined to limit the rates and therefore the treatment effectiveness of certain passive treatment process units (e.g., Hedin et al. 1994, Younger et al. 2002). Kirby et al (1999) conducted field work and developed a model examining iron oxidation kinetics in several passive systems. They found that above pH 5, treatment effectiveness was dictated by pH, temperature and dissolved oxygen concentrations and stated that “failure to consider Fe(II) oxidation rates in treatment system design may result in insufficient iron removal”. Dempsey et al. (2001) found that oxygen transfer limits ferrous iron oxidation in pond-type passive systems in Pennsylvania. They also found that, because of its profound effects on pH, degassing of dissolved CO_2 played a significant role. Dempsey et al. (2001) concluded that greater O_2 and CO_2 transfer and higher heterogeneous rates were provided in systems of active mixing (e.g., channels as opposed to ponds). Hedin (2009) identified iron oxidation as the rate limiting step in a series of ponds receiving large flows of net alkaline, Fe(II)-rich mine drainage. In downstream wetlands, particulate settling of oxidized iron solids limited retention.

It is apparent that effective iron removal via aerobic mechanisms requires oxygenation of untreated mine drainage, which in turn consumes oxygen. Each mole of O_2 can oxidize 4 moles of Fe^{+2} (or each mg of O_2 can oxidize 7 mg of Fe^{+2}). Although oxygen solubility is temperature dependent, according to Watzlaf et al. (2004), a maximum practical dissolved oxygen level of 8 mg/L is realistic in passive treatment systems. At this level, only about 56 mg/L of Fe^{+2} can be oxidized without re-oxygenation of the water.

In most situations, the mass transfer of oxygen into the water column of passive treatment systems occurs either via passive wind-induced mixing or entrainment over aeration structures like stone or wooden barriers (either within or between process units) or through channelized flow. Mass transfer of oxygen into a completely mixed body of water may be described as a first order process (equation 1.3).

$$\frac{d[\text{O}_2]}{dt} = k_L a_t [\text{O}_2]_{\text{sat}} - [\text{O}_2] \quad \text{Equation 1.3}$$

where k_L is the bulk liquid film transfer rate coefficient and a_t is the total specific surface area. As oxygen is continually consumed by water column processes (e.g., iron oxidation), additional oxygen enters the water column under given solubility constraints. Because homogenous and heterogeneous iron oxidation rates are both first order with respect to O_2 , effective oxygen transfer plays a vital role in iron retention.

For effective passive retention of iron from net alkaline mine drainage, mass transfer of O₂ into the water column is not the only important gas-water interface process. Mass transfer of CO₂ out of the water column is also vitally important, in part because of its considerable effects on pH. Mine waters often have elevated CO₂ partial pressures on the order of 10^{-0.8} to 10^{-0.2} atm. Because these values greatly exceed atmospheric CO₂ partial pressures (~10^{-3.5} atm), CO₂ tends to exsolve from mine waters during retention in passive treatment systems. This process decreases dissolved CO₂ and exchanges bicarbonate alkalinity for hydroxyl ions, thus increasing pH but not affecting alkalinity (reaction 1.4).



Because homogenous and heterogeneous iron oxidation rates are second order and first order, respectively, with respect to pH, CO₂ degassing plays a vital role in iron retention in aerobic passive treatment systems.

Because many mine drainage discharges contain greater than a nominal 50-60 mg/L Fe⁺², re-aeration after initial treatment is necessary. As iron oxidizes, hydrolyzes and precipitates, entrainment structures like rip-rap barriers often coat rapidly with accumulated iron oxyhydroxides rendering them relatively useless. Channels may fill with accumulated precipitates, detrimentally impacting hydrologic flow paths and treatment effectiveness. Also, although effective and efficient, fossil-fuel powered aerators like those common in municipal wastewater treatment lagoons are not a passive option. Renewable energy-driven aeration devices, providing power off the grid, were examined in this study to determine if they are an effective option.

1.2 Re-aeration of vertical flow bioreactor effluents in re-aeration ponds

Vertical flow bioreactors have become common passive treatment system process units (Kepler and McCleary 1994, Younger et al. 2002, Watzlaf et al. 2004, Nairn et al. 2009). Also called vertical flow cells or ponds, these units are applicable to net acidic mine waters and are typically designed for vertically-oriented water flow through a layer of waste organic substrate (e.g., spent mushroom compost, various manures, yard wastes) overlying a layer of limestone gravel. They produce alkalinity through bacterial sulfate reduction (BSR; reaction 1.5) and limestone (CaCO₃) dissolution (reaction 1.6) and are typically followed by aerobic ponds.



Although biological alkalinity generation in vertical flow bioreactors is primarily provided by BSR, other microbially-mediated reductive processes occur. In temperate regions, the contribution of biological processes to overall alkalinity production is seasonal (Watzlaf 1996) while abiotic processes occur at a relatively constant rate year-round. Significant metal sequestration may occur in vertical flow bioreactors via sulfide precipitation (e.g., Hedin and Nairn 1993, Willow et al. 1998, Crisp et al. 1998, Nairn et al. 1999, Athay et al. 2003, Athay 2003). However, excess sulfide is often produced leading to odor and toxicity problems in the effluent (Porter 2004, Porter and Nairn 2008, Nairn et al 2009, C. McCool, personal communication 2009, Porter and Nairn 2010). In addition, as the organic substrates are microbially acted upon, elevated BOD may be present. At least during initial operational start up, vertical flow bioreactor effluent waters are often chemically reduced, containing elevated H₂S and BOD and lacking oxygen, and may be detrimental to receiving streams. In effect, one problem (elevated metals) may be traded for another (elevated oxygen demand).

Properly designed passive treatment systems include aerobic process units after vertical flow bioreactors. These aerobic units are typically ponds or wetlands and rely on passive mass transfer of atmospheric oxygen into the water column (see equation 1.3) to offset any oxygen demand. In some cases, aeration structures (steps, channels, etc.) may be included. However, it is well-documented that passively aerated ponds or wetlands may be unable to effectively re-aerate these organic-rich waters (e.g., Yopez and Nairn 2012). They are not unlike municipal or agricultural wastewaters. Aeration devices, preferably powered off the grid by renewable-energies, may provide sufficient active mixing to address these problems.

1.3 Water column re-aeration using renewable energy sources

Submerged aeration systems are commonly used in aquaculture, lake and reservoir management and lagoon operations to promote mixing and to increase dissolved oxygen levels (e.g., Westerman and Zhang 1997, Boyd 1998, DeMoyer et al. 2003). A typical system consists of a renewable power source that builds pressure in an air compressor. The pressure is released through a valve and line to a submerged diffuser at the bottom of the pond which produces a “bubble plume” that rises to the surface. The bubbles cause vertical and lateral circulation by entraining water as they rise. The bubble interfaces help to transfer oxygen to the water as they rise as well. At the pond surface, further oxygen mass transfer occurs due to turbulence at the air-water interface. Although the available literature does not address the exsolution of carbon dioxide by these types of systems, they should work just as well for this purpose. In general, two power options exist for renewable-energy based water column re-aeration devices: wind and solar.

Windmill-powered re-aeration is a well-established technology for aquaculture. According to Superior Windmill Aeration Systems (2009), these systems have the ability to develop a steady stream of air at more than 30 pounds of pressure “*enabling deep placement of the diffuser for*

maximum cleansing action” The towers are typically 12-20 feet in height with the compressor mounted directly behind the fan blades. A single diaphragm compressor can produce 1.5 cubic feet per minute (cfm) and a dual diaphragm compressor can produce 3 cfm, both at a nine mile per hour (mph) wind speed.

Solar powered units use small solar panels to generate energy for a battery-driven compressor. Because the panels continuously charge the battery, these units will continue to work at night and on cloudy days. According to Solar Aerators (2009), these units can run continuously for two weeks of cloudy days. Using a single 0.5 amp, 18-volt solar panel and a standard 12-volt automobile battery, these units can pump 1.0 cfm; use of multiple diffusers can pump up to 4 cfm.

2.0 Project Description

2.1 Purpose, goal and objectives

The purpose of this project was to examine sustainable, low-maintenance and cost-effective passive treatment methods for abandoned coal mine drainage discharges, a topic of considerable interest to the Office of Surface Mining Reclamation and Enforcement (OSMRE). The project specifically addressed *"the implementation and evaluation of aeration devices which do not require power from the grid"*, identified as High Priority Topic #2 in the OSMRE FY2010 Applied Science Cooperative Agreements Announcement.

The work was completed by personnel from the Center for Restoration of Ecosystems and Watersheds (CREW) at the University of Oklahoma (OU), which maintains a well-established research program (<http://crew.ou.edu>) centered on applications of ecological engineering - the design and construction of sustainable ecosystems that integrate human society with its natural environment for the benefit of both (Mitsch and Jorgensen 2004). CREW currently focuses on passive treatment of coal and metal mine waters and has access to five state-of-the-art, full-scale passive treatment systems in the Mid-Continent Region. The CREW team is multidisciplinary and consists of engineers and scientists (faculty, staff and students) of diverse expertise and interests who together are attempting to “unlock the black box” of passive treatment.

The overall goal of the project was to advance passive treatment technology for use in remote locations by implementing renewable energy-driven (wind- and solar-powered) aeration devices to improve oxidative treatment mechanisms in aerobic ponds. Aerobic ponds are utilized in two ways in comprehensive passive treatment systems; i) to promote oxidative iron removal mechanisms and ii) to re-aerate waters discharging from anaerobic process units (e.g., vertical flow bioreactors). In both cases, methods that enhance performance and which do not require power from the grid may help to decrease system size and thus reduce construction and maintenance costs. It is important to note that many abandoned mine drainage discharges may

only be addressed by non-profit watershed groups with limited funding and resources. Therefore, effective methods to reduce costs are both economically attractive and environmentally necessary.

It was hypothesized that relatively simple, renewable energy-driven re-aeration devices will effectively enhance aerobic passive treatment processes by re-oxygenating and mixing the water column. Commercially available wind- and solar-powered re-aeration systems are commonly used in aquaculture and lake or pond management. The project addressed the effectiveness of these devices in both oxidation (designed for iron oxidation, hydrolysis and settling) and re-aeration (designed for re-oxygenation to promote sulfide and biochemical oxygen demand conversion) ponds. The project was conducted at three field sites, two of which were included in the original proposal (Mine #6 and Rock Island #7) and a third (Mayer Ranch) added due to flow problems at one of the original sites.

Three related objectives were pursued in completion of the project goal. Objective 1 was to comprehensively evaluate water quality changes and hydraulic performance of two passive treatment systems, through collection of water quality and water quantity information and performance of tracer studies. Objective 2 was to enhance the iron retention performance of oxidation ponds through design, installation and monitoring of sustainable aeration devices. Objective 3 was to enhance the oxygenation performance of re-aeration ponds through design, installation and monitoring of sustainable aeration devices and to evaluate hydrogen sulfide (H₂S) and biochemical oxygen demand (BOD) removal.

2.2 Project tasks

Six project work tasks were initially identified to address the project purpose, goal and objectives. They are reiterated here for clarity and references are provided to appropriate portions of this final report where each task is addressed.

Task 1 focused on inflow/outflow and within-system water quality. Comprehensive water quality sampling and analyses were completed at all three study sites and included regular (monthly) visits. Task 2 addressed water quantity (e.g., volumetric flow rate) characterization to fully evaluate system performance with and without operation of re-aeration devices. Task 3 focused on use of conservative tracer studies to more fully evaluate the effects of aeration on hydraulic characteristics of the system. Task 4 was the procurement, installation and operation of wind- and solar-powered aeration units. Task 5 evaluated passive treatment water quality improvement performance and optimization. Task 6 included data analysis and dissemination to end users and Task 7 was regular project reporting.

Tasks, 1, 2, 3, 5 and 6 are addressed in Section 4.0 Results and Discussion. Task 4 is described in Section 3.0 Study Sites. Task 7 included previously submitted Quarterly Progress Reports,

this final report and associated deliverables. Additional publications, presentation and other project outputs are discussed in Appendix A.

2.3 *Experimental and analytical procedures*

Input/output water quality/quantity monitoring at each of the sites was initially conducted on at least a monthly basis. Water quality samples were collected only from flowing waters (e.g., sample of stagnant water were not collected), thus limiting water quality data collection efforts at some sites. Spatial water quality at selected locations within the ponds was also conducted. All water quality sampling and analyses followed USEPA, APHA or USGS methods (USEPA 1983; APHA 1998; USGS, 2003). Because of the highly mineralized nature of the mine waters and likely presence of substantial alkalinity, certain water quality parameters were analyzed either *in situ* or immediately upon collection. Measurements of pH, dissolved oxygen (both as concentration and as percent saturation), specific conductance, conductivity, resistivity, salinity, total dissolved solids, oxidation-reduction potential (ORP) and temperature were obtained *in situ* using a multi-parameter water quality instrument (YSI 600QS with 650MDS controller). Turbidity was determined on a portable Hach 2100P Ratio Turbidimeter. Total alkalinity was measured via Hach Digital Titrator (Method 8203) with sulfuric acid cartridges of the appropriate normality and volumetric glassware. All field instruments will be properly calibrated and maintained and appropriate Quality Assurance/Quality Control procedures were followed.

For each sampling event (location-date pair), samples were collected for analysis of total and dissolved metals (e.g., Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn), anions (Br^- , Cl^- , F^- , NO_2^- , NO_3^- , PO_4^{3-} and SO_4^{2-}), biochemical oxygen demand (BOD), mineral acidity and total sulfide (S^{2-}). Water samples were gathered in pre-cleaned 1-L HDPE bottles at sampling locations between appropriate process units. Sample for anions, mineral acidity, and BOD analyses were left unpreserved. Samples for total metals analyses were field-acidified with trace-metal grade HNO_3 to a pH <2 to prevent precipitation of dissolved metals. Another sample was field-filtered upon collection (through a 0.45 μm in-line filter) and field-acidified to pH < 2 for dissolved metals analyses. Samples for total sulfide analysis were field-preserved with zinc acetate and sodium hydroxide. All samples were placed on ice in insulated coolers and stored at 4°C upon collection. All samples were returned to the CREW laboratories at the University of Oklahoma for laboratory analysis.

Total and dissolved metals were analyzed by EPA 6000 series methods via inductively coupled plasma-optical emission spectroscopy after hot acid microwave digestion (USEPA Methods 3015 and 6010b; USEPA 2006). Anions were determined by ion chromatography following USEPA 300 Series Methods (USEPA 1993). Hot mineral acidity was determined by the modified H_2O_2 titration method, BOD by the five-day incubation BOD test and sulfide by spectrophotometry following development of standard curves (APHA 1998).

Flow measuring devices were installed to gather accurate volumetric discharge rates at all sites. At Rock Island #7 and Mayer Ranch, pressure transducers were installed in final effluent pipes allowing the use of the Chezy-Manning equation to estimate flow. At Mine #6, similar calculations were done using a deployable Sontek Argonaut Acoustic Doppler Velocimeter (ADV) to estimate open channel flows. Volumetric flow rates were also obtained during sampling events by using a calibrated bucket and stopwatch or Sontek FlowTracker Hand-Held ADV, where appropriate. By using concentration and discharge rate pairs, contaminant mass load calculations were completed for all sampled locations.

To complete conservative tracer studies, pulsed injections of Rhodamine were completed at all three sites, with aeration systems both on and off. Rhodamine has very little natural background concentration (Smart and Laidlaw 1977) and was detectable at 0.5 µg/L using a YSI 600 Optical Monitoring System (OMS) datasonde equipped with Rhodamine-specific sensors.

In addition, data-recording water quality monitoring sondes (YSI 6000 and YSI 600 series) were deployed for various periods at all sites. These units, after proper maintenance and calibration, were deployed to collect near-continuous (typically 15 minute interval) water quality data including pH, dissolved oxygen (both as concentration and as percent saturation), specific conductance, conductivity, resistivity, salinity, total dissolved solids, oxidation-reduction potential (ORP) and temperature.

3.0 Study Sites

3.1 Mine #6 passive treatment system (Arkansas)

The Mine # 6 passive treatment system was constructed by the Arkansas Department of Environmental Quality (ADEQ), with assistance provided by OSMRE, in 2009 (Figure 3.1). Located near Huntington, AR, the system receives water from the abandoned Central Coal and Coke Mine #6 underground complex which was mined in the early 1900s. Prior to treatment, a net acidic (pH 5.5, net acidity 143 mg/L, Fe 39 mg/L, Mn 2 mg/L) flow of approximately 660 liters per minute (174 gallons per minute) discharged from an abandoned air shaft. The passive treatment system was designed with a vertical anoxic limestone drain (VALD), initial oxidation pond (1820 m²), vertical flow bioreactor (2800 m²) and final aeration pond (1380 m²; McCool 2010). The approximately 86-m VALD includes a dolomitic stone overlain by high quality limestone. Elevation drops throughout the system were limited by local topography and available area, so a pipe header, rock bed, and header cell were implemented to improve flows. According to McCool (2010), H₂S gas was commonly noted and dissolved oxygen was < 0.2 mg/L in the final aeration pond.

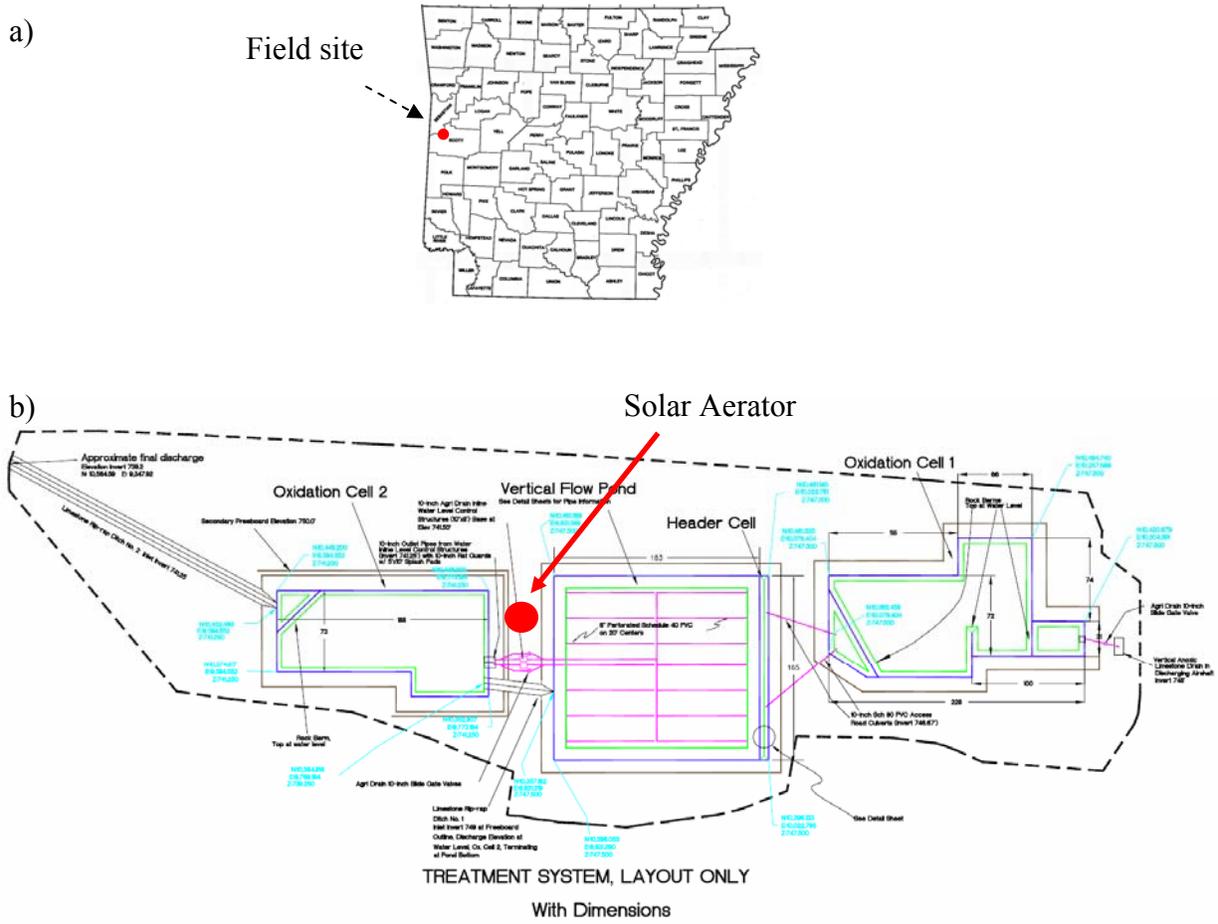


Figure 3.1. a) Location of the Mine #6 passive treatment system in Sebastian County, AR and b) plan view design showing vertical anoxic limestone drain, oxidation pond (oxidation cell 1), vertical flow bioreactor (vertical flow pond) and re-aeration pond (oxidation cell 2). In this figure, mine water flows from right to left through these process units.

The focus of the study at this site was the re-aeration pond (after the vertical flow bioreactor). The pond had a nominal depth of 0.6 m, allowing not only analysis of the effects of re-aeration, but the possible implications of re-suspension of accumulated organic matter from the pond bottom. The system was readily accessible and had influent and effluent sampling locations allowing establishment of continuous flow monitoring stations and tracer deployment/recovery sites. Adequate land area was readily available on system dikes for establishment of multiple diffuser solar-driven re-aeration units. Given the site topography, wind-driven re-aeration units were unlikely to be successfully implemented.

As part of this project, the ADEQ installed a Keeton Industries Inc. SB-3 Sollar Lake Bed Aeration System at this site (Keeton Industries 2013). The system included two 125-watt, 7.1-amp solar panels mounted 8 feet above grade, two high volume brushless continuous DC compressors with air output of 1.8 cfm in continuous duty operation, a 30-amp charge control center, cooling manifold with pressure relief valve and pressure gauge, three 9-inch Duraplate diffusers fitted with 10" fine bubble dura-disk flexible membranes connected to Alpine self-weighted PVC tubing, a single 255-amp hour deep cycle solar battery and a 12/24 volt smart box converter.

Data collection at the Mine #6 site began in January 2011. However, substantial variability in volumetric flow rates were immediately noted. Although the system was designed for flows of about 175 gallons per minute, continuous monitoring data shows a flashy hydrology with flows near 1000 gallons per minute and extended periods of zero flow, which significantly impeded project progress. Based on information provided in Quarterly Project Reports (QPRs), related telephone conversations with OSMRE (November 17, 2011) and emails, and site visits on November 29 and December 13, 2011 and January 12, 2012, continuing the project research at the Mine #6 site was deemed to be significantly problematic. **Given the approval of OSMRE via email on December 5, 2011, it was decided to remove the Mine #6 site from further study and instead include the paired re-aeration cells at the Mayer Ranch passive treatment system near Commerce, OK.** Therefore, further discussion of the Mine #6 site is limited to available water quality and quantity data only and is provided for reference.

3.2 Rock Island #7 passive treatment system (Oklahoma)

Through a cooperative effort of the OSMRE, Oklahoma Conservation Commission, University of Oklahoma, and others, the Rock Island #7 passive treatment system, aka Whitlock/Jones 145 CSI AML Project or Hartshorne passive treatment system, was constructed in late 2005 to treat an abandoned (ca. 1930s) underground discharge from the Rock Island Coal Company #7 mine near the town of Hartshorne, Pittsburg County, Oklahoma (Figure 3.2). Prior to construction, the mine discharge was sampled periodically for several years and showed considerable fluctuation in both water quality and quantity. Measured discharge rates ranged from <1 to approximately 75 liters per minute (~0.25 to 20 gallons per minute). Metal and anion concentrations varied

with each sampling event, although temperature, pH, and dissolved oxygen remained relatively consistent. The acidic nature of the discharge, coupled with median concentrations of Fe and Mn of 765 and 18 mg/L, respectively, warranted a plan for treatment.

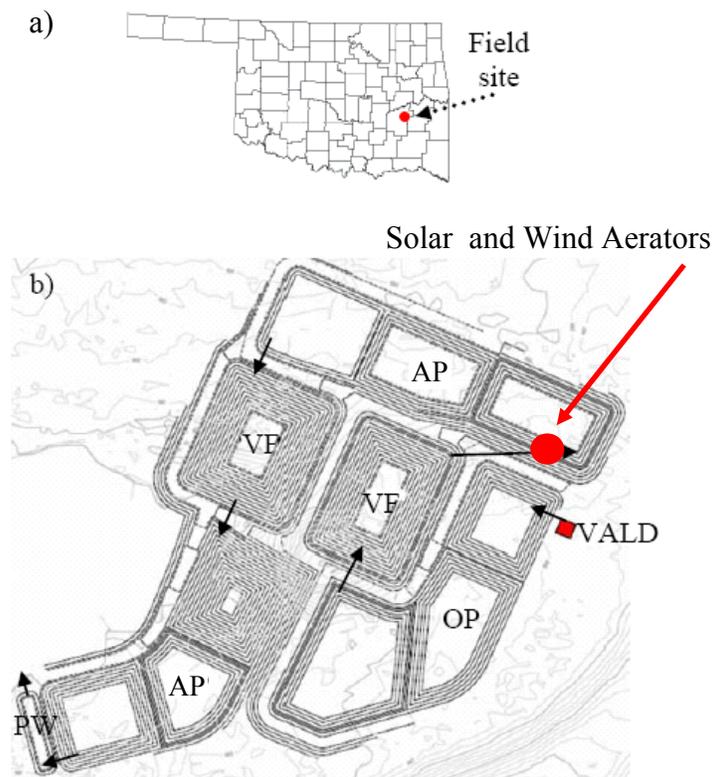


Figure 3.2. a) Location of the Rock Island #7 passive treatment system in Pittsburg County, OK and b) plan view of system showing process units (VALD = vertical anoxic limestone drain, OP = oxidation pond, VF = vertical flow bioreactor, AP = aeration pond and PW = polishing wetland).

An abandoned fan shaft (total depth approximately 56 m) from which the water discharged in an artesian manner was converted to a VALD and serves as the first process unit in the passive treatment system. The VALD was designed to perform similarly to a traditional horizontally-oriented anoxic limestone drain. The shaft was first filled with approximately 34 m of local dolomitic stone (to provide long-term stability) which was then covered by 22 m of high calcite limestone (to provide alkalinity generation capacity). An effluent header pipe directs water from the VALD to the remainder of the passive treatment system. The first oxidation pond (total surface area = 1215 m²) was designed for iron retention via oxidation, hydrolysis and settling and includes three sub-cells separated by limestone re-aeration structures. Although designs called for a 0.30-m drop between sub-cells, final construction yielded variable elevation differences. This cell discharges to a vertical flow cell (650 m²) containing a spent mushroom substrate layer over limestone which was designed for alkalinity generation via biotic and abiotic mechanisms. This first vertical flow cell discharges to an aeration pond (1215 m²) again including three sub-cells separated by limestone re-aeration structures. This pond is followed by another vertical flow cell (650 m²). This second vertical flow cell is followed by another aerobic pond (1215 m²) again including three sub-cells separated by limestone re-aeration structures. This cell discharges into a small polishing wetland before entering an existing on-site pond. Final construction of the system left limestone re-aeration structures in each of the three aerobic process units with variable and in some cases, quite limited (~ 0.04 m), vertical elevation changes.

The Rock Island #7 site provides excellent conditions for the project research. The focus of the study was the first oxidation pond and first aeration pond (after the first vertical flow bioreactor). The surface areas of both ponds are divided into three distinct sub-cells of different design water depths. The first sub-cell A has a nominal water depth of 1.5 m, while sub-cells B and C have nominal water depths of 1.2 and 0.9 m, respectively. The system is readily accessible and has well-established and maintained influent and effluent sampling locations. Establishment of continuous flow monitoring stations and tracer deployment/recovery sites was straightforward. Adequate land area was readily available on system dikes for establishment of both wind- and solar-driven re-aeration units.

For wind-powered re-aeration at the Rock Island #7 oxidation pond, an Outdoor Water Solutions (OWS) 20-foot Deluxe Windmill was selected and installed in early 2011. This system features a 20-foot galvanized steel tower, 12 73"-blades mounted on a self-governing head, one-piece hub assembly, and a head-mounted vertical displacement compressor capable of producing 3-4.5 cfm at 30 psi depending on wind speed, self-weighted line and two diffusers.

For solar-powered re-aeration in the Rock Island #7 aeration pond, a Pennington Equipment Company EKBS-15 Solar Aerator System was selected and installed in early 2011. This system

features an integrated 45-W power source (three 15-W solar panels) with 14.5 volt output, a PEC 45 0.6 amp-hour pump house containing four compressors with air output of 0.3 cfm continuous duty operation, solar charge controller, single rubber diaphragm bubble diffuser, self-weighted tubing, and a 12-V deep cycle marine battery.

Although plagued by similar, yet nowhere near as extreme, flow variability problems like Mine #6, data collection at the Rock Island #7 site continued throughout the period of study. During significant portions of 2011, 2012 and 2013, flows at Rock Island #7 decreased to zero at the final effluent, although small amounts of mine water continued to enter the system. On less frequent occasions, mine water inflows also ceased. Flows between process units within the system varied in a like manner and appeared to be strongly dependent on local precipitation availability. The installed solar- and wind-powered aeration devices continue to operate after project completion.

3.3 Mayer Ranch passive treatment system (Oklahoma)

The Mayer Ranch passive treatment system is located in the Tar Creek Superfund Site, the Oklahoma portion of the abandoned Tri-State Lead-Zinc Mining District of Oklahoma, Kansas and Missouri. Although not addressing coal mine drainage, the system was included in this project starting in January 2012 after the failure of the Mine #6 site to meet project needs. It already included both solar- and wind-powered re-aeration devices previously funded and installed through the U.S. Environmental Protection Agency (USEPA) project "*Design, Construction and Evaluation of a Passive Treatment System for Contaminated Mine Waters*", Project X7-97682001-0 through USEPA's Region 6 CWA 104(b)(3) program to OU CREW.

Installation of the Mayer Ranch passive treatment system and associated aeration devices was completed in November 2008. It was designed to address approximately 1000 liters per minute (264 gallons per minute) of net alkaline, circum-neutral pH mine waters containing 189 mg/L Fe, 10 mg/L Zn, 70 µg/L Pb and 18 µg/L Cd. The system consists of ten distinct process units including two parallel trains (Figure 3.3). Waters from three discharges (SA, SB, and SD) flows 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 by Nairn et al. 2009.

a)



b)

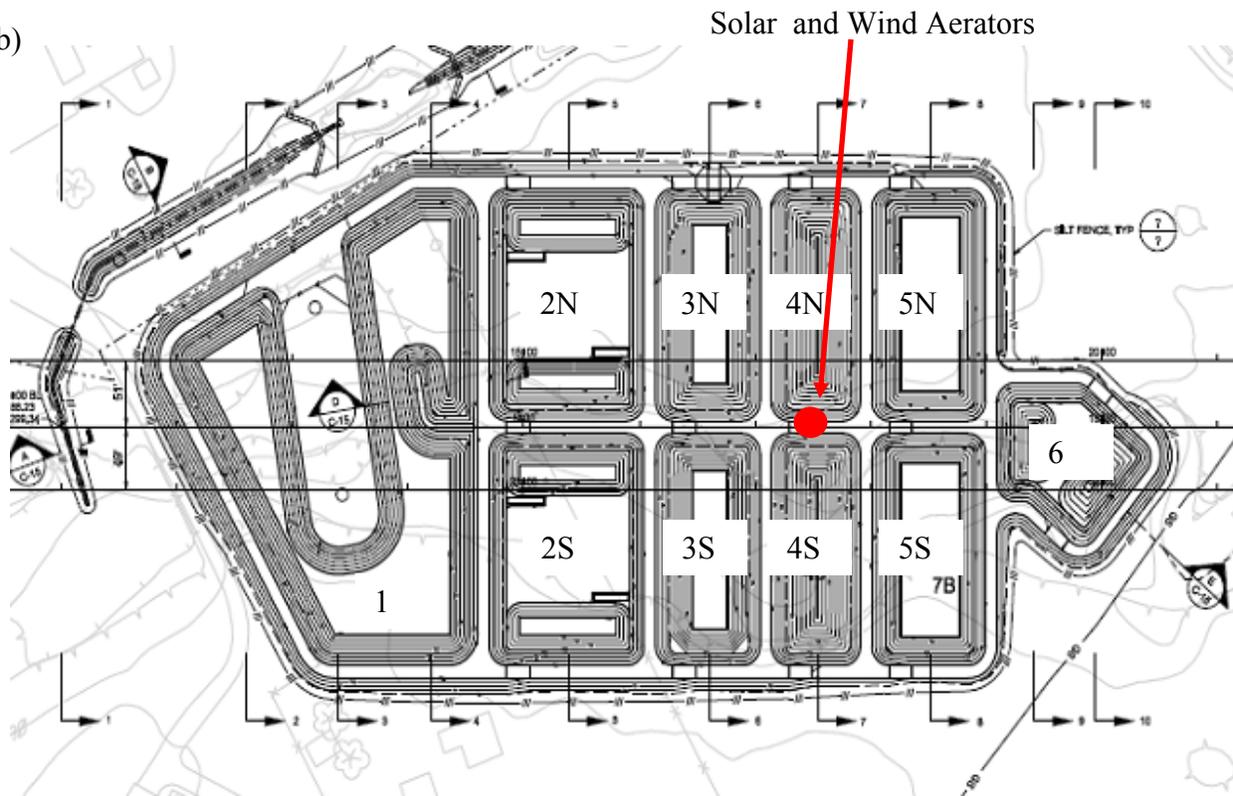


Figure 3.3. a) Location of the Mayer Ranch passive treatment system in Ottawa County, OK and b) plan view of system showing process units: initial oxidation pond (1), followed by parallel surface-flow aerobic wetlands/ponds (2N and 2S), vertical-flow bioreactors (3N and 3S), re-aeration ponds (4N and 4S), horizontal-flow limestone beds (5N and 5S), and a single polishing pond/wetland (6).

The north re-aeration pond (4N) includes a Superior Windmill Aeration System including a 20-foot tower, 70" 12-blade upwind turbine, Jet Stream direct drive compressor producing 30 PSI and 1.5 cfm at wind speed of nine mph and operational to 40 mph and dual rubber diaphragm bubble diffusers. The system has been in continual operation for over five years.

The south re-aeration pond (4S) includes a Keeton Industries SB-1 Solear Lake Bed Aeration System. This system includes a single 120-W solar panel, high volume compressor, 30-amp charge control center, 210 amp-hour deep cycle solar battery, 12/24 volt smart box converter and dual rubber diaphragm bubble diffusers. Like the windmill aeration system, the solar system has been in continual operation for over five years.

Flows at the Mayer Ranch system were perennial throughout the study period and were consistently measurable at the final system effluent. However, for a brief time during the project period, excessively high water levels in selected process units inhibited data collection. The vertical flow bioreactors experienced excessively high water levels due to a combination of precipitation, animal activity and organic layer permeability problems. Water was diverted from these cells while a repair was put in place, this eliminating flow from these units into the re-aeration cells. They were put back online as rapidly as possible. The installed solar- and wind-powered aeration devices continued to operate in the re-aeration cells during this period and continue to operate after project completion.

4.0 Results and Discussion

As described in Section 2.3 *Experimental and analytical procedures*, data collection was accomplished either through field site visits (and associated sampling, analyses and sample and/or data collection) or near-continuous monitoring with deployed datasondes. For purposes of this section, the data are described sequentially for each study site. Overall water quality changes and hydraulic performance are examined to determine the effects of aeration.

4.1 Overall system water quality performance

4.1.1 Mine #6 passive treatment system

Although the Mine #6 passive treatment system was eliminated from study in late 2011, a brief data summary is provided. Near-continuous flow monitoring was established at the final outflow of the passive treatment system (Cell 3 out) and data were generated on 5-minute intervals. Both stage and volumetric discharge rates were flashy and quite variable (Figure 4.1). Perhaps most problematic, they ceased completely during the summer and fall of 2011 for extended periods of time.

At this time, eastern Oklahoma and western Arkansas were in the midst of an ongoing and prolonged regional drought. Through 2011, the East Central and Southeast Climate Regions of Oklahoma were at 78% and 69% of normal and were down 10 and 16 inches, respectively, from expected rainfall amounts (data not available for western Arkansas). In addition, at the Mine #6 site, discussions with ADEQ personnel indicated that mine waters that would typically enter the passive treatment system were discharging at another lower elevation point on adjacent land. Several conversations indicated that the problem was unlikely to be rectified any time soon (the adjacent landowner was utilizing the mine pool discharge as stock water and did not want it be eliminated from flowing on his land). Specifically, cattle had apparently caused a standpipe to dislodge, thus draining the mine pool at this lower elevation than the inflow to the Mine #6 passive treatment system. Conversations with ADEQ and OSMRE personnel (C. McCool 2011; P. Behum 2011) both indicated that a speedy solution, although likely feasible, was unlikely to happen.

From April 2011, the Mine #6 passive treatment system received little to no inflow. A single measurable system effluent discharge of approximately 0.02 gallons per minute was obtained over this period of study. The Mine #6 site was selected for this study in part because design flow rates were several hundred gallons per minute, much greater than any anticipated flow at the Hartshorne site, thus providing significant opportunity for evaluation of off-the-grid re-aeration performance under different hydrologic conditions. Given the lack of flow, and the unlikelihood of flow re-establishment, the Mine #6 site was eliminated from further evaluation under this project in late 2011.

Table 4.1 provides a statistical summary of the limited set of general water quality data collected at the Mine #6 passive treatment system. The waters discharging from the VALD (Cell 1 In) maintained circum-neutral pH and contained considerably alkalinity. However, it was somewhat surprising that they contained dissolved oxygen of greater than 1 mg/L (9-15 % saturation), perhaps indicative of the great difficulty in collecting valid samples with such low flow rates. After passing through the vertical flow bioreactor (Cell 3 In), alkalinity and circum-neutral pH was maintained. Dissolved oxygen and oxidation-reduction potential both decreased substantially. The system final effluent (Cell 3 Out), appeared to be positively influenced by solar-driven re-aeration, with increased dissolved oxygen concentrations and positive oxidation-reduction potential.

BOD concentrations (Figure 4.2) demonstrate considerable variation for the limited data set. Mean BOD concentrations were higher in the cell 3 effluent than in those waters exiting the vertical flow bioreactor. However, BOD values were well below problematic values (typical wastewater treatment plant target effluent concentrations are 30 mg/L). However, given the limited sample size, and the lack of data collection from the system with the aerators not running, firm conclusions are unable to be made.

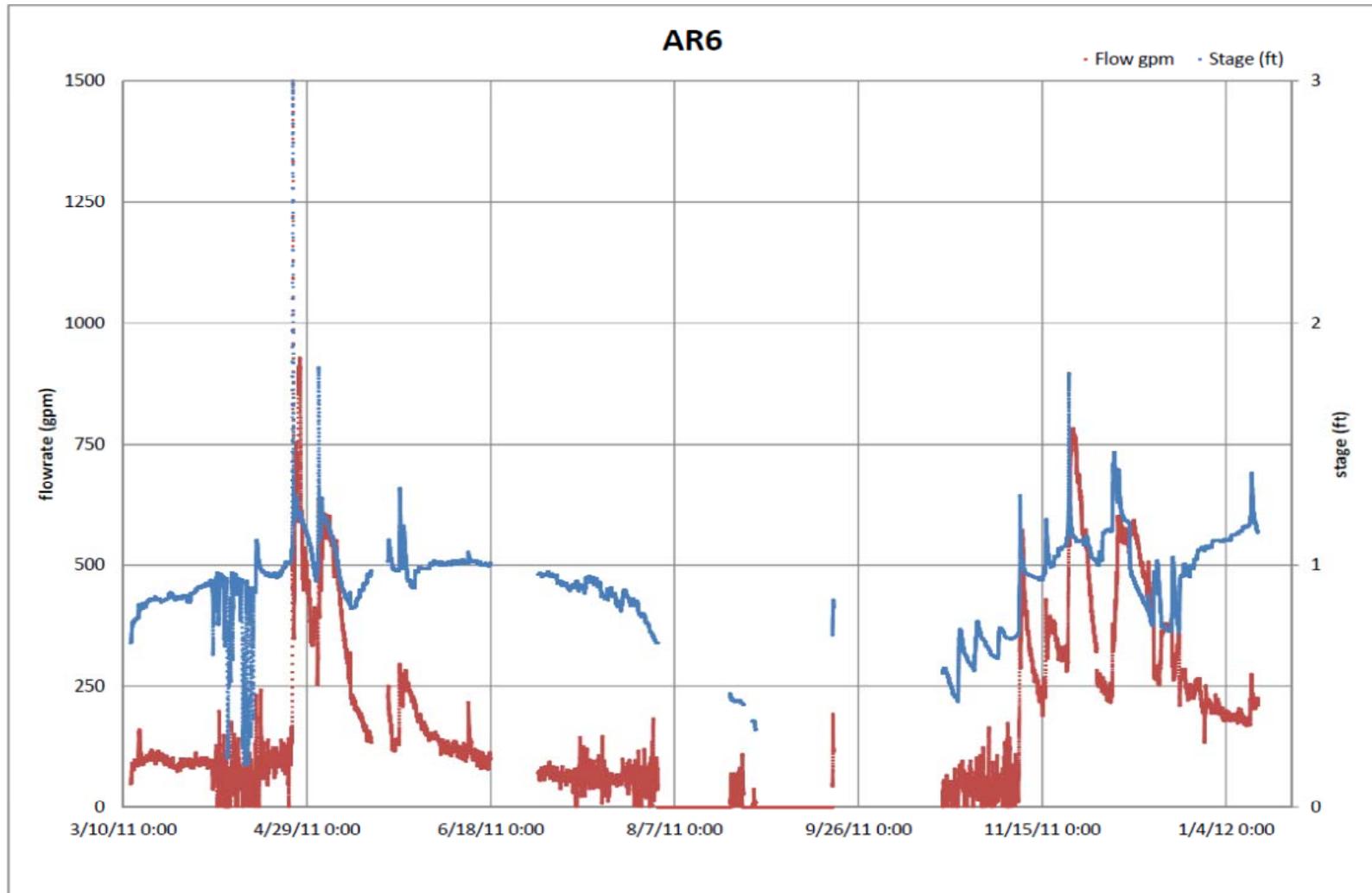


Figure 4.1. Near-continuously monitored stage and volumetric discharge rate at the final effluent of the Mine #6 passive treatment system (Cell 3 Out). Note the flashy nature of the hydrology and extended periods of little or no flow.

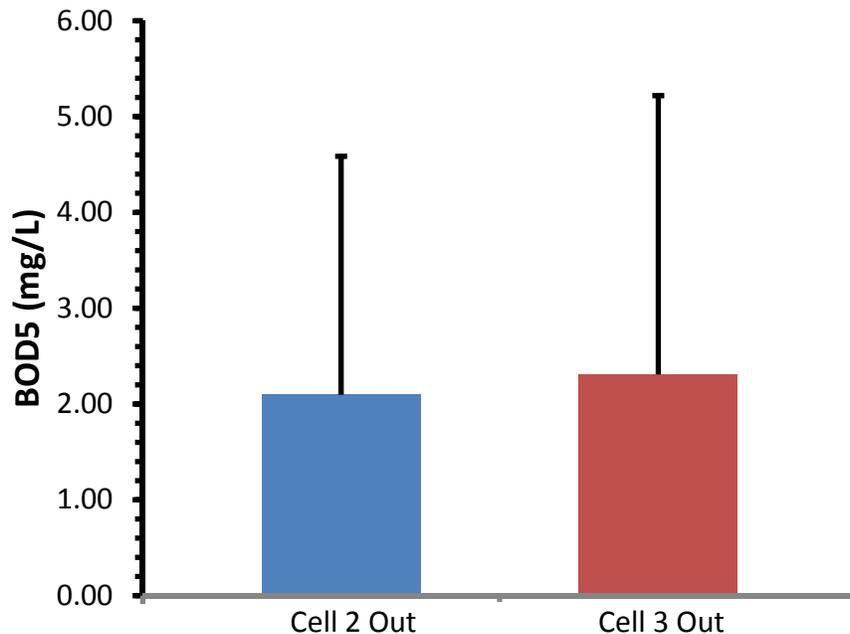


Figure 4.2. Biochemical oxygen demand (BOD) values for the Mine #6 re-aeration process unit.

4.1.2 Rock Island #7 passive treatment system

The Rock Island #7 passive treatment system also experienced substantial flow variability over the study period. On many sampling visits, flow was either nonexistent or very low. On other occasions, discernible flow was found only at a limited subset of the sampling locations between cells, likely indicating the variable nature of the mine pool discharge and/or the effects of precipitation on the system itself.

Figure 4.3 shows a portion of the near-continuous discharge data for the final system effluent (Cell 5 Out). Despite a number of substantial peaks after large storm events, the mean discharge rate was 26.49 ± 70.75 liters per minute (7.00 ± 18.69 gallons per minute). These values are near the system design flow rate of 10 gallons per minute. Water quality data and samples were able to be collected for at least one system location on 21 of 30 sampling events.

Water quality physical parameters are summarized in Table 4.2. The VALD added substantial alkalinity to the mine drainage discharge (300-400 mg/L total alkalinity) and maintained a circum-neutral pH. The apparent elevated DO concentrations in the system influent may be representative of the difficulty of sampling the VALD effluent. Water rises in the limestone-filled mine shaft, enters a horizontal header structure and then is directed to three influent pipes

Table 4.1. Summary statistics for water quality physical parameter data (temperature, specific conductance, dissolved oxygen as percent saturation and concentration, oxidation-reduction potential, total alkalinity and turbidity) for the Mine #6 passive treatment system. Sample sizes at each location varied from 4-6 depending on flow. "SE" refers to standard error of the mean; "Max." and "Min." refer to maximum and minimum values, respectively.

	Temp. (°C)	SC (mS/cm)	DO (%Sat)	DO (mg/L)	pH (su)	ORP (mV)	T. Alk. (mg/L CaCO ₃)	Turb. (NTU)
Mine #6 VALD (Cell 1 In)								
Mean	14.70	0.687	15.35	1.53	6.57	-61	105	1.12
SE	1.60	0.017	4.42	0.39	0.30	40	2.30	0.08
Max.	16.96	0.711	21.60	2.08	6.99	-5	109	1.23
Min.	12.44	0.663	9.10	0.97	6.14	-117	102	1.01
Mine #6 Cell 2 (Vertical Flow Bioreactor) Out								
Mean	19.52	0.840	14.60	1.30	6.70	-119	306	2.65
SE	2.21	0.037	1.38	0.07	0.08	4	51	0.97
Max.	29.37	0.972	21.00	1.60	6.99	-99	494	8.43
Min.	11.67	0.709	10.00	1.06	6.41	-141	116	0.31
Mine #6 Cell 3 (Re-aeration Pond) Out								
Mean	19.93	0.768	86.78	7.57	7.40	20	202	12.64
SE	2.55	0.017	10.21	0.47	0.13	6	23	2.04
Max.	33.89	0.850	145.30	10.27	7.93	45	319	23.03
Min.	12.19	0.713	56.70	6.03	6.93	-9	115	3.14

fitted with 90° elbows. Under low flow conditions, obtaining valid DO concentrations at these locations is challenging. The outflow of the first oxidation pond maintained elevated DO concentrations but varied from net alkaline to net acidic depending on sampling event, with pH ranging from 4.01 to 6.34. Cell 2 is a vertical flow bioreactor and outflows showed consistent alkalinity and circum-neutral pH, along with negative ORP values and low DO concentrations. The next aeration unit (Cell 3) increased DO concentrations substantially with a mean of 9.69 ± 0.78 , greater than saturation at near 111% on average. ORP values were consistently positive but alkalinity values varied widely, likely due to changes in influent acidity and alkalinity. The final system effluent (Cell 5 Out) maintained a consistent circum-neutral pH, measurable alkalinity, positive ORP values, and on average increased DO concentrations (67% saturation). Despite the inclusion of two vertical flow bioreactors in the system producing anaerobic waters, the final effluent waters were appropriate for discharge to an existing farm pond and subsequent receiving stream.

The Rock Island #7 passive treatment system had a dramatic and significant effect on mine drainage metals concentrations (Table 4.3). The first process unit, an oxidation pond (Cell 1), substantially decreased iron concentrations in the alkaline and circum-neutral pH conditions created by the VALD. Calcium and magnesium concentrations, indicative of limestone dissolution in the VALD, were elevated throughout the system, and especially so in the first process unit. Magnesium is typically considered to be conservative in passive systems and concentrations through the Rock Island #7 systems support this concept.

With the notable exceptions of lead, nickel and zinc, trace metal concentrations in the Rock Island system were at or below detectable limits. Overall, lead, nickel and zinc were retained in the system both in oxidation cells (likely due to iron oxyhydroxide sorption and co-precipitation) and in the vertical flow bioreactors (likely due to exchange, sorption and sulfide precipitation). The Rock Island #7 mine waters are somewhat unique in displaying elevated mean potassium (39 mg/L) and sodium (850 mg/L) concentrations. It is speculated that the mine pool may be hydraulically connected to an oil field waste disposal site in an adjacent reclaimed surface mine. Manganese concentrations do not change substantially with flow through the system.

The temporal variability of selected total and dissolved metals concentrations at the Rock Island #7 passive treatment system are displayed in Figures 4.4 through 4.11. Total and dissolved metals track closely, and with the single exception of aluminum concentrations in Cell 3 Out samples, were not significantly different ($p > 0.05$, two-tailed tests assuming equal variance). Despite the significant flow variability throughout the Rock Island #7 system, water quality improvement via metal retention was consistent for total and dissolved iron, zinc, nickel and lead. Manganese concentrations exhibited both temporal and spatial variability throughout the system. Although sample matching problems (the assumption that water exiting a selected

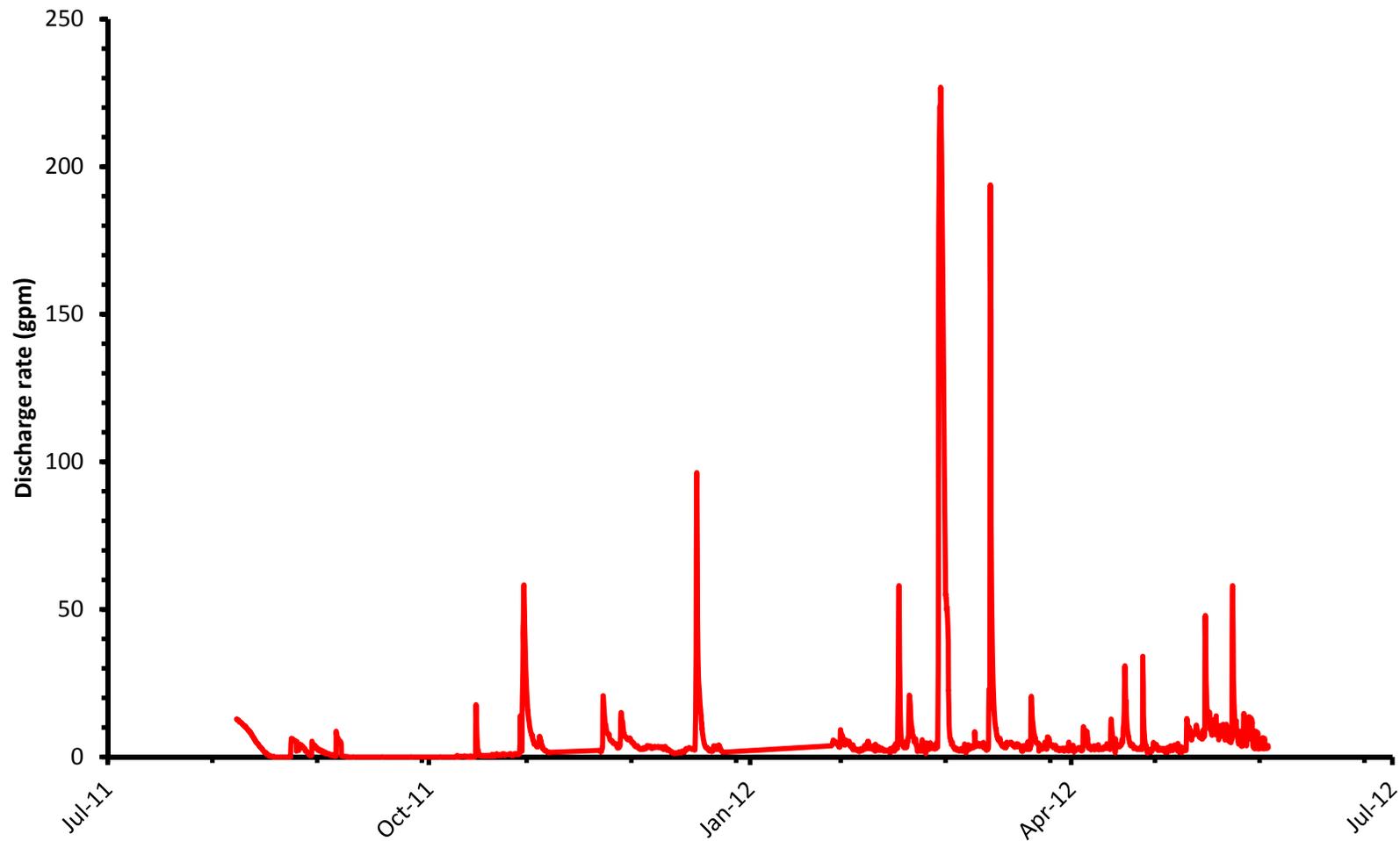


Figure 4.3. Near-continuously volumetric discharge rate at the final effluent of the Rock Island #7 passive treatment system (Cell 5 Out). Note the flashy nature of the hydrology and extended periods of little or no flow.

Table 4.2. Summary statistics for water quality physical parameter data (temperature, specific conductance, dissolved oxygen as percent saturation and concentration, oxidation-reduction potential, total alkalinity and turbidity) for the Rock Island #7 passive treatment system. Sample sizes at each location varied from 13-21 depending on flow. "SE" refers to standard error of the mean; "Max." and "Min." refer to maximum and minimum values, respectively.

	Temp. (°C)	SC (mS/cm)	DO (%Sat)	DO (mg/L)	pH (su)	ORP (mV)	T. Alk. (mg/L CaCO ₃)	Turb. (NTU)
RI#7 VALD (Cell 1 In)								
Mean	20.33	6.15	23.40	2.09	6.23	-27	343	1.97
SE	0.39	0.51	6.19	0.55	0.04	3	9	0.46
Max.	20.94	8.91	62.30	5.50	6.43	-13	394	4.80
Min.	16.45	4.39	4.70	0.41	5.94	-47	315	0.57
RI#7 Cell 1 (Oxidation Pond) Out								
Mean	20.82	6.39	89.73	8.02	6.34	111	45	32.14
SE	1.89	0.30	4.15	0.45	0.23	22	8	5.71
Max.	31.43	9.13	116.70	11.72	7.53	265	136	86.00
Min.	6.49	4.51	36.70	3.20	4.01	22	0	3.80
RI#7 Cell 2 (Vertical Flow Bioreactor) Out								
Mean	21.01	6.45	23.44	1.98	6.54	-86	94	3.80
SE	1.59	0.42	8.74	0.70	0.06	25	10	1.48
Max.	28.24	9.29	75.50	6.29	6.81	97	165	15.50
Min.	12.14	4.58	2.10	0.19	6.29	-174	54	0.95
RI#7 Cell 3 (Re-aeration Pond) Out								
Mean	19.78	6.72	110.64	9.69	7.50	195	65	10.17
SE	1.89	0.50	7.46	0.78	0.29	42	7	1.40
Max.	29.99	11.35	152.30	16.86	8.70	480	118	20.40
Min.	6.77	3.36	47.60	4.11	3.86	17	22	0.40
RI#7 Cell 5 (Final System) Out								
Mean	21.79	5.83	67.39	7.34	7.06	228	51	14.99
SE	1.43	0.33	9.94	1.07	0.14	26	9	4.26
Max.	28.90	7.35	92.70	13.19	7.49	296	93	36.00
Min.	16.40	4.48	14.90	3.63	6.29	68	25	4.00

Table 4.3. Summary of total metals concentrations for the Rock Island #7 passive treatment system. "N" refers to the number of samples for which concentrations of any given analyte were above detection limit. "BDL" refers to below detection limits. "SD" and "SE" refer to the standard deviation and standard error of the mean.

		Al	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
		-----mg/L-----														
VALD																
	Mean	0.02	BDL	506	0.03	0.004	0.005	0.004	255	38.18	148	3.65	850	0.04	0.14	0.04
	N	21		21	21	8	6	16	21	21	21	21	21	21	21	21
	SD	0.02		96.46	0.02	0.002	0.003	0.001	153	9.06	49.91	2.14	334	0.02	0.05	0.04
	SE	0.00		21.05	0.004	0.001	0.001	0.0003	33.32	1.98	10.89	0.47	72.92	0.005	0.01	0.01
C1 Out																
	Mean	0.03	BDL	490	0.01	0.002	BDL	0.004	47.53	40.59	155	4.03	902	0.02	0.06	0.02
	N	21		21	10	5		16	21	21	21	21	21	20	18	21
	SD	0.02		65.94	0.01	0.001		0.001	82.96	10.00	42.79	2.99	275	0.01	0.04	0.01
	SE	0.01		14.39	0.004	0.0003		0.0002	18.10	2.18	9.34	0.65	59.95	0.003	0.01	0.003
C5 Out																
	Mean	0.03	BDL	471	BDL	BDL	BDL	0.01	0.16	39.66	159	3.40	952	0.01	0.03	0.02
	N	13		13				11	13	13	13	13	13	11	13	12
	SD	0.02		69.92				0.003	0.13	7.67	34.12	3.92	212	0.01	0.01	0.02
	SE	0.01		19.39				0.001	0.04	2.13	9.46	1.09	58.70	0.002	0.002	0.01

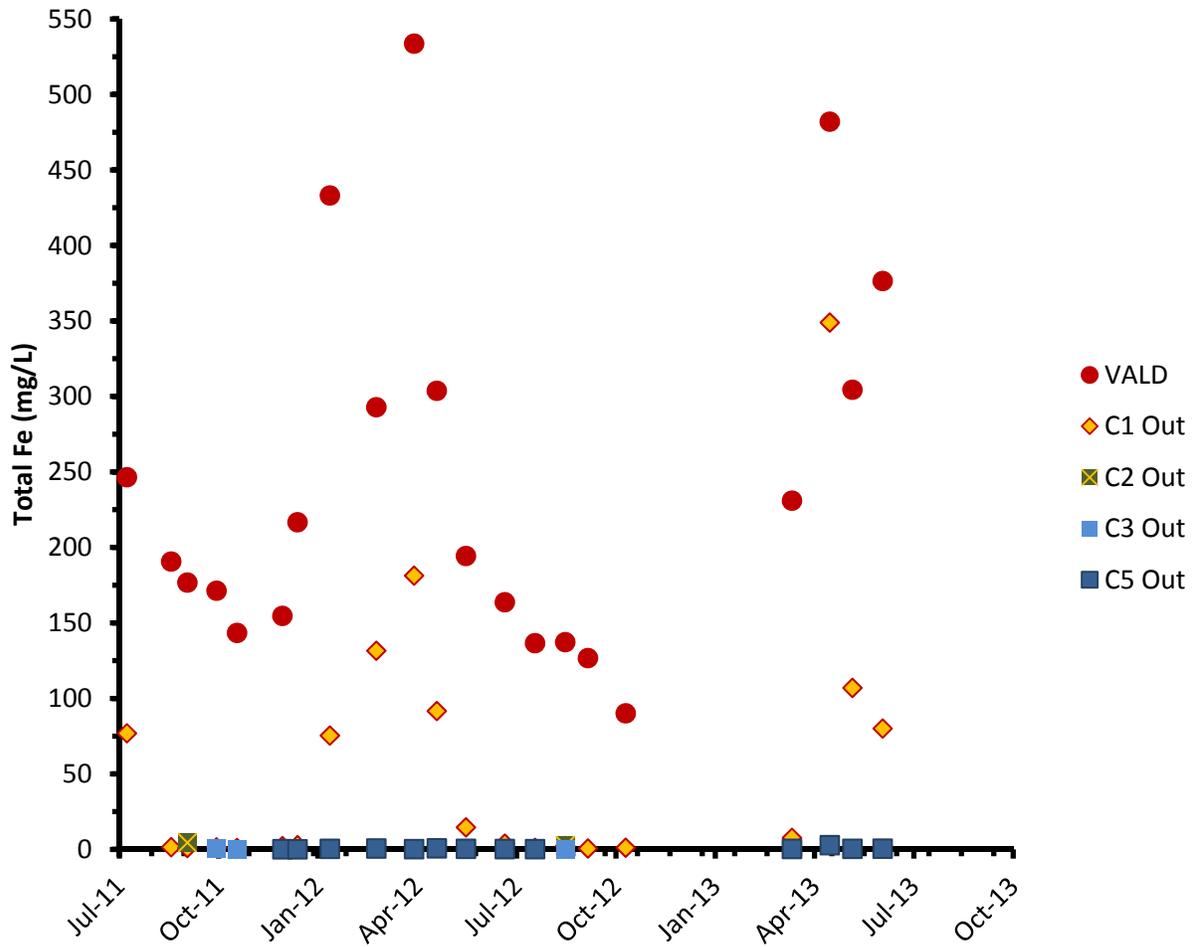


Figure 4.4. Total iron concentrations versus time at the Rock Island #7 passive treatment system. VALD represents waters discharging from the vertical anoxic limestone drain (mine drainage source), and C1, C2, C3 and C5 Out represent effluents from the initial oxidation pond, first vertical flow bioreactor, re-aeration pond, and the full system (after an additional vertical flow bioreactor and second re-aeration pond), respectively.

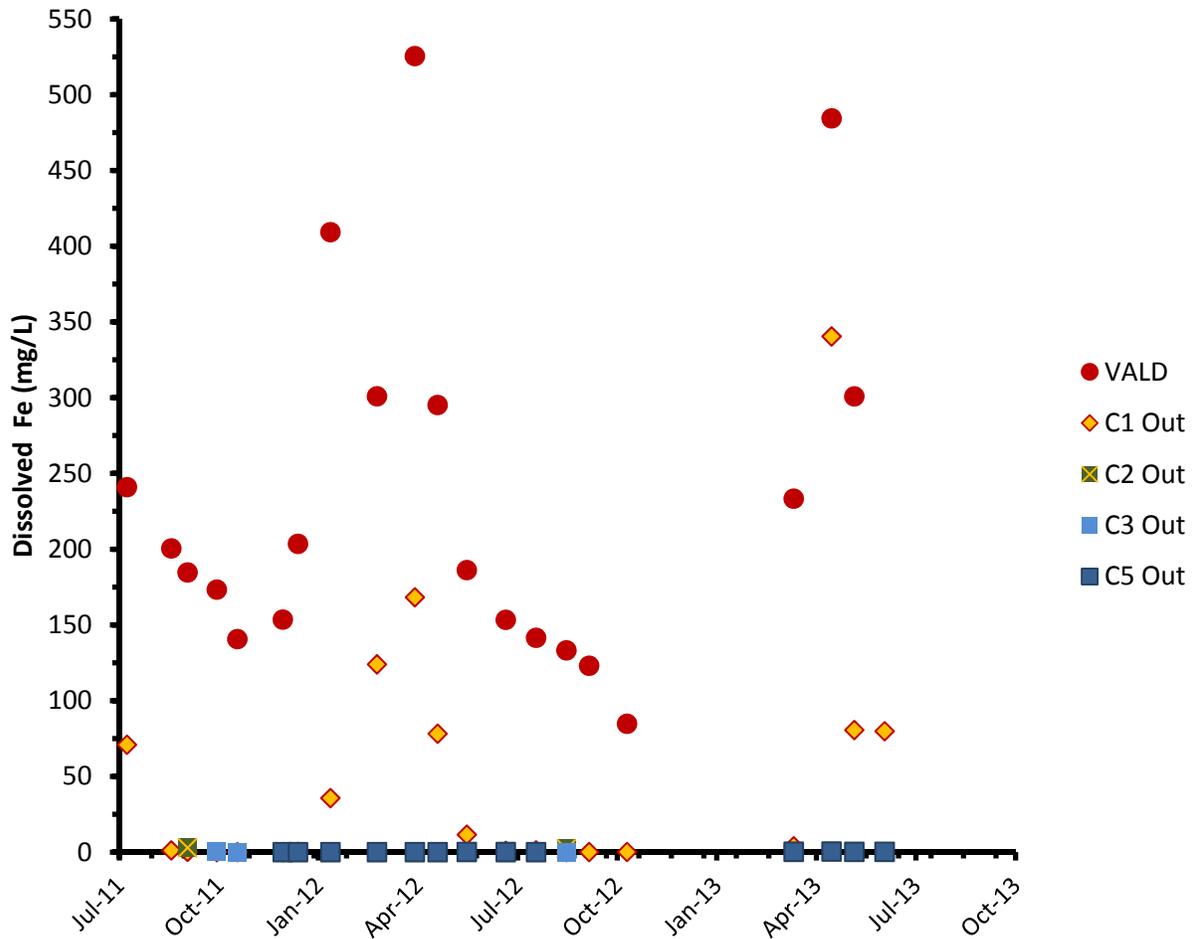


Figure 4.5. Dissolved iron concentrations versus time at the Rock Island #7 passive treatment system. VALD represents waters discharging from the vertical anoxic limestone drain (mine drainage source), and C1, C2, C3 and C5 Out represent effluents from the initial oxidation pond, first vertical flow bioreactor, re-aeration pond, and the full system (after an additional vertical flow bioreactor and second re-aeration pond), respectively.

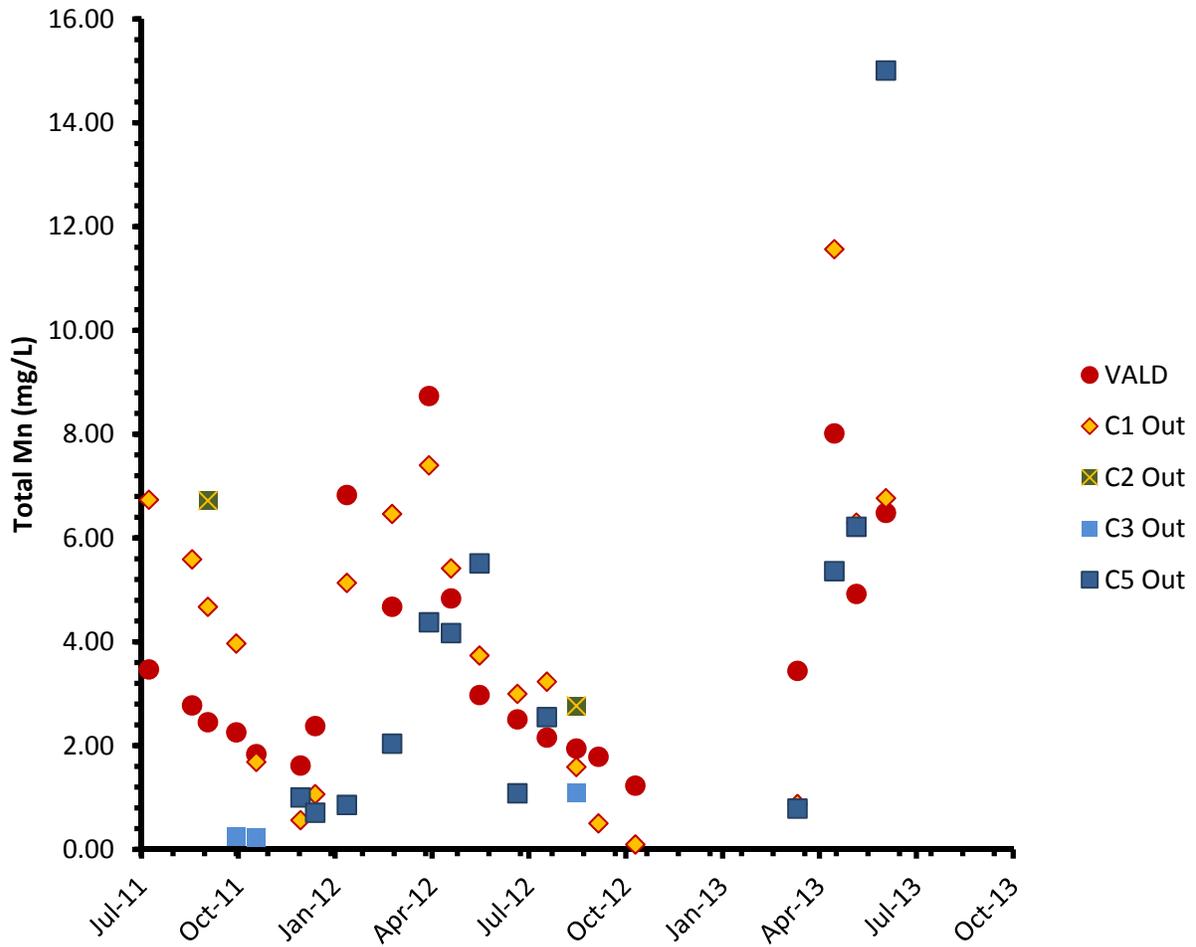


Figure 4.6.. Total manganese concentrations versus time at the Rock Island #7 passive treatment system. VALD represents waters discharging from the vertical anoxic limestone drain (mine drainage source), and C1, C2, C3 and C5 Out represent effluents from the initial oxidation pond, first vertical flow bioreactor, re-aeration pond, and the full system (after an additional vertical flow bioreactor and second re-aeration pond), respectively.

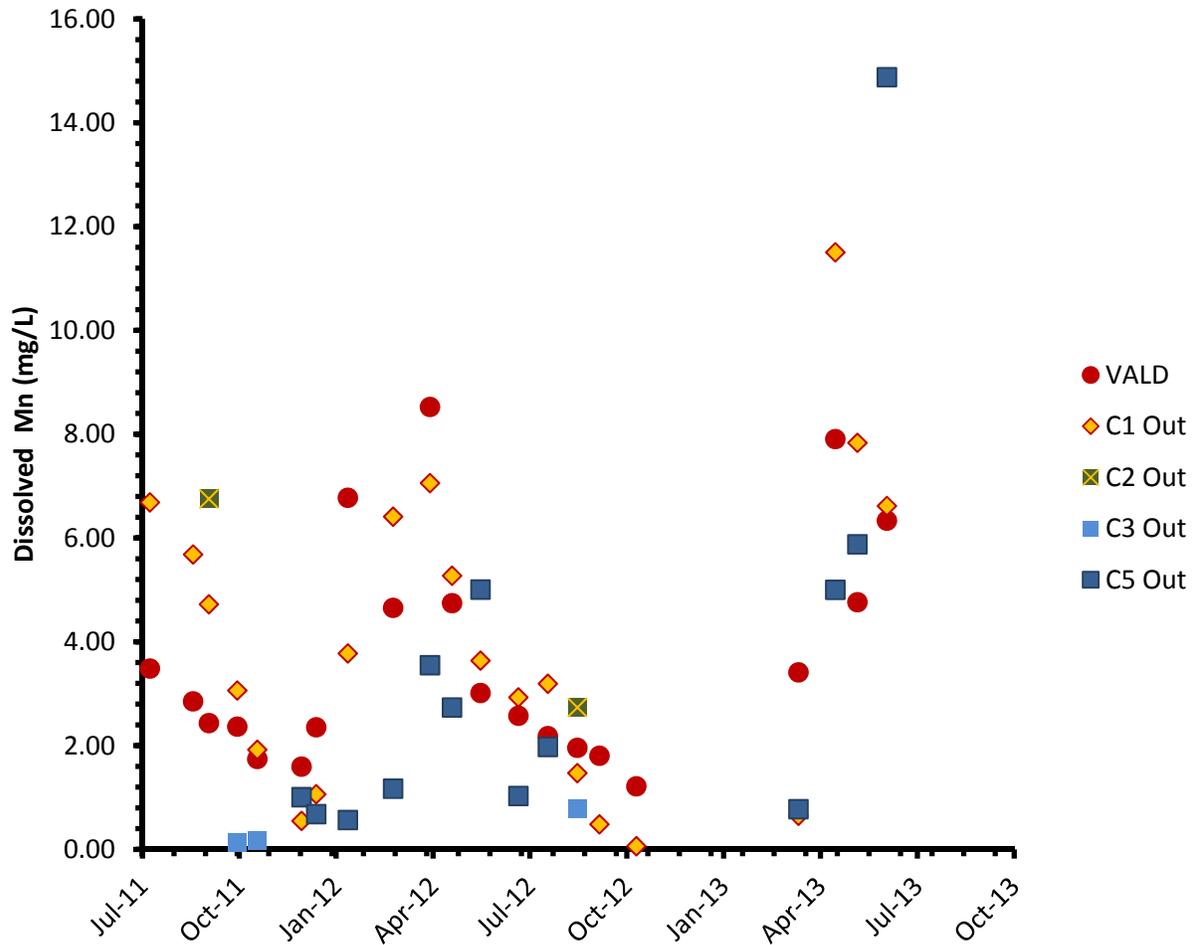


Figure 4.7. Dissolved manganese concentrations versus time at the Rock Island #7 passive treatment system. VALD represents waters discharging from the vertical anoxic limestone drain (mine drainage source), and C1, C2, C3 and C5 Out represent effluents from the initial oxidation pond, first vertical flow bioreactor, re-aeration pond, and the full system (after an additional vertical flow bioreactor and second re-aeration pond), respectively.

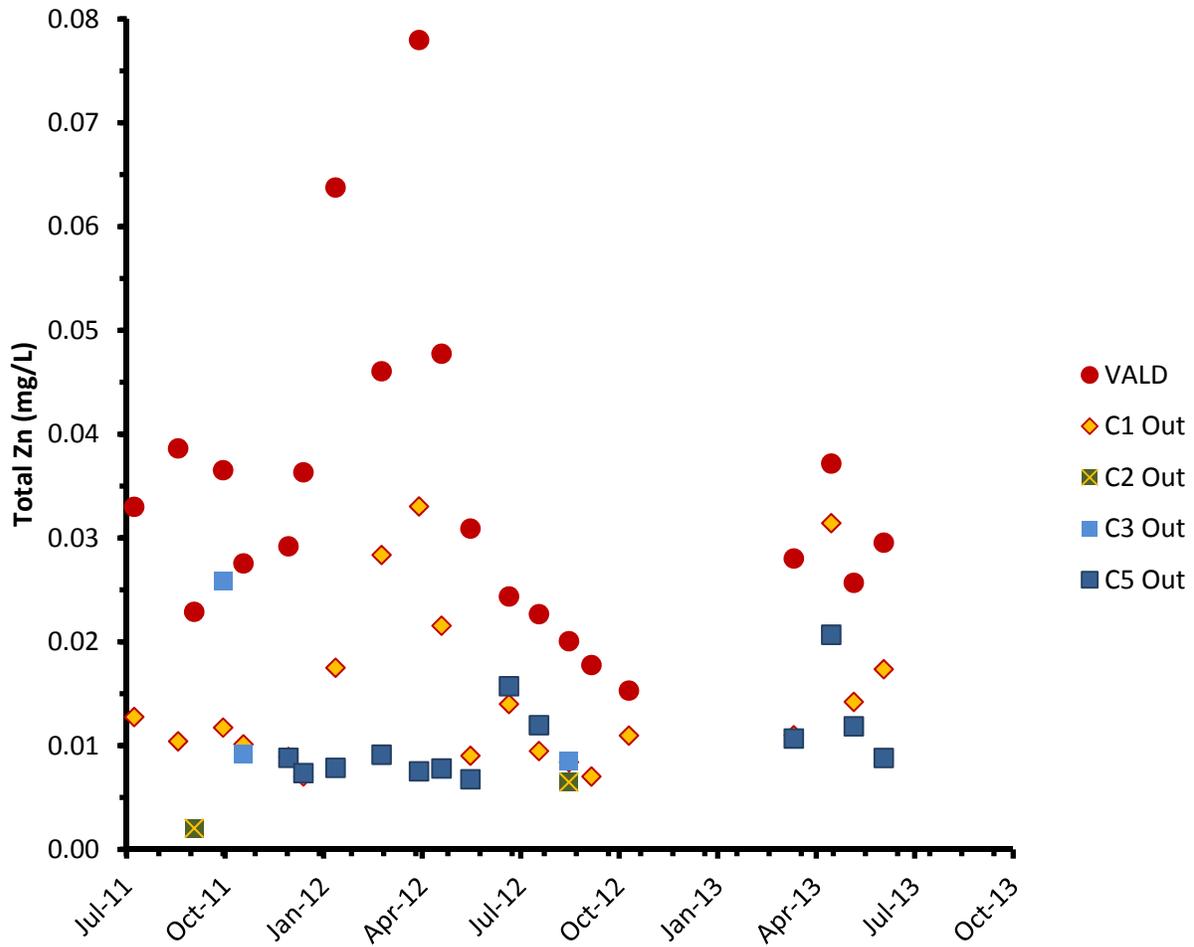


Figure 4.8. Total zinc concentrations versus time at the Rock Island #7 passive treatment system. VALD represents waters discharging from the vertical anoxic limestone drain (mine drainage source), and C1, C2, C3 and C5 Out represent effluents from the initial oxidation pond, first vertical flow bioreactor, re-aeration pond, and the full system (after an additional vertical flow bioreactor and second re-aeration pond), respectively.

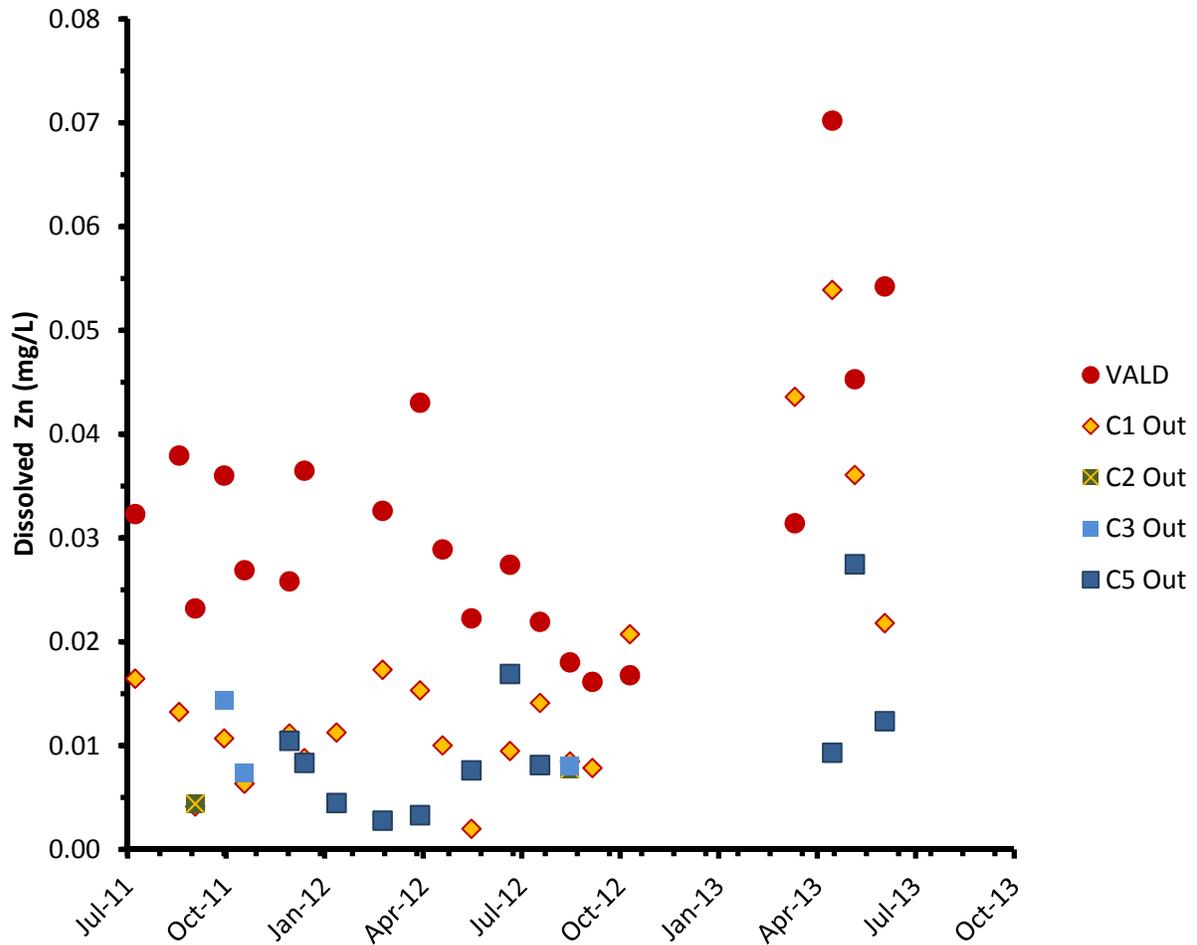


Figure 4.9. Dissolved zinc concentrations versus time at the Rock Island #7 passive treatment system. VALD represents waters discharging from the vertical anoxic limestone drain (mine drainage source), and C1, C2, C3 and C5 Out represent effluents from the initial oxidation pond, first vertical flow bioreactor, re-aeration pond, and the full system (after an additional vertical flow bioreactor and second re-aeration pond), respectively.

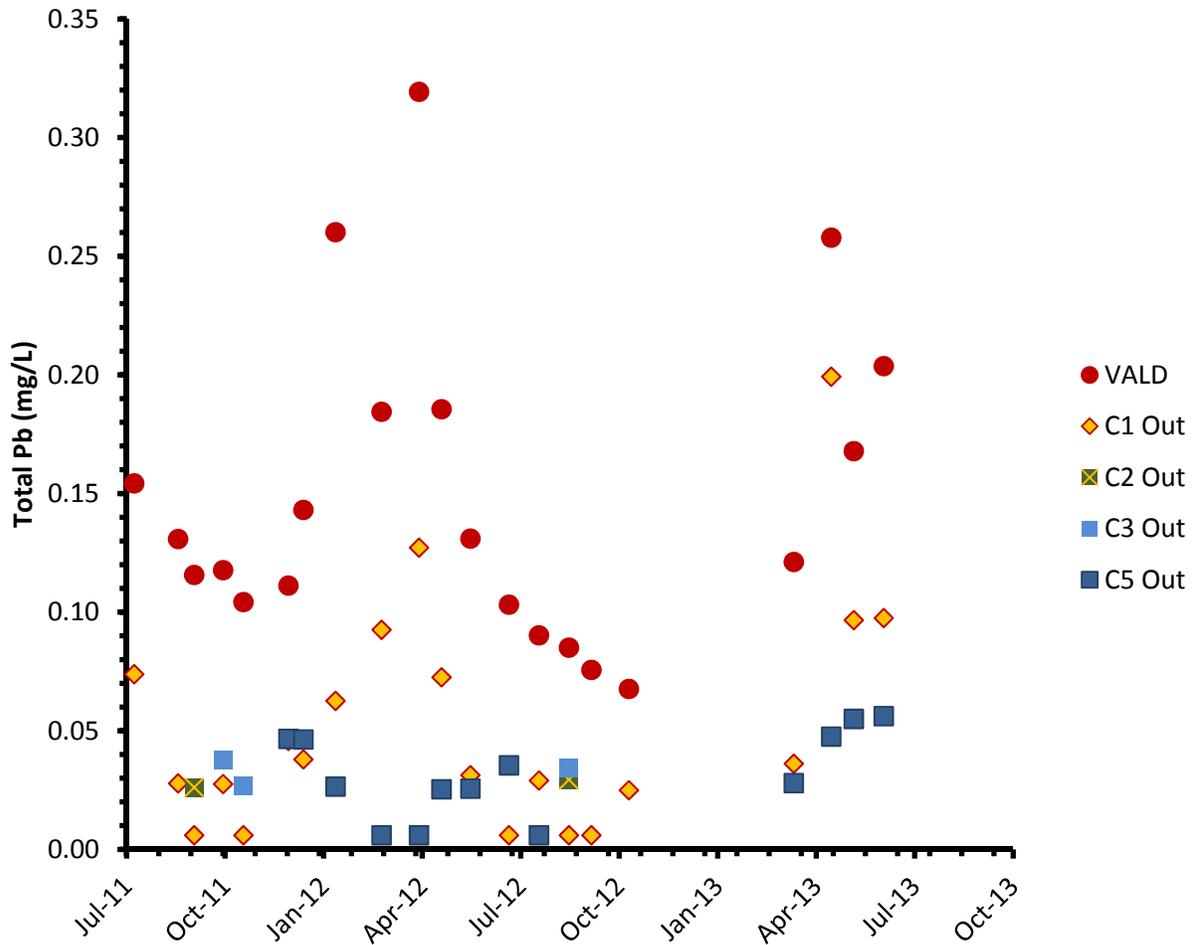


Figure 4.10. Total lead concentrations versus time at the Rock Island #7 passive treatment system. VALD represents waters discharging from the vertical anoxic limestone drain (mine drainage source), and C1, C2, C3 and C5 Out represent effluents from the initial oxidation pond, first vertical flow bioreactor, re-aeration pond, and the full system (after an additional vertical flow bioreactor and second re-aeration pond), respectively.

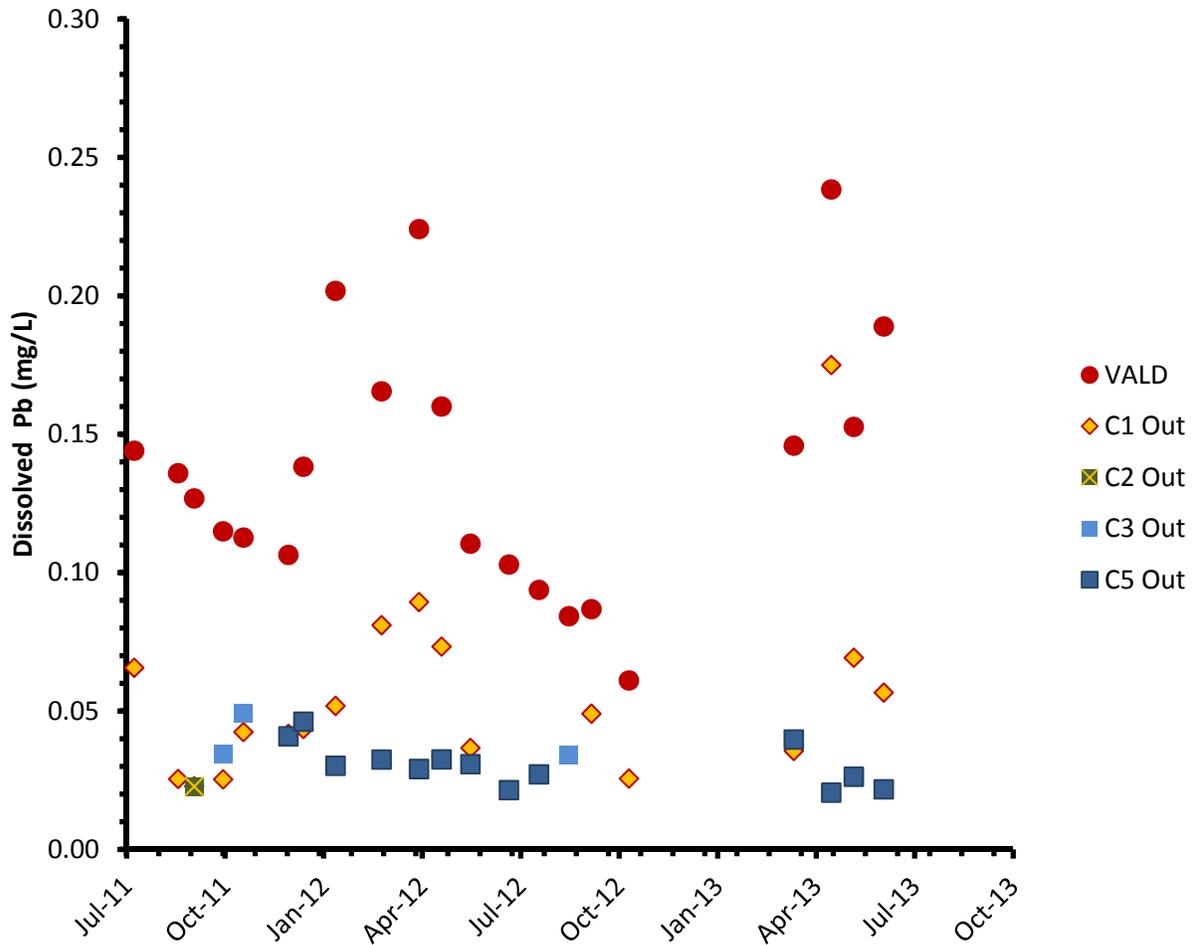


Figure 4.11. Dissolved lead concentrations versus time at the Rock Island #7 passive treatment system. VALD represents waters discharging from the vertical anoxic limestone drain (mine drainage source), and C1, C2, C3 and C5 Out represent effluents from the initial oxidation pond, first vertical flow bioreactor, re-aeration pond, and the full system (after an additional vertical flow bioreactor and second re-aeration pond), respectively.

process unit was identical upon entering the unit to the water entering that unit on a given day) complicates this analysis, especially given the low flow rates and resulting long retention times in this system, it does appear that manganese dynamics may be linked to leaching from the vertical flow bioreactor substrates.

In terms of oxygen demanding substances produced by vertical flow bioreactors, the Rock Island #7 system re-aeration process unit had a significant effect on concentrations (Figures 4.12 and 4.13). BOD values from the first vertical flow bioreactor (Cell 2) were 3.93 ± 3.81 mg/L, showing considerable temporal variability but much less than expected concentrations and considerably lower than those typically thought to be problematic. The re-aeration process unit (Cell 3) decreased BOD values to 2.54 ± 2.37 mg/L. Total sulfide concentrations in the vertical flow bioreactors effluent were 5.90 ± 6.08 mg/L, again showing considerable temporal variability (Figure 4.14). Despite the range of influent values, aeration cell total sulfide effluent concentrations were significantly different ($p < 0.005$) and measured 0.02 ± 0.02 mg/L.

Overall, the Rock Island #7 passive treatment system, including both wind- and solar-powered re-aeration devices, had substantial and statistically significant impacts on mine water quality. Although temporal flow variability complicated evaluations of overall system performance, mean water quality changes, both from a mine drainage constituent and oxygen demanding substances perspective, indicate that the system effluent has a positive influence on receiving stream water quality. Final effluents had lower metals, BOD, and sulfide values, and higher dissolved oxygen concentrations than influent waters.

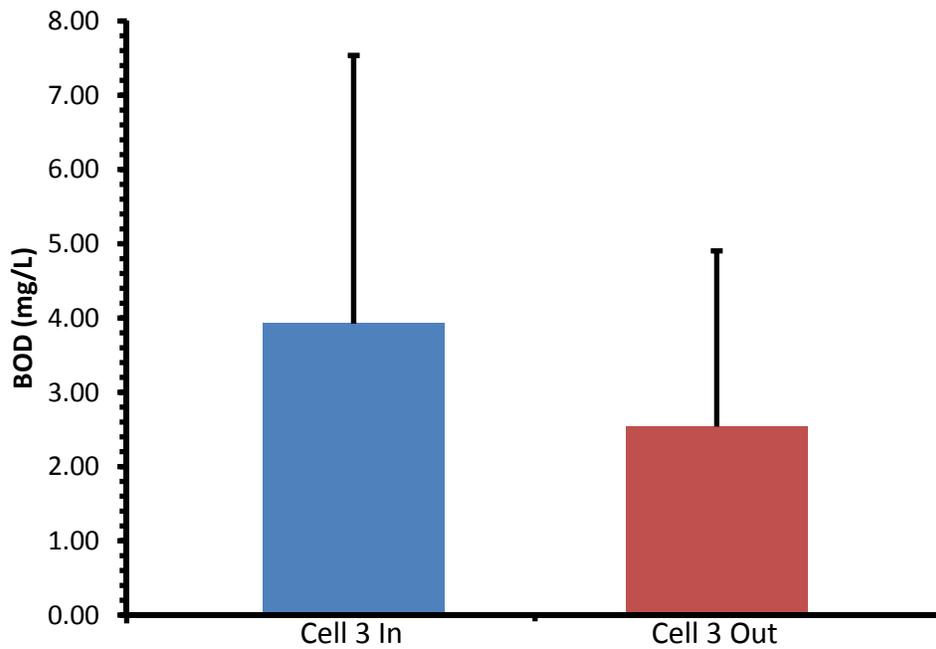


Figure 4.12. Biochemical oxygen demand values at the Rock Island #7 passive treatment system. Error bars represent one standard deviation.

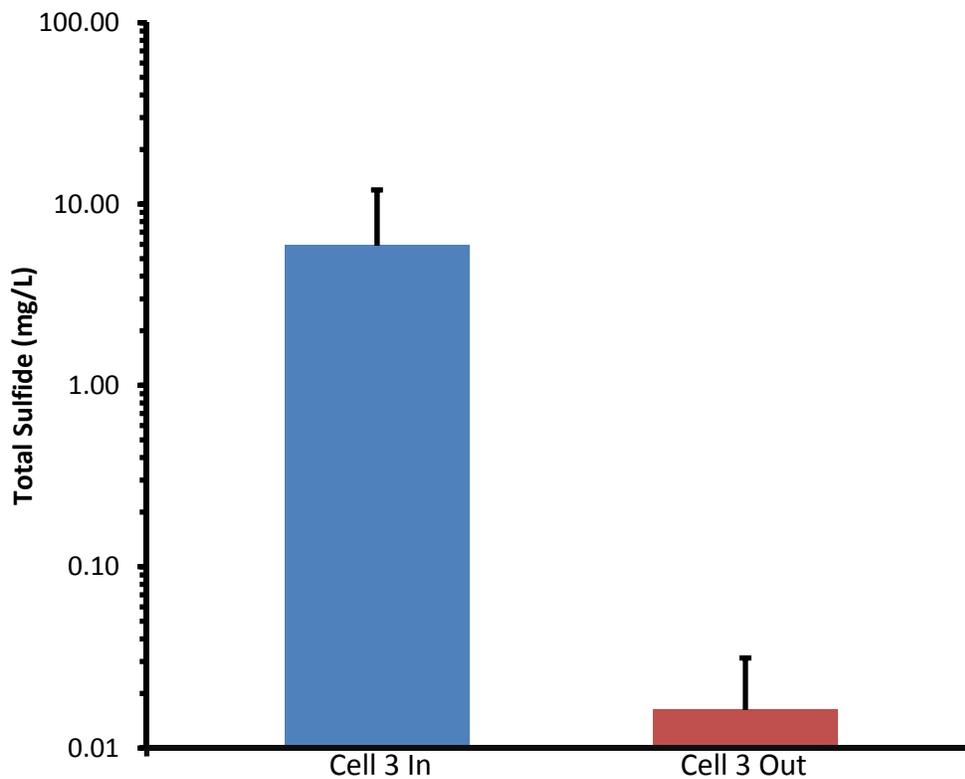


Figure 4.13. Total sulfide values at the Rock Island #7 passive treatment system. Error bars represent one standard deviation. Note the logarithmic y-axis for this plot.

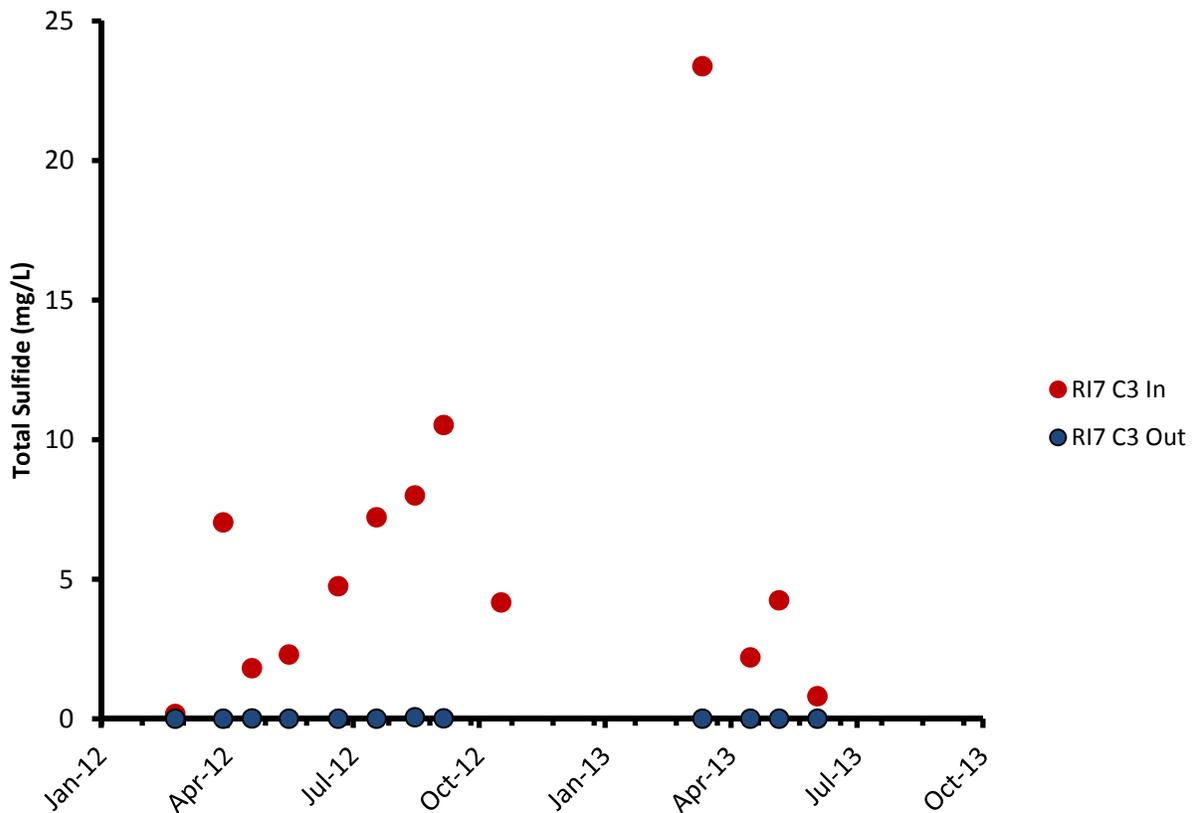


Figure 4.14. Total sulfide concentrations versus time at the Rock Island #7 passive treatment system showing the temporal variability of sulfide production and nearly complete removal in the re-aeration cell.

4.1.3 Mayer Ranch passive treatment system

The Mayer Ranch passive treatment system maintained consistent and perennial flow throughout the study period and throughout the process units. Although lower than design flows, measured influent volumetric discharge rates were greater than 380 liters per minute (100 gallons per minute) on all sampling dates.

Because the water quality data set for the Mayer Ranch system is more robust and complete than for the other sites, and the wind- and solar-powered re-aeration units have been in place since system construction was completed, these data are summarized for the life of the system (approximately five years) rather than for the shorter period of this study.

Table 4.4 summarizes physical parameter water quality data for the Mayer Ranch passive treatment system. Source waters (SA, SB and SD) were net alkaline with circum-neutral pH, due

to the limestone host rock in this area. Elevated dissolved carbon dioxide concentrations (calculated to be 0.16 atm) suppressed pH in the upwelling mine waters, which visually fizzed as they exited to the surface as the CO₂ degassed. DO concentrations and turbidity values appeared to be slightly elevated due to the challenges of sampling these waters. Net alkalinity and circum-neutral pH were maintained at the outflows of aerobic process units (Cells 1, 2N and 2S). Oxidation of iron consumes oxygen in the initial oxidation pond (Cell 1) but oxygen was successfully added to the waters in the surface flow wetlands (Cells 2N and 2S).

In the vertical flow bioreactors (Cells 3N and 3S), DO was effectively stripped and the circum-neutral pH and net alkaline character of the mine water was maintained. Additional alkalinity was added through a combination of limestone dissolution and bacterial processes. The re-aeration ponds (Cells 4N and 4S) consumed limited amounts of alkalinity and showed temporal variability in oxygen additions. Overall, however, the effects of re-aeration on DO values were quite limited. The anoxic nature of the horizontal flow limestone beds (Cells 5N and 5S) decreased DO concentrations but did little to change any other water quality parameters. The final process unit (cell 6) slightly increased DO concentrations. Final effluent waters were net alkaline with circum-neutral pH and typically had positive ORP values.

Table 4.5 provides a summary of metals concentration changes for the Mayer Ranch passive treatment system. The system had a dramatic and significant impact on targeted metals concentrations. Elevated arsenic concentrations are retained via sorption to and co-precipitation with iron oxyhydroxides in the initial oxidation pond (Cell 1) with concentrations below detectable limits after the first process unit. Iron concentrations are decreased in this same unit through oxidation, hydrolysis and precipitation, as well as the following aerobic units (surface flow wetlands Cells 2N and 2S). At the final effluent, iron concentrations were near 0.5 mg/L on average. Both cadmium and lead concentrations were decreased dramatically in Cell 1, presumably via the same processes as arsenic retention. Nickel and zinc concentrations decreased in Cells 1, 2N and 2S, but the bulk of retention occurred in the vertical flow bioreactors, Cells 3N and 3S, through exchange, sorption and sulfide precipitation. Cells 4N, 4S, 5N, 5S and 6 have little impact overall on metals concentrations, given load limitations by this pint in the treatment system. Both calcium and magnesium are elevated in the source waters due to the local geology, and are maintained at these concentrations throughout the passive treatment system. Manganese and aluminum, not metals of concern at this site, are less than 0.1 and 2 mg/L in the source water, respectively. Other trace metals (cobalt, chromium and copper) are at low concentrations as well. Both sodium and potassium are found in the 10s to 100s of mg/L throughout the system and appear to act conservatively. Based on changes in concentrations for these constituents, dilution appears to play little overall role in overall metals concentration decreases in this system.

Table 4.4. Summary statistics for water quality physical parameter data (temperature, specific conductance, dissolved oxygen as percent saturation and concentration, oxidation-reduction potential, total alkalinity and turbidity) for the Mayer Ranch passive treatment system. Sample sizes at each location varied from 27-31. "SE" refers to standard error of the mean; "Max." and "Min." refer to maximum and minimum values, respectively.

	Temp. (°C)	SC (mS/cm)	DO (%Sat)	DO (mg/L)	pH (su)	ORP (mV)	T. Alk. (mg/L CaCO ₃)	Turb. (NTU)
SA (mine drainage source)								
Mean	17.81	3.30	14.58	1.37	5.99	39	409	2.86
SE	0.01	0.09	2.45	0.23	0.03	18	4	0.71
Max.	17.92	3.63	75.30	7.09	6.64	140	450	17.93
Min.	17.73	1.28	2.50	0.23	5.75	-116	361	0.47
SB (mine drainage source)								
Mean	17.43	3.36	15.94	1.55	5.97	46	386	7.68
SE	0.40	0.05	2.40	0.26	0.03	17	7	2.96
Max.	17.98	3.60	55.80	6.67	6.60	148	424	72.75
Min.	6.26	2.72	2.60	0.24	5.69	-99	215	0.55
SD (mine drainage source)								
Mean	17.97	3.47	15.88	1.49	5.98	38	396	6.98
SE	0.04	0.04	4.23	0.40	0.03	18	3	0.87
Max.	18.27	3.66	123.00	11.53	6.59	140	411	19.90
Min.	17.56	2.84	3.40	0.32	5.74	-114	347	1.35
Cell 1 (Initial Oxidation Pond) Out								
Mean	15.77	3.25	39.71	3.99	6.04	175	172	116.70
SE	1.32	0.03	5.80	0.58	0.05	23	7	10.89
Max.	26.17	3.45	133.00	13.00	6.71	373	249	318.20
Min.	4.01	2.69	3.40	0.37	5.60	-16	114	52.23
Cell 2N (Surface Flow Wetland) Out								
Mean	18.22	3.25	89.81	8.49	6.42	191	149	42.42
SE	1.83	0.04	7.05	0.66	0.07	22	4	4.24
Max.	31.48	3.56	216.00	20.24	7.14	360	215	94.10
Min.	2.60	2.61	27.20	2.54	5.85	-134	98	5.60
Cell 2S (Surface Flow Wetland) Out								
Mean	18.06	3.22	92.58	8.71	6.49	173	152	38.70
SE	1.83	0.05	6.09	0.54	0.07	22	5	3.90
Max.	33.10	3.57	165.30	15.64	7.28	345	223	91.47
Min.	2.52	2.46	26.50	3.57	5.87	-151	106	6.66

Table 4.4 (Continued). Summary statistics for water quality physical parameter data (temperature, specific conductance, dissolved oxygen as percent saturation and concentration, oxidation-reduction potential, total alkalinity and turbidity) for the Mayer Ranch passive treatment system. Sample sizes at each location varied from 27-31. "SE" refers to standard error of the mean; "Max." and "Min." refer to maximum and minimum values, respectively.

	Temp. (°C)	SC (mS/cm)	DO (%Sat)	DO (mg/L)	pH (su)	ORP (mV)	T. Alk. (mg/L CaCO ₃)	Turb. (NTU)
Cell 3N (Vertical Flow Bioreactor) Out								
Mean	16.43	3.27	11.68	1.27	6.78	-77	244	10.65
SE	1.74	0.05	2.77	0.32	0.03	31	16	2.21
Max.	31.93	3.75	61.30	7.12	7.06	210	508	65.47
Min.	1.49	2.69	-3.70	-0.28	6.46	-408	64	1.05
Cell 3S (Vertical Flow Bioreactor) Out								
Mean	16.62	3.26	11.06	1.18	6.78	-67	233	11.92
SE	1.78	0.04	2.93	0.30	0.03	31	13	1.90
Max.	32.09	3.70	70.40	6.63	7.21	214	433	41.80
Min.	1.56	2.67	-9.30	-0.70	6.50	-340	147	2.70
Cell 4N (Re-aeration Pond) Out								
Mean	17.20	3.19	36.17	3.92	7.01	46	223	44.66
SE	1.78	0.07	5.15	0.61	0.05	39	13	8.53
Max.	31.40	3.70	86.40	9.66	7.49	298	403	150.33
Min.	1.16	2.03	0.10	0.01	6.58	-350	141	4.56
Cell 4S (Re-aeration Pond) Out								
Mean	16.73	3.24	31.78	3.57	6.99	45	216	41.07
SE	1.76	0.05	5.50	0.66	0.03	37	12	5.96
Max.	32.17	3.64	101.90	12.34	7.30	289	378	112.67
Min.	1.52	2.62	1.20	0.09	6.55	-341	138	4.26
Cell 5N (Horizontal Flow Limestone Bed) Out								
Mean	15.83	3.22	11.87	1.33	6.92	12	209	6.55
SE	1.71	0.05	2.64	0.33	0.02	37	10	1.25
Max.	29.64	3.65	52.60	6.68	7.11	296	320	25.17
Min.	1.45	2.52	-0.80	-0.07	6.69	-310	140	0.95
Cell 5S (Horizontal Flow Limestone Bed) Out								
Mean	16.25	3.20	9.65	1.06	6.92	-2	207	8.28
SE	1.73	0.05	2.08	0.24	0.02	36	11	1.31
Max.	30.57	3.61	40.40	3.93	7.16	321	308	29.03
Min.	1.82	2.50	-2.30	-0.18	6.65	-319	131	1.30
Cell 6 (Polishing Pond/Wetland) Out								
Mean	16.56	3.18	32.40	3.47	7.03	115	206	29.07
SE	1.77	0.06	3.73	0.46	0.04	31	10	7.33
Max.	30.91	3.61	68.70	7.84	7.43	338	321	139.67
Min.	1.73	2.42	4.10	0.33	6.57	-203	137	0.77

Table 4.5. Summary of total metals concentrations for the Mayer Ranch passive treatment system. "N" refers to the number of samples for which concentrations of any given analyte were above detection limit. "BDL" refers to below detection limits. "SD" and "SE" refer to the standard deviation and standard error of the mean.

		Al	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
		-----mg/L-----														
SA	Mean	0.09	0.06	727	0.02	0.06	0.004	0.003	168	25.17	189	1.41	100	0.91	0.07	7.89
	N	31	31	31	31	31	12	30	31	31	31	31	31	31	31	31
	SD	0.03	0.01	31.58	0.01	0.01	0.002	0.001	8.73	1.57	14.13	0.08	7.95	0.06	0.01	0.53
	SE	0.01	0.001	5.67	0.001	0.001	0.001	0.0002	1.57	0.28	2.54	0.01	1.43	0.01	0.002	0.10
SB	Mean	0.10	0.06	724	0.02	0.06	0.002	0.003	176	25.83	191	1.44	99.95	0.91	0.07	7.70
	N	31	31	31	31	31	7	29	31	31	31	31	31	31	31	31
	SD	0.02	0.01	35.70	0.01	0.01	0.001	0.001	9.25	1.72	11.78	0.09	8.12	0.06	0.01	0.52
	SE	0.004	0.001	6.41	0.001	0.001	0.0002	0.0001	1.66	0.31	2.12	0.02	1.46	0.01	0.002	0.09
SD	Mean	0.10	0.06	727	0.02	0.07	0.002	0.004	178	25.13	190	1.54	99.63	0.94	0.08	8.59
	N	29	29	29	29	29	4	27	29	29	29	29	29	29	29	29
	SD	0.03	0.01	36.56	0.01	0.01	0.001	0.01	11.48	1.65	12.74	0.09	8.43	0.06	0.01	0.59
	SE	0.01	0.001	6.79	0.001	0.001	0.0004	0.002	2.13	0.31	2.37	0.02	1.56	0.01	0.002	0.11
C1 Out	Mean	0.10	BDL	724	0.004	0.06	0.002	0.003	34.72	25.38	191	1.41	100	0.83	0.03	6.25
	N	29		31	27	31	2	30	31	31	31	31	31	31	19	31
	SD	0.12		32.33	0.002	0.01	0.001	0.001	22.96	1.80	14.12	0.14	9.42	0.07	0.01	0.83
	SE	0.02		5.81	0.0005	0.002	0.001	0.0002	4.12	0.32	2.54	0.03	1.69	0.01	0.002	0.15
C2N Out	Mean	0.20	BDL	724	0.002	0.05	0.003	0.003	7.08	25.24	192	1.43	101	0.77	0.03	5.17
	N	31		31	12	31	3	31	31	31	31	31	31	31	1	31
	SD	0.33		33.13	0.002	0.02	0.0004	0.003	10.50	1.87	16.48	0.45	9.47	0.10		1.47
	SE	0.06		5.95	0.001	0.003	0.0002	0.0005	1.89	0.34	2.96	0.08	1.70	0.02		0.26
C2S Out	Mean	0.10	BDL	724	0.002	0.05	0.003	0.003	6.93	25.27	192	1.49	101	0.77	0.03	5.15
	N	31		31	12	31	5	31	31	31	31	31	31	31	3	31
	SD	0.10		31.49	0.002	0.02	0.001	0.001	10.71	1.95	14.53	0.60	9.93	0.12	0.001	1.62
	SE	0.02		5.66	0.001	0.004	0.001	0.0002	1.92	0.35	2.61	0.11	1.78	0.02	0.001	0.29

Table 4.5 (Continued). Summary of total metals concentrations for the Mayer Ranch passive treatment system. "N" refers to the number of samples for which concentrations of any given analyte were above detection limit. "BDL" refers to below detection limits. "SD" and "SE" refer to the standard deviation and standard error of the mean.

		Al	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
		-----mg/L-----														
C3N																
Out	Mean	0.14	BDL	743	0.001	0.01	0.003	0.003	1.69	27.08	191	1.30	101	0.19	0.03	1.04
	N	29		31	6	18	3	31	31	31	31	31	31	31	1	31
	SD	0.18		58.20	0.0002	0.01	0.001	0.001	2.14	6.07	21.16	0.82	11.80	0.21		1.23
	SE	0.03		10.45	0.0001	0.003	0.0004	0.0002	0.38	1.09	3.80	0.15	2.12	0.04		0.22
C3S																
Out	Mean	0.30	BDL	742	0.002	0.02	0.005	0.004	1.66	26.34	191	1.19	101	0.23	BDL	1.16
	N	30		31	4	17	10	31	31	31	31	31	31	31		31
	SD	0.30		51.72	0.001	0.02	0.004	0.003	2.87	3.64	17.39	0.58	11.36	0.26		1.26
	SE	0.05		9.29	0.0003	0.004	0.001	0.001	0.51	0.65	3.12	0.10	2.04	0.05		0.23
C4N																
Out	Mean	0.20	BDL	733	0.001	0.01	0.003	0.01	0.99	26.93	189	1.32	101	0.16	BDL	0.69
	N	30		30	3	15	5	30	30	30	30	30	30	30		30
	SD	0.16		63.76	0.0002	0.01	0.001	0.01	1.27	9.30	19.52	0.82	11.96	0.17		0.89
	SE	0.03		11.64	0.0001	0.003	0.001	0.003	0.23	1.70	3.56	0.15	2.18	0.03		0.16
C4S																
Out	Mean	0.09	BDL	730	0.00	0.02	0.003	0.003	1.10	26.37	188	1.25	101	0.18	BDL	0.87
	N	31		31	2	16	8	31	31	31	31	31	31	31		31
	SD	0.10		58.57	0.0003	0.01	0.002	0.001	1.70	4.48	18.16	0.57	11.22	0.21		1.05
	SE	0.02		10.52	0.0002	0.004	0.001	0.0002	0.30	0.80	3.26	0.10	2.02	0.04		0.19

Table 4.5 (Continued). Summary of total metals concentrations for the Mayer Ranch passive treatment system. "N" refers to the number of samples for which concentrations of any given analyte were above detection limit. "BDL" refers to below detection limits. "SD" and "SE" refer to the standard deviation and standard error of the mean.

		Al	As	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn
		-----mg/L-----														
C5N																
Out	Mean	0.20	BDL	725	0.001	0.01	0.002	0.003	0.59	27.04	189	1.19	102	0.14	0.03	0.38
	N	30		30	1	10	6	30	30	30	30	30	30	30	2	30
	SD	0.28		68.07		0.01	0.001	0.001	0.63	10.67	20.78	0.93	12.23	0.17	0.003	0.65
	SE	0.05		12.43		0.003	0.0002	0.0002	0.12	1.95	3.79	0.17	2.23	0.03	0.002	0.12
C5S																
Out	Mean	0.44	BDL	722	0.001	0.02	0.003	0.003	0.83	25.58	185	1.18	100	0.17	BDL	0.50
	N	30		30	1	11	14	30	30	30	30	30	30	30		30
	SD	0.43		66.72		0.02	0.002	0.001	1.26	4.01	20.27	0.64	12.01	0.23		0.83
	SE	0.08		12.18		0.005	0.001	0.0002	0.23	0.73	3.70	0.12	2.19	0.04		0.15
C6 Out																
	Mean	0.05	BDL	723.91	0.001	0.01	0.003	0.004	0.51	26.25	187	1.21	100.83	0.15	0.02	0.38
	N	29		30	3	10	8	30	30	30	30	30	30	29	1.00	30
	SD	0.05		67.70	0.0002	0.01	0.001	0.002	0.46	7.70	21.92	0.68	12.42	0.19		0.62
	SE	0.01		12.36	0.0001	0.004	0.0004	0.0003	0.08	1.41	4.00	0.12	2.27	0.04		0.11

The temporal variability of selected metals concentration changes for the Mayer Ranch passive treatment system are shown in Figures 4.15 - 4.19. For iron concentrations, it is quite apparent that the bulk of removal takes place via aerobic mechanisms in Cells 1, 2N and 2S. Zinc is predominately removed in the vertical flow bioreactors, Cells 3N and 3S via exchange, sorption and sulfide precipitation. Lead and cadmium are retained via sorptive mechanisms in Cells 1, 2N and 2S, as well as in Cells 3N and 3S. Exchange, sorption and sulfide precipitation play a dominant role in retention of these trace metals. Manganese is not effectively retained by this system. Similar to the Rock Island #7 system, it appears that the substrates in the vertical flow bioreactors may contribute manganese to the bulk water, via substrate leaching. Dissolved metals data track total metals data and are not presented.

The vertical flow bioreactors at Mayer Ranch produced substantial concentrations of oxygen demanding substances. BOD values from the vertical flow bioreactors were 2.89 ± 1.13 mg/L and 2.44 ± 1.49 mg/L, for north and south cells, respectively. The re-aeration ponds decreased BOD concentrations to 1.11 ± 1.30 mg/L and 1.21 ± 1.29 mg/L, for north and south cells, respectively (Figure 4.20). Although overall concentrations decreased, and it appears both wind- and solar-powered aeration had positive impacts on BOD concentrations, no significant statistical difference was observed due to the great variability in these data. In any case, BOD values were low enough to not be considered problematic.

Total sulfide concentrations in the vertical flow bioreactor effluents were elevated and widely variable: 30.63 ± 53.57 mg/L and 38.41 ± 60.84 mg/L, for the north and south cells, respectively. Concentrations decreased dramatically in the re-aeration cells to 1.90 ± 4.36 mg/L and 4.24 ± 7.53 mg/L, respectively (Figure 4.21). Despite the substantial variability in these data, effluent concentrations were significantly different from influent concentrations for both the wind- and solar-powered re-aeration cells ($p < 0.05$). The considerable temporal variability in sulfide production appeared to be seasonal (Figure 4.22) in nature, with extremely high values seen in the hot, dry summer of 2012. These concentrations (> 100 mg/L) are directly toxic to wildlife. Although still elevated (> 1 mg/L), re-aeration cell effluent values were considerably lower and were further decreased in the remaining passive treatment system process units.

Overall, the Mayer Ranch passive treatment system, including both wind- and solar-powered re-aeration devices, had substantial and statistically significant impacts on both mine water quality and oxygen demanding substances concentrations. The system effluent had a positive influence on receiving stream water quality. No significant differences were seen between wind- and solar-powered re-aeration devices in their effects on water quality; both technologies had a positive impact. The selection of a given technology would therefore likely be driven by available resources (both financial and natural, e.g., the availability of wind and solar energy) on a given project site.

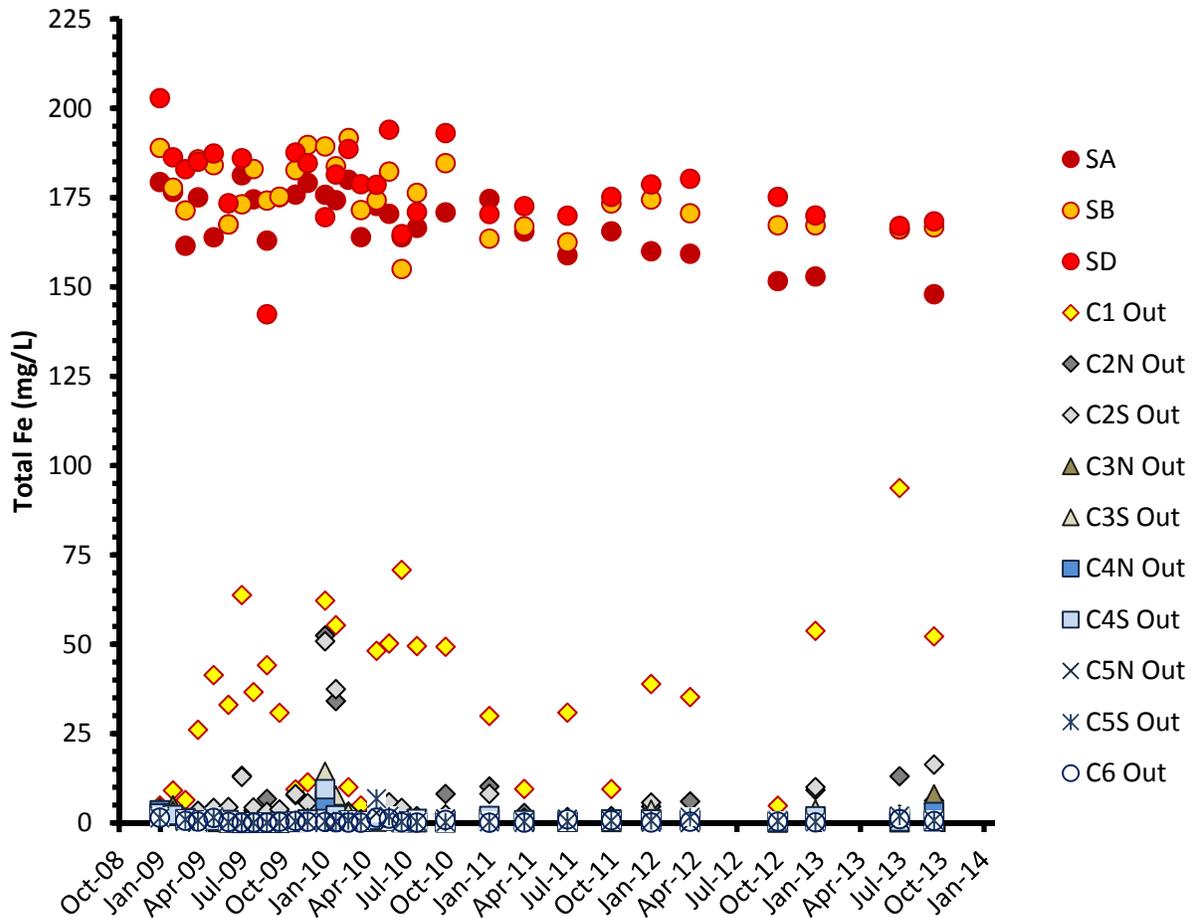


Figure 4.15. Total iron concentrations versus time at the Mayer Ranch passive treatment system. SA, SB and SD represent three separate source waters discharging via artesian flow into the system. C1 Out is the effluent of the initial oxidation pond. C2N Out and C2S Out are the effluents of the north and south surface flow wetlands. C3N Out and C3S Out are the effluents of the north and south vertical flow bioreactors. C4N Out and C4S Out are the effluents of the north and south re-aeration ponds. C5N Out and C5S Out are the effluents of the north and south horizontal flow limestone beds. C6 Out is the system effluent after the final polishing wetland/pond.

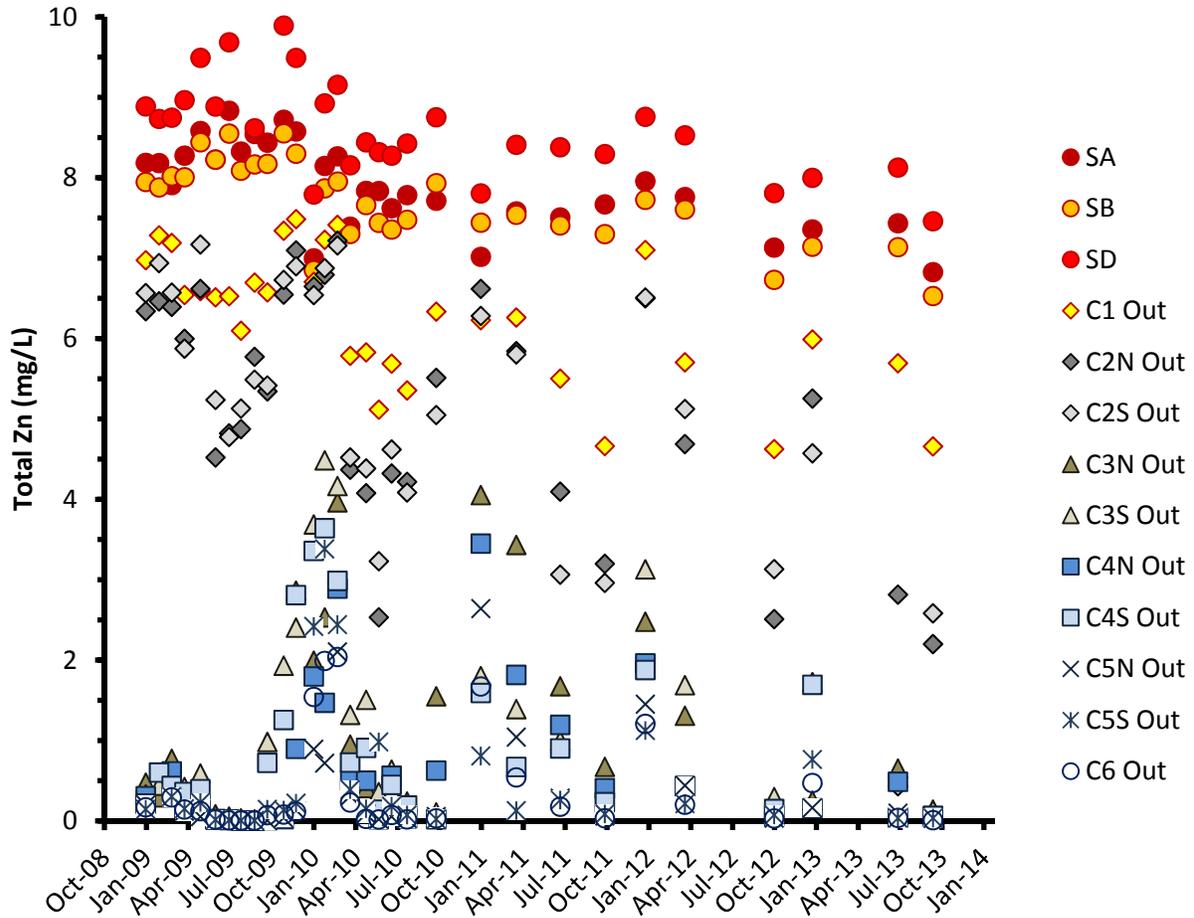


Figure 4.16. Total zinc concentrations versus time at the Mayer Ranch passive treatment system. SA, SB and SD represent three separate source waters discharging via artesian flow into the system. C1 Out is the effluent of the initial oxidation pond. C2N Out and C2S Out are the effluents of the north and south surface flow wetlands. C3N Out and C3S Out are the effluents of the north and south vertical flow bioreactors. C4N Out and C4S Out are the effluents of the north and south re-aeration ponds. C5N Out and C5S Out are the effluents of the north and south horizontal flow limestone beds. C6 Out is the system effluent after the final polishing wetland/pond.

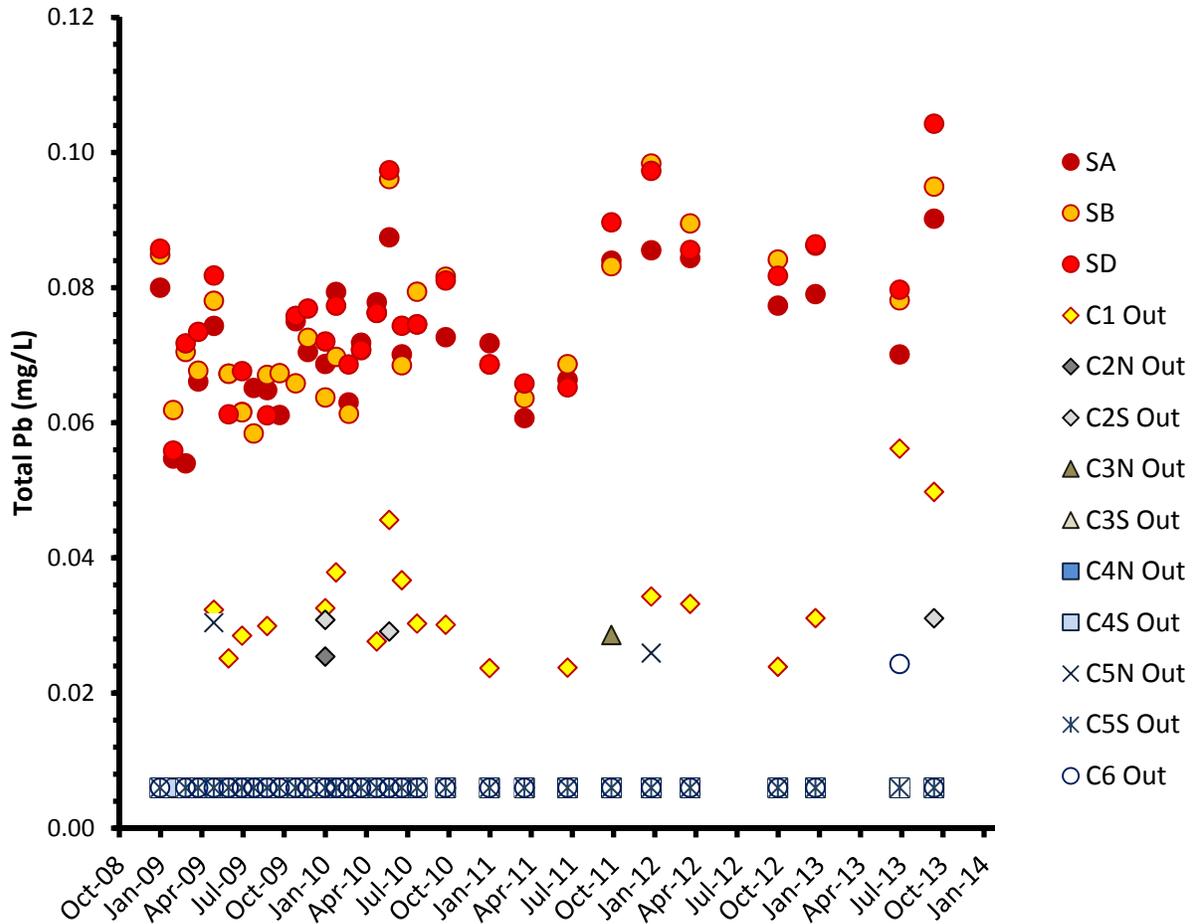


Figure 4.17. Total lead concentrations versus time at the Mayer Ranch passive treatment system. SA, SB and SD represent three separate source waters discharging via artesian flow into the system. C1 Out is the effluent of the initial oxidation pond. C2N Out and C2S Out are the effluents of the north and south surface flow wetlands. C3N Out and C3S Out are the effluents of the north and south vertical flow bioreactors. C4N Out and C4S Out are the effluents of the north and south re-aeration ponds. C5N Out and C5S Out are the effluents of the north and south horizontal flow limestone beds. C6 Out is the system effluent after the final polishing wetland/pond. Data below detectable limits were plotted as one-half the detection limit (0.006 mg/L).

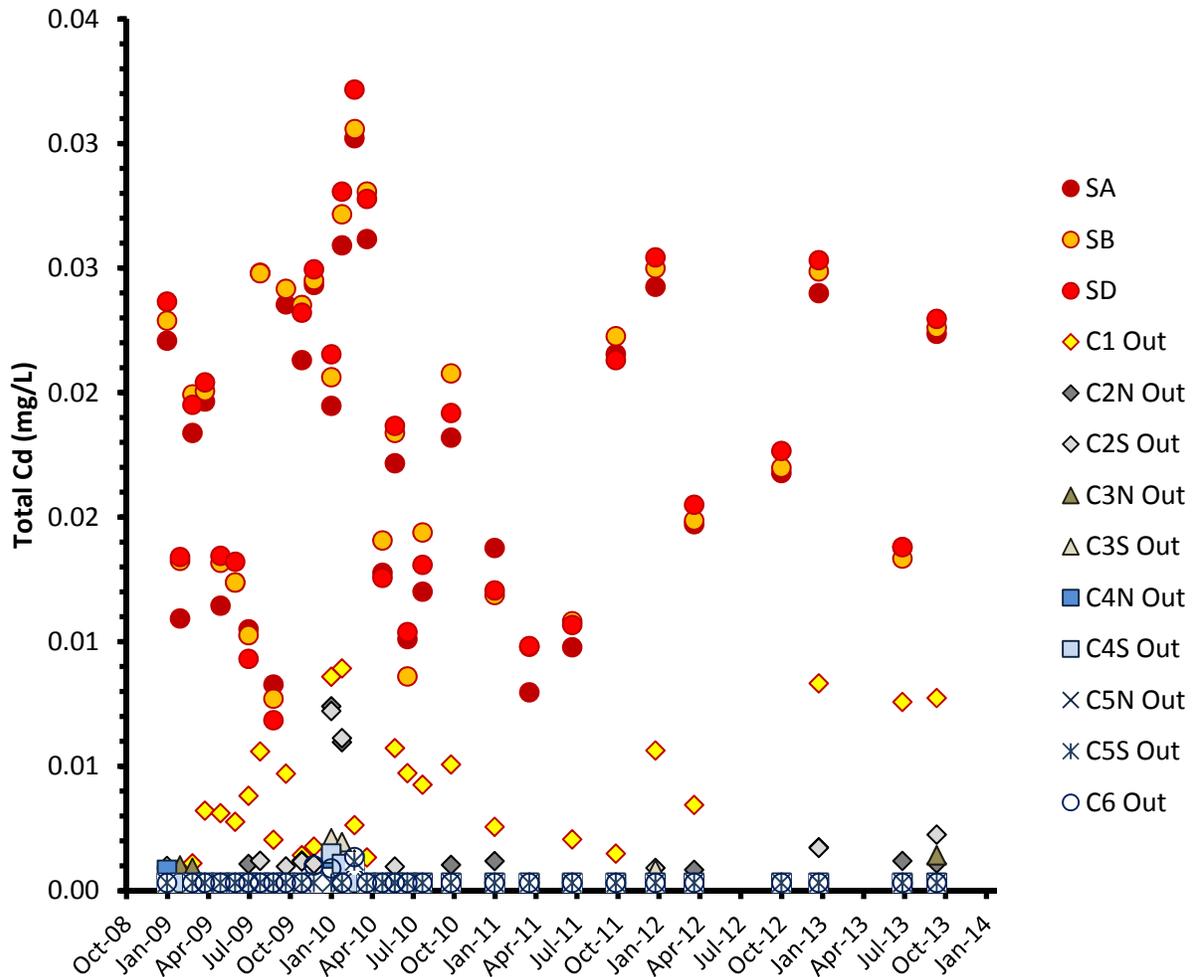


Figure 4.18. Total cadmium concentrations versus time at the Mayer Ranch passive treatment system. SA, SB and SD represent three separate source waters discharging via artesian flow into the system. C1 Out is the effluent of the initial oxidation pond. C2N Out and C2S Out are the effluents of the north and south surface flow wetlands. C3N Out and C3S Out are the effluents of the north and south vertical flow bioreactors. C4N Out and C4S Out are the effluents of the north and south re-aeration ponds. C5N Out and C5S Out are the effluents of the north and south horizontal flow limestone beds. C6 Out is the system effluent after the final polishing wetland/pond. Data below detectable limits were plotted as one-half the detection limit (0.00032 mg/L).

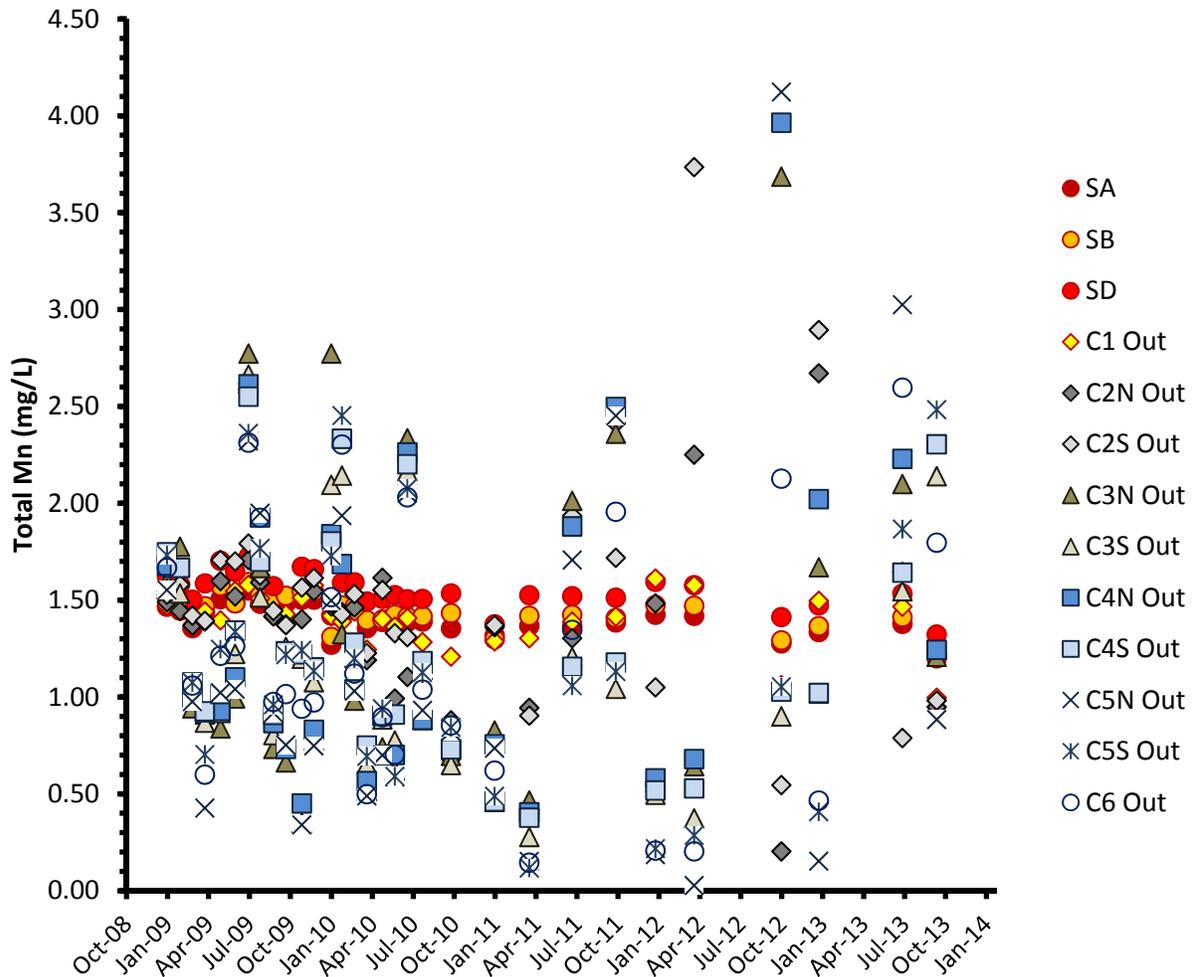


Figure 4.19. Total manganese concentrations versus time at the Mayer Ranch passive treatment system. SA, SB and SD represent three separate source waters discharging via artesian flow into the system. C1 Out is the effluent of the initial oxidation pond. C2N Out and C2S Out are the effluents of the north and south surface flow wetlands. C3N Out and C3S Out are the effluents of the north and south vertical flow bioreactors. C4N Out and C4S Out are the effluents of the north and south re-aeration ponds. C5N Out and C5S Out are the effluents of the north and south horizontal flow limestone beds. C6 Out is the system effluent after the final polishing wetland/pond.

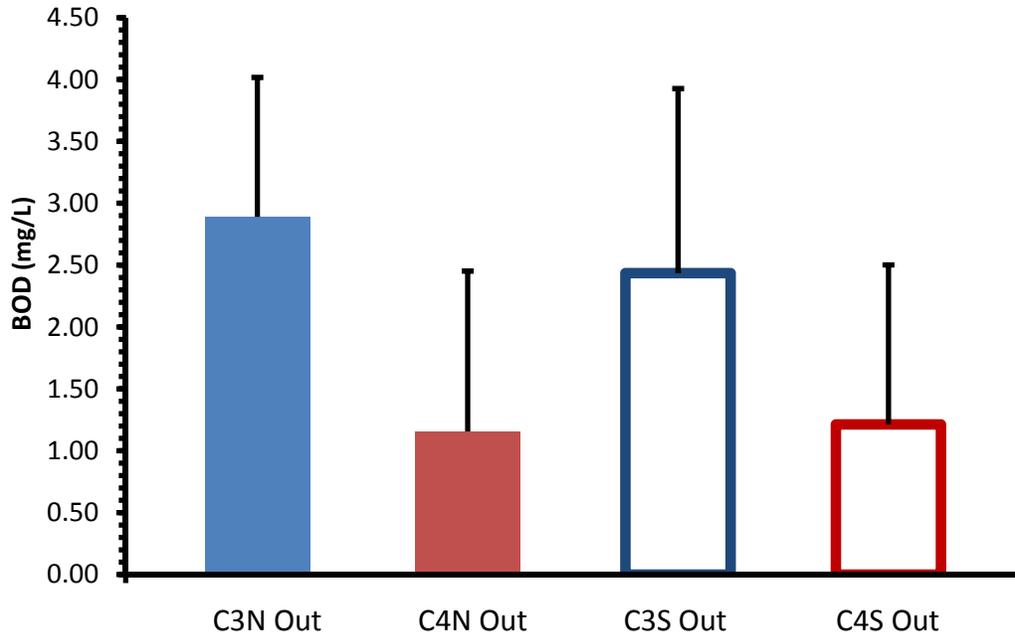


Figure 4.20. Biochemical oxygen demand values at the Mayer Ranch passive treatment system. Error bars represent one standard deviation.

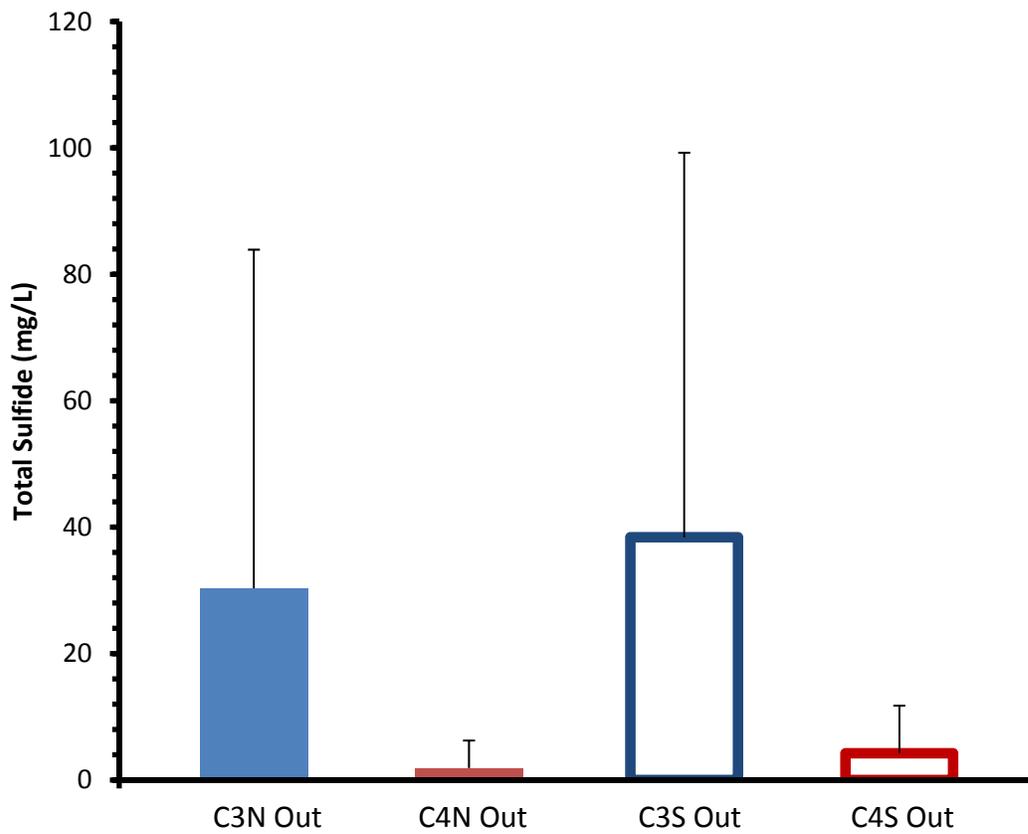


Figure 4.21. Total sulfide values at the Mayer Ranch passive treatment system. Error bars represent one standard deviation.

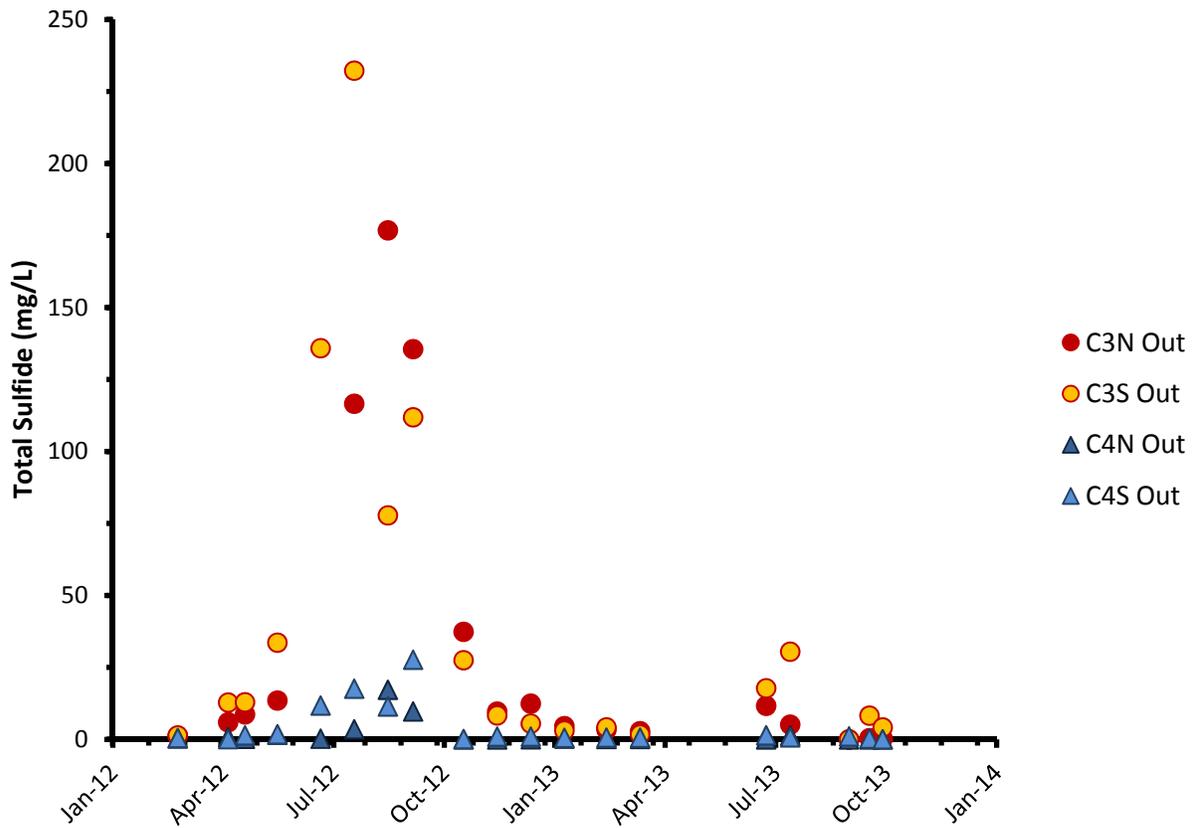


Figure 4.22. Total sulfide values versus time at the Mayer Ranch passive treatment system.

4.2 Hydraulic performance

In order to determine the impact of aeration on the hydraulic retention time of the systems, tracer studies were completed and preferential flow patterns analyzed. The tracer selected for this study needed to meet a set of predetermined characteristics. First, the tracer was to be a conservative chemical that would mimic fluid flow. Second, the degradation rate (via photo- or biological mechanisms) would need to be minimized, but ultimate degradation must be obtainable to prevent long term tracer residue concentrations in the environment. Finally, the tracer must be able to be analyzed via continuous data monitoring.

Two types of tracers were initially evaluated, viz. salt and fluorescent dyes. Salt tracers are often used in ground water studies due to their conservative natures. In environments with high chloride concentrations or high conductivity, chloride detection can be hampered due to the high background chloride concentration (Chua et al., 2007). Salt tracers are generally not used in

mining systems due to the high total dissolved solids concentrations and high specific conductivity levels. For these reasons, artificial fluorescent dyes were evaluated. Fluorescent dyes are commonly utilized due to their ease of analysis, practical cost, and environmental safety (Aldous and Smart, 1988). Fluorescent dyes are large organic molecules that when exposed to light, adsorb shorter wavelength light and emit a longer wavelength light and fluoresce (Sabatini and Austin, 1991). These dyes contain ionic functional groups (e.g., COO^- and SO_3^-) that increase their aqueous solubility (Sabatini et al., 1999). Sometimes these ionic groups have the potential of sorbing to other surfaces by interacting with oppositely charged surface charges undergoing ion exchange (Sabatini et al., 1999). Rhodamine WT (RWT), a stable red fluorescent dye, was selected as the best fluorescent dye tracer for this project due to its low detectable concentration (detectable at $0.5 \mu\text{g/L}$), relative resistance to the effects of pH, low natural background concentration and resistance to suspended sediment (Smart and Laidlaw, 1977; Smart, 1988).

Through use of the tracer breakthrough curves (TBCs), many hydrologic characteristics of a treatment system can be determined such as dispersion, residence time, time of travel, flow patterns, dead-volume, and index of short-circuiting. However, before these characteristics were evaluated, the effectiveness of the tracer study was determined. The effectiveness of the tracer was based on mass recovery, divergence, sensor saturation, and initial injection concentration.

A larger mass recovery is characteristic of conservative tracers whereas a non-conservative tracer will often result in a lower yield. The lower yield in the field can be due to several reasons such as biodegradation, partitioning to organic constituents, photolysis, or an alternative flow path through underground fissures or groundwater seepage in those situations (Aldous and Smart, 1988; Sabatini and Austin, 1991; Sabatini et al., 1999; Field and Pinsky, 2000). Each tracer study was evaluated for a total mass recovery and tracer injection was repeated for percent recoveries below 70%.

Other factors that affect TBC are dispersion, divergence, and initial injection concentrations (Aldous and Smart, 1988). Any one of these factors could affect the analysis; as an example, a greater concentration of tracer was necessary when completing the windmill tracer in order to accurately detect the tracer in the mine water. Injection concentrations were increased to maintain a detectable effluent concentration, yet minimized to reduce affecting the environment.

Flow in the passive treatment cells can be characterized as a non-ideal flow pattern. Levenspeil (1972) described two methods for the characterization of non-ideal flow pattern: plug flow and dispersion models. The plug flow model or commonly known as the tanks-in-series model, describes the flow pattern by indicating the number of completely mixed reactors flowing in series (N) that would result in the same retention time distribution. The dispersion model represents a flow that deviates in some extent from plug flow. Both models use one-parameter

analysis. The parameters of both models are calculated from the measured retention time (\bar{t}) and the variance (σ^2) of a conservative tracer. The measured retention time is the centroid (equation 4.1) of the break-through curve for which the variance is the spread (equation 4.2) of the TBC. The variance of the time-concentration curve describes the distribution of effluent leaving the cell.

$$\bar{t} = \frac{\int_0^{\infty} tC dt}{\int_0^{\infty} C dt} \quad \text{Equation 4.1}$$

$$\sigma^2 = \frac{\int_0^{\infty} t^2 C dt}{\int_0^{\infty} C dt} - \bar{t}^2 \quad \text{Equation 4.2}$$

where C is defined as the mass concentration (mg/L) of a conservative tracer and t is time (hours). A YSI 600 OMS sonde equipped with optical sensor was deployed at the effluent of the treatment cells and set to collect mass concentration data every 15 minutes.

The retention time distribution curve is often shown as the normalized effluent TBC with respect to time. Normalization of tracer concentration is completed with the initial concentration (mg/L) of a conservative tracer while the time function is normalized by the theoretical hydraulic retention time (HRT). Thus, the tank-in-series model can be described by equation 4.3.

$$N = \frac{\bar{t}^2}{\sigma^2} \quad \text{Equation 4.3}$$

If $N=1$, the flow pattern is complete mixing and if $N=\infty$, the flow pattern approaches ideal plug flow.

For the dispersion model, a dispersion number (equation 4.4) is a measure of the amount of mixing.

$$d = \frac{D}{vL} \quad \text{Equation 4.4}$$

Where D is defined as the dispersion coefficient (m^2/s), v is the average velocity (m/s) and L is the length (m) from the influent to effluent structures. If d approaches zero, the flow pattern is ideal plug flow and d approaches one, the flow pattern is completely mixed.

The dispersion number (d) can be determined from a pulse tracer injection from the following analysis of the TBC (equation 4.5).

$$d = 0.5 \frac{\sigma^2}{\bar{t}^2} \quad \text{Equation 4.5}$$

The TBC analysis is also used to determine the fraction of dead-volume per bulk volume of treatment cell. The fraction of these stagnant pockets is determined using the measured detention time and the theoretical hydraulic retention time (equation 4.6).

$$Vf = \left(1 - \frac{\bar{t}}{\tau}\right) 100 \quad \text{Equation 4.6}$$

Where τ is the theoretical retention time (hours).

Finally, TBC analysis is used to describe the mixing behavior (equation 4.7) in the non-ideal flow pattern using the index of short-circuiting (α_s).

$$\alpha_s = \frac{\bar{t} - t_p}{\bar{t}} \quad \text{Equation 4.7}$$

Where t_p is the time to reach the maximum concentration or peak retention time. At a value of zero, there is no short-circuiting. When there is a large extent of short-circuiting, the index will approach the extreme boundary value of one.

4.2.2 Rock Island #7 passive treatment system tracer studies

The first series of tracer studies completed were performed on the current system for Cell 3 (Figure 4.23). This cell is a horizontal-flow re-aeration pond in series between two vertical-flow ponds. The influent enters from the south end and travels to the far northwest corner of the cell. As seen in Figure 4.23, Cell 3 is a series of three small cells (all horizontal-flow). Each cell is separated by a rock berm that was original designed to provide aeration. Each of the two rock berms create a hydrologic head differential (Figure 4.24). Although the piezometric head varies throughout the season, a constant drop from Cell 3a to Cell 3b was visually present through the study under normal flow conditions. Rarely was there a visible difference in the piezometric surface from Cell 3b to Cell 3c. Monthly maintenance was needed to remove vegetation (primarily Bermuda grass) from the first rock berm.

Following a period of consistent inflow, rhodamine was added to the influent pipe using an access hole at the top of a riser elbow. The pulse of rhodamine was monitored using a YSI 600 OMS sonde equipped with optical sensor that was deployed at the effluent of the treatment cell and set to collect mass concentration data every 15 minutes (Figure 4.25). The tracer concentration was monitored well past the expected TBC time to allow for the system to reach background concentrations of RWT.



Figure 4.23. Rock Island #7. Cell 3 is outlined in yellow. The white arrows indicated two rock-aeration berms.

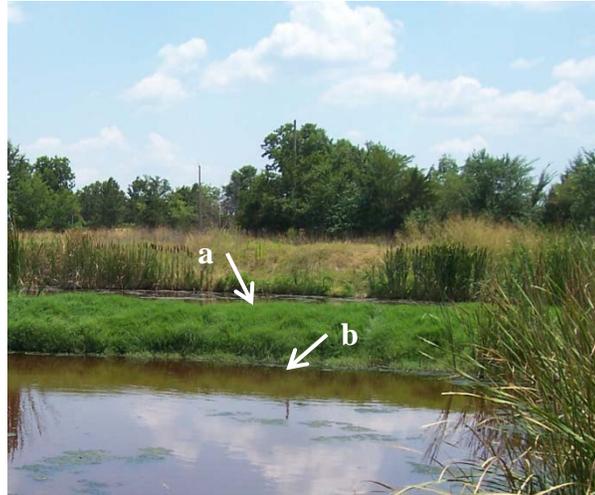


Figure 4.24. Rock berm initially covered with Bermuda grass. Water level *a* is upstream of water level *b*.



Figure 4.25. YSI OMS suspended above the effluent pipe which is below the water level.

Five independent tracer studies were completed at the Rock Island #7 system. The first tracer study was eliminated due to low mass concentration. It was assumed that the initial concentration of rhodamine was insufficient to achieve a reliable TBC. Based on rhodamine concentration measured at the effluent, the initial mass of the tracer was increased. The fourth tracer was discarded due to a mass recovery of 61% which was below our target of >70%. The low mass recovery was assumed to be the result of a rain event that may have increased the cell

water depth to a level above the emergency spill way on the eastern end of the cell. The remaining three tracer studies are presented in Figure 4.26.

A step-wise integration of the product of mean tracer concentration and increment time per differential time was used to determine the actual hydraulic detention time. Tracer studies were complete with an average flow variance of 4.1 gallons per day. This variance in flow was an anticipated experimental error, and can be accounted for by the use of a mean concentration rather than averaging actual retentions time. As seen in Figure 4.26, a broadening of the tracer concentration along the peak edge is indicative of completely mixed systems, while the sharp rising limb is a characteristic plug flow systems. The broadening and falling limb of the tracer analysis could be the result of the two rock berms within Cell 3. Although not evaluated experimentally, visual observation of tracer pooling in the first segment of Cell 3 and subsequent distribution along the rock berm between the first and second segments does support this statement. It was further concluded that the rock berms provided some deviation from short circuiting and thus reduction of void volume.

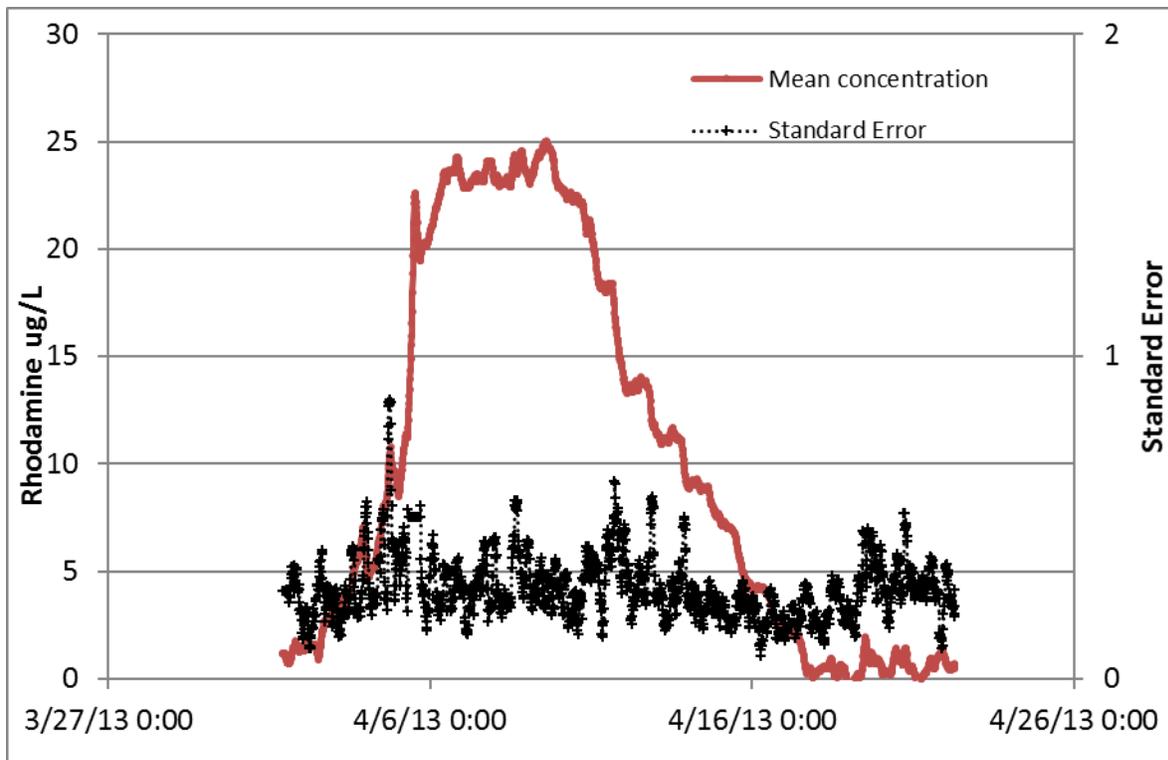


Figure 4.26. Mean concentration of Rhodamine WT with standard error for Cell 3 without additional aeration units.

Hydraulic characteristics of Cell 3, viz. measured retention time (\bar{t}), number of completely mixed reactors flowing in series (N), dispersion number (d), volume per bulk volume (V_f), and the index of short-circuiting (α_s), are presented in Table 4.6. The plug-flow modeling parameter, N , confirms observations made above with regards to Figure 4.26. The value of ca. 500 indicates that the flow regime is a mix of ideal plug flow and completely mixed. The fraction of voids, 55.1%, indicates that the current system is not optimized and the presence of the rock berms does have an impact of the void volume. Further, over half of the flow is short-circuiting the system. This is most likely due to preferential flow paths established within the system and through the rock berms.

Table 4.6 Hydraulic characteristics of Rock Island #7 Cell 3 without aeration modifications

Parameter	Cell 3
T (days)	9.1
N	518.5
d	0.8×10^{-3}
α_s	0.44

Two subsequent tracers were performed on Cell 3 (Figure 4.23), with the addition an aeration stone placed in the first segment, or Cell 3a. The aerating stone was suspended from a floating platform with a constant submerged depth of 24 inches below surface water level (SWL). Using this configuration, the aeration stone maintained a constant depth below SWL. Aeration was supplied either by a battery powered air pump or mechanical bladder pump (Figure 4.27). The battery was recharged using a solar panel connected to a voltage regulator. The bladder air pump was connected to a windmill. Only one aerator was operated for each of the two sets of tracer studies: solar power and windmill power, each completed in triplicates. Care was taken to ensure that within each tracer study, set similar flow, water elevation, and tracer concentration were maintained. An uncontrolled experimental variable, aeration flow rate, was not regulated within the triplicates or among the two different aeration units.

Hydraulic characteristics of Cell 3, viz. measured retention time (\bar{t}), number of completely mixed reactors flowing in series (N), dispersion number (d) and the index of short-circuiting (α_s), are presented in Table 4.7. There was a significant increase in the actual hydraulic detention time between the two aeration units. The solar aeration unit did not significantly (CI 95%, t -test) increase the hydraulic detention time of the tracer as compared to the control system (no aeration). However, a nearly 67% increase in the hydraulic detention time was observed for the windmill aeration unit. The observed detention time of 15 days for Cell 3 with the windmill aeration unit approximated the theoretical hydraulic detention time using averaged flow and system volume. This resulted in a significant ($p < 0.05$) decrease flow short circuiting.



Figure 4.27. Solar panel (left) and windmill (right) placed on high terrace between Cell 1 (background) and Cell 3 (foreground).

Table 4.7 Hydraulic characteristics of Rock Island #7 Cell 3 with aeration modifications

Parameter	Solar	Windmill
T (days)	9.4	15
N	562.6	8.7×10^{16}
d	8.8×10^{-4}	5.8×10^{-18}
α_s	0.43	0.27

The desired result to improve hydraulic retention time was clearly achieved with the windmill aeration unit. Both the dispersion number and number of completely mixed reactors flowing in series for this configuration identified that the system approached a complete mixed flow regime. Although some caution should be noted that the consistency of this completely mixed flow regime may fluctuate with wind speed. The solar powered aeration unit did not significantly increase the hydraulic retention time, and it was observed that the sparging rate was lower for the unit as compared visually for the windmill aeration unit. It must be noted that the solar unit at Rock Island #7 was considerably smaller and less expensive than the units deployed at Mine #6 and Mayer Ranch. Airflow and bubble production was considerably lower, perhaps impacting these conclusions,

4.2.3 Mayer Ranch System tracer studies

The tracer studies completed at Mayer Ranch were performed on Cells 4S and 4N of the system (Figure 4.28). These cells are a set of parallel non-vegetated free water surface (FWS) ponds that act as re-aeration and settlement basins. The cells have two submerged and independent aeration systems, the main purpose of which is to speed the aeration of the water in the ponds.



Figure 4.28. MRPTS aerial photo. Cells 4S and 4N in red. The green circle indicates the location of the aeration systems and the arrow points the water flow direction.

The aeration systems are powered by renewable power sources; aeration in Cell 4S is powered by a solar panel and Cell 4N is powered by a windmill (Figure 4.29). Water flows in the cells from a set of perforated pipes under the limestone layer in vertical flow bioreactor Cells 3N and 3S and it flows out by a set of underground pipes that connect to Cells 5S and 5N.

In order to perform the tracer studies, a known volume of rhodamine was injected into the Agri-drain flow control structure connecting the process units (Figure 4.30) located at the inflow points of Cells 4S and 4N, using a funnel and tubing system. The pulse of rhodamine was monitored using two YSI 600 OMS sondes equipped with an optical sensor. These sondes were deployed at the outflow Agri-drains of cell 4S and 4N and they were set to collect mass concentration data every 15 minutes. The tracer concentration was monitored well past the expected TBC time to allow for the system to reach background concentrations of rhodamine.



Figure 4.29. Solar panel (left) and windmill (right) placed between Cell 4S and 4N at the Mayer Ranch system.



Figure 4.30. Agri-Drain flow control structure (view from above).

Four independent tracers studies were completed, two in Cell 4S and two in Cell 4N. The first set of tracer studies was performed with the aeration units OFF, and the second set was performed with the aeration units ON.

In the first set of tracer studies (Figure 4.31), the aeration system in Cell 4S and 4N were turned OFF and 300 mL of rhodamine was introduced into the systems. A step-wise integration of the product of tracer concentration and increment time per differential time was used to determine

the actual retention time in each Cell. Figure 4.32 is an example of the breakthrough curve obtained in Cells 4S and 4N.

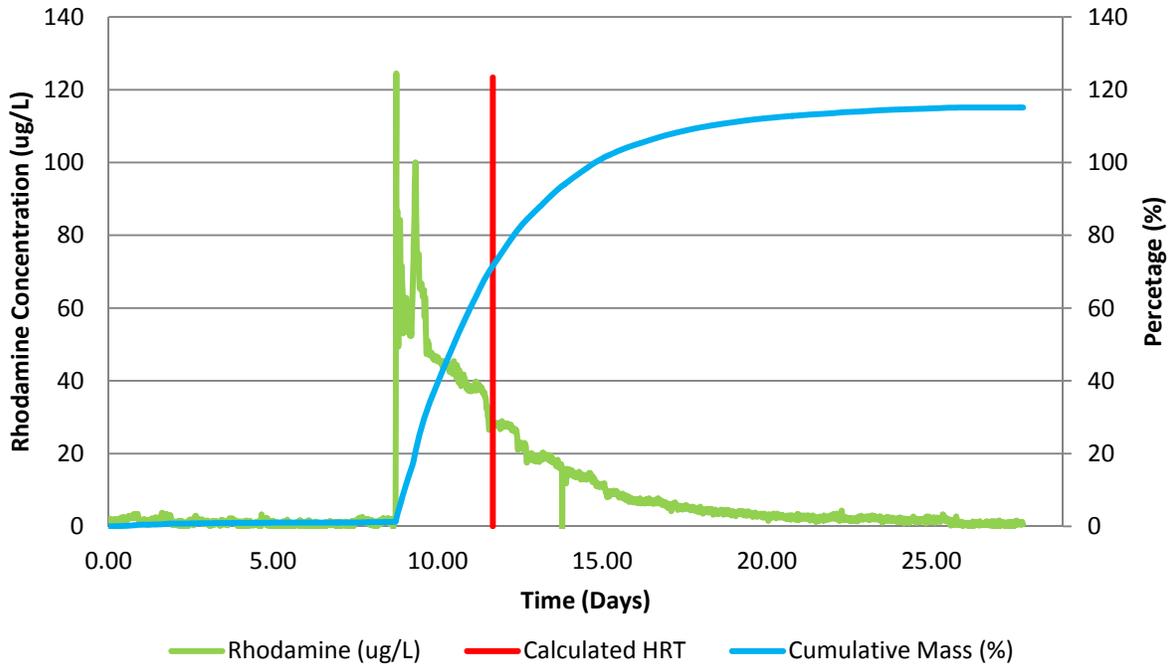


Figure 4.32. Tracer Study Cell 4N Aerator OFF

As seen in Figure 4.32 the mass recovery for rhodamine was >100% in both Cells, thus indicating that there was no loss of dye during the period when the tracer study took place and that our target of >70% mass recovery was exceeded which indicates that the test is reliable.

Hydraulic characteristics as number of completely mixed reactors flowing in series (N), dispersion number (d) and the index of short-circuiting (α_s), are presented in Table 4.8.

With the aeration system OFF, Cell 4S and Cell 4N presented a flow pattern that approached ideal plug flow (d is closer to 0). The systems do not contain dead volume or significant short circuiting areas; this can be inferred because the calculated Hydraulic Retention Time (HRT) is bigger than the theoretical HRT and the α_s does not approach to the extreme boundary of 1.

Table 4.8. Hydraulic characteristics of Mayer Ranch Cells 4S and 4N with aeration off.

Parameter	4S (Solar)	4N (Windmill)
T (days)	11.67	10.82
N	14.48	21.13
d	0.03	0.02
α_s	0.25	0.16

In the second set of tracer studies (Figure 4.33), the aeration systems in Cell 4S and 4N were turned ON and 350 mL of rhodamine was introduced in the Cells. A step-wise integration of the product of tracer concentration and increment time per differential time was used to determine the actual retention time in each Cell. In this scenario the mass recovery for rhodamine in Cells 4S and 4N was >100% in both Cells; thus indicating that there was no loss of dye during the period where the tracer study took place and that our target of >70% mass recovery was exceeded which indicates that the test is reliable. Hydraulic characteristics as number of completely mixed reactors flowing in series (N), dispersion number (d), and the index of short-circuiting (α_s), are presented in Table 4.9.

Table 4.9. Hydraulic characteristics of Mayer Ranch Cells 4S and 4N with aeration on.

Parameter	4S (Solar)	4N (Windmill)
T (days)	16.16	17.01
N	28.34	32.01
d	0.01	0.01
α_s	0.18	0.17



Figure 4.33. RWT flowing through Cell 4N aerator ON (side view).

With the aerator system on, Cell 4S and Cell 4N still presented a flow pattern that approaches ideal plug flow. The system does not present any dead volume or short circuiting areas. It is important to mention that with the aeration systems ON there was almost a 73% increase in the HRT in both cells, and the number of completely mixed reactors flowing in series (N) and the index of short-circuiting (α_s) also increased. This indicates that the aeration system is helping the water to get more mixing in both cells. Between the aeration systems being powered by the

solar panel and windmill, there was no significant difference, which indicates that both methods are appropriate for the system.

4.2.4 Spatial water quality

In addition to tracer studies, the effects of aeration were evaluated at the Rock Island #7 site by collecting spatial DO data in Cell 1 and Cell 3.. For aeration off analyses, aeration was turned off for one week before the DO measurements were taken. For aeration on analyses, aeration was turned on for more than one week before the DO measurements were taken. Data were collected with a YSI Optical DO probe, at 1 foot below water level (Figures 4.34 and 4.35).

Although differences in the spatial pattern of DO did exist, no substantial patterns of consequence emerged. As expected, DO concentrations were lower closer to the location of the aerators when they were turned off. However, DO did substantially increase with flow through the process unit whether aerators were turned off or on. The internal rock berms in these two cells likely helped to increase DO concentrations regardless of the addition of off the grid aeration. It is apparent that the location of the front of low DO water is impacted by the presence of operating aerators.



Figure 4.34. Spatial patterns of DO (% saturation) in Cells 1 and 3 at the Rock Island #7 passive treatment system with aerators off.



Figure 4.35. Spatial patterns of DO (% saturation) in Cells 1 and 3 at the Rock Island #7 passive treatment system with aerators on.

5.0 Conclusions

Methods to enhance aerobic passive treatment are necessary to decrease passive treatment system size and thus reduce construction and maintenance costs. Effective methods would be both economically attractive and environmentally necessary. For this project, it was hypothesized that relatively simple, renewable energy-driven re-aeration devices requiring limited operation and maintenance would effectively enhance aerobic passive treatment processes by re-oxygenating and mixing the water column, thus positively affecting iron oxidation and retention rates and/or sulfide and biochemical oxygen demand (BOD) removal. Cost-effective wind- and solar-powered re-aeration systems are commercially available and are commonly used in aquaculture and lake or pond management and, with little modification, can produce an adequate amount of pressure to sustainably re-aerate oxygen depleted mine waters, thus improving water quality. The efficacy of two different re-aeration devices (wind- and solar-powered) were evaluated specifically as to their effect on mine water quality improvement, oxygen demanding substance removal and hydraulic performance. Through a combination of water quality and quantity analyses (both temporal inflow/outflow and in situ spatial studies) and tracer studies (to determine retention times and other characteristics), the effects of these enhancements on treatment performance was evaluated.

Significant challenges were presented at the two original study sites (Mine #6, Arkansas and Rock Island #7 Oklahoma) due to climatic and weather-related phenomena. Lack of consistent mine water flows eliminated Mine #6 from further study. The Mayer Ranch system at the Tar Creek Superfund Site was added.

The effects of aeration on iron oxidation and retention were evaluated at only a single location, Rock Island #7 Cell 1. Aeration resulted in locally increased DO concentrations near the air stones, and thus positively influenced rates of iron retention in the initial treatment pond. However, these effects were limited in scope and difficult to quantify due to the wide variation in both mine drainage water quality and quantity at this site. Installation of solar- and wind-powered re-aeration devices at a site with perennial flows, consistent iron concentrations and reasonable retention times (e.g., Mayer Ranch) may help to explore these questions and reach definitive conclusions. Iron retention at Rock Island #7 may be limited by the pond-like nature of the initial oxidation pond, as opposed to a channel configuration. With such low flows entering the system, flows are essentially stagnant the great majority of time.

The effects of re-aeration on oxygen demanding substances produced by vertical flow bioreactors was evaluated at three sites, Mine #6, Rock Island #7 Cell 3, and Mayer Ranch Cells 4N and 4S. Although BOD concentrations were not high enough at any site to be deemed problematic and they varied temporally over a large concentration range, substantial decreases in

BOD occurred when aerators were in place and operational, although they were not statistically different either between or among sites.

Despite a similarly wide range of measured concentrations, significant differences in performance did exist for total sulfide removal in ponds with both solar- and wind-powered re-aeration devices installed. Overall, sulfide concentrations were lower after re-aeration than before, although great variability did exist in paired concentrations for any given sampling event. No statistical difference in performance existed between the types of aeration devices utilized for oxygen demanding substance removal.

In terms of the effects of aeration on hydraulic performance, mixed results were found depending on the study site. At Rock Island #7, windmill aeration had a statistically significant effect on hydraulic parameters, when compared to solar-driven re-aeration. This was not the case at the side by side comparison of technologies at Mayer Ranch. However, it is uncertain whether this result is indicative of a true technological advantage, or if it is simply reflective of the type of solar units employed in this study. Continuous water quality data do demonstrate that properly maintained solar units are able to function under a mix of conditions, and because they store energy in a battery, are not as substantially influenced by time of day, season or weather patterns as wind-driven devices. Wind-driven units effectively aerate only when the wind is blowing at a minimum speed to turn the turbine blades. Aeration is therefore nil during calm periods, common at certain times of day and year.

The overall effectiveness of off the grid aeration technologies may be summarized as follows.

- Solar- and wind-driven re-aeration devices demonstrated a considerable positive influence on retention of traditional mine drainage constituents of concern, e.g. metals. At all study sites, effluent metal concentrations were significantly lower than influent concentrations and apparent rates of metal retention were similar to expected values.
- Solar- and wind-driven re-aeration devices also had a demonstrable effect on dissolved oxygen concentrations, oxygen percent saturation and oxidation-reduction potential values. The limited local influence of individual air stones appears to be a function of system water quality, process unit depth and placement of the aerator. Multiple air stones may be necessary to see consistent and dramatic effects on whole system oxygen concentrations.
- Concentrations of oxygen demanding substances (BOD and total sulfide) in vertical flow bioreactor effluents were effectively decreased by subsequent solar- and wind- driven re-aeration in downstream ponds. Although concentrations varied widely over time, overall decreases were documented. Although measurable, BOD concentrations were not found to be of significant concern at any site. Total sulfide, on the other hand, was found to be

at seasonably toxic concentrations. Re-aeration devices helped decrease sulfide concentrations and may represent an effective sulfide removal technology.

- Re-aeration may have considerable influence on the hydraulic characteristics of passive treatment system process units. Wind-driven re-aeration resulted in considerable differences in several hydraulic parameters at the Rock Island #7 passive treatment system (e.g., retention time, number of reactors in series, dispersion number and index of short-circuiting). At Mayer Ranch, however, aeration did not substantially change these values, perhaps due to the deeper, more pond-like design of these units than the shallower wetland-type process units at Rock Island #7.
- Overall capital costs for solar- and wind-driven aeration devices were found to be modest. The large three-diaphragm solar unit at Mine #6 cost just more than \$11,000 in 2010. The smaller solar unit at Mayer Ranch cost \$5,200 in 2008. Capital costs for the windmills at Mayer Ranch and Rock Island #7 were approximately \$2,000-\$2,500 each. The much smaller solar unit at Rock Island #7 was purchased for \$2300. Similarly, maintenance commitments were likewise modest. Air stones must be periodically checked for clogging, lines examined for air leaks, and moving parts kept greased and oiled on an annual basis.
- Overall, off the grid aeration shows promise as a passive treatment tool. Enhanced removal of nuisance constituents like sulfide produced by vertical flow bioreactors shows potential for further application. The influence of these devices on iron oxidation removal rates warrants further study at a suite of sites with appropriate flow and system conditions. Further inquiry into hydraulic performance is also warranted, as the relationship between specific hydraulic characteristics and water quality improvement performance are evaluated.

6.0 Personnel Summary

A total of 22 scientists, engineers and other interested individuals directly contributed to this project. The breakdown included two faculty members, four doctoral students, eight masters students, two undergraduates at the University of Oklahoma, two undergraduates at regional colleges (Northeast Oklahoma A&M College) and three undergraduates who participated in summer programs, and one high school student. Through OU classes (e.g., CEES 5363 Ecological Engineering Science, CEES 4324 Environmental Biology and Ecology and BIOL 4970 Wetlands Science and Management), approximately another 150 other students were exposed to the project.

7.0 Resulting Presentations and Publications

Two conference proceedings published abstracts and presentations have been produced from this project so far and are included in Appendix A. Although no refereed journal articles have been submitted as of yet, they may be in the future as data analyses continues.

8.0 Literature Cited

- Aldous, P.J. and Smart, P.L. 1988. Tracing Ground-Water Movement in Abandoned Coal Mined Aquifers Using Fluorescent Dyes. *Ground Water*, 26(2): 172-178
- APHA. 1998. Standard Methods for the Examination of Water and Wastewater. 19th Edition American Public Health Association. Washington, DC.
- Athay, D., R.W. Nairn and K.A. Strevett. 2001. Biotic and abiotic iron oxidation kinetics in alkaline mine drainage. In: R.I. Barnhisel, B.A. Buchanan, D. Peterson and J.J. Pfeil (eds.), *Land Reclamation – A Different Approach, Proceedings, 18th Annual National Meeting of the American Society for Surface Mining and Reclamation*, Albuquerque, NM, pp. 524-528
- Athay, D. 2003. Water quality and substrate analysis of an acid mine drainage treatment wetland system, Masters of Environmental Science thesis, University of Oklahoma, Norman, OK, 191 pp.
- Athay, D., R.W. Nairn and K.A. Strevett. 2003. Mine drainage treatment wetland substrate analysis. In: R. Barnhisel (ed.), *Working Together for Innovative Reclamation, Proceedings of a Joint Conference, 9th Billings Land Reclamation Symposium and 20th Annual Meetings of the American Society of Mining and Reclamation*, Billings, MT, pp. 2-16.
- Behum, P. 2011. Personal communication regarding Mine #6 passive treatment system, Office of Surface Mining Reclamation and Enforcement
- Boyd, C.E. 1998. Pond water aeration systems. *Aquacultural Engineering* 18(1): 9-40.
- Chua, L.H.C., Robertson, A.P., Yee, W.K., Shuy, E.B., Lo, E., Lim, T.T., and Tan, S.K., 2007. Use of Fluoresceine as a Ground Water Tracer in Brackish Water Aquifers. *Ground Water*, 45(1): 85-
- Crisp, T., R.W. Nairn, K.A. Strevett, J.W. Everett and B. Chen. 1998. Passive treatment using coal combustion products: results of a column study. *Abstracts, 25th Anniversary and 15th Annual National Meeting of American Society for Surface Mining and Reclamation*, St. Louis, MO.
- DeMoyer, C.D., E.L. Schierholz, J.S. Gulliver and S.C. Wilhelms. 2003. Impact of bubble and free surface oxygen transfer on diffused aeration systems. *Water Research* 37: 1890-1904.
- Dempsey, B.A., H.C. Roscoe, R. Ames, R. Hedin and B-H Jeon. 2002. Ferrous iron chemistry in passive abiotic systems for the treatment of mine drainage. *Geochemistry, Exploration, Environment, Analysis* 1: 81-88
- EPA. 1983. Methods for the Chemical Analysis of Water and Wastes. EPA/440/4-90/003, Environmental Monitoring and Support Laboratory, Cincinnati, OH.
- Field, M.S. and Pinsky, P.F. 2000. A Two-Region Nonequilibrium Model for Solute Transport in Solution Conduits in Karstic Aquifers. *Journal of Contaminant Hydrology* 44: 329-351
- Flanagan, N., W.J. Mitsch, and K. Beach. 1994. Predicting metal retention in a constructed mine drainage wetland. *Ecological Engineering* 3:135-159

- Gusek, J.J. 2001. Why do some passive treatment systems fail while others work? In: *Proceedings of the National Association of Abandoned Mine Land Programs*, Athens, Ohio, 14 pp.
- Hedin, R. 2009. Iron removal by a passive system treating alkaline coal mine drainage. *Mine Water and the Environment* 27:200-209
- Hedin, R.S. 2004. The use of measured and calculated acidity values to improve the quality of mine drainage datasets. In: R. Barnhisel (ed.), *21st National Conference of the American Society of Mining and Reclamation and 25th West Virginia Surface Mine Drainage Task Force Symposium*, Morgantown, WV, pp. 879-898.
- Hedin, R.S. and R.W. Nairn. 1993. Contaminant removal capabilities of wetlands constructed to treat coal mine drainage. In: G.A. Moshiri (ed.), *Constructed Wetlands for Water Quality Improvement*, CRC Press, Lewis Publishers, Inc. Chelsea, MI pp. 187-195.
- Hedin, R.S., R.W. Nairn and R.L.P. Kleinmann. 1994. Passive Treatment of Coal Mine Drainage. U.S. Bureau of Mines Information Circular 9389. 37 pp.
- Jageman, T.C., R.A. Yokley and G.W. Heunisch, 1988. The Use of Pre-Aeration to Reduce the Cost of Neutralizing Acid Mine Drainage. In: *Proceedings of the 1988 Mine Drainage and Surface Mine Reclamation Conference*, Pittsburgh, PA, pp. 131-135.
- Kepler, D.A. and E.C. McCleary. 1994. Successive alkalinity producing systems (SAPS) for the treatment of acidic mine drainage. U.S. Bureau of Mines Special Publication SP 06A-94, Volume 1. pp. 195-204.
- Kirby, C. S.; H. Thomas; G. Southam; R. Donald, 1999, Relative contributions of abiotic and biological factors to Fe(II) oxidation kinetics in acid mine drainage, *Applied Geochemistry* , 14, 4, 511-530.
- Kirby, C.S., and J.A. Elder. 1998. Field determination of Fe²⁺ oxidation rates in acid mine drainage using a continuously-stirred tank reactor, *Applied Geochemistry* 13(4): 509-520
- Levenspiel, O. 1972. *Chemical Reaction Engineering*, Wiley, New York, pp. 411-416.
- McCool, C. 2009. Personal communication regarding Mine #6 passive treatment system, Arkansas Department of Environmental Quality
- McCool, C. 2011. Personal communication regarding Mine #6 passive treatment system, Arkansas Department of Environmental Quality
- Mitsch, W. J. and K.M. Wise, 1998. Water quality, fate of metals, and predictive model validation of a constructed wetland treating acid mine drainage. *Water Research* 32: 1888-1900.
- Mitsch, W.J. and J.G. Gosselink. 2000. *Wetlands*. 3rd Ed. John Wiley and Sons, Inc. New York. 920 pp.
- Mitsch, W.J. and S.E. Jorgensen. 2004. *Ecological Engineering and Ecosystem Restoration*. John Wiley and Sons, NY. 411 pp.
- Nairn, R.W. and R.S. Hedin. 1992. Designing wetlands for the treatment of polluted coal mine drainage. In: M. C. Landin (ed.), *Wetlands: Proceedings of the 13th Annual Conference of the Society of Wetland Scientists*, New Orleans, LA, South Central Chapter, Society of Wetland Scientists, Utica, MS, pp. 224-229.
- Nairn, R.W., M.N. Mercer, and J.W. Everett. 1999. Passive treatment using coal combustion products: An innovative vertical flow constructed wetland field study. In: *Mining and Reclamation for the Next Millennium, Proceedings, 16th Annual National Meeting, American Society for Surface Mining and Reclamation*, Scottsdale, AZ.

- Nairn, R.W., A.D. O'Sullivan and J. Coffey. 2002. Iron oxidation in net alkaline CO₂-rich mine waters. *In: R. Barnhisel and M. Collins (eds.), Reclamation with a Purpose*, Proceedings of the 19th Annual National Conference of the American Society of Mining and Reclamation, and 6th International Conference of the International Affiliation of Land Reclamationists, Lexington, KY, pp. 1133-1136.
- Nairn, R.W., T. Beisel, R.C. Thomas, J.A. LaBar, K.A. Strevett, D. Fuller, W.H. Strosnider, W.J. Andrews, J. Bays, and R.C. Knox. 2009. Challenges in Design and Construction of a Large Multi-Cell Passive Treatment System for Ferruginous Lead-Zinc Mine Waters. *Proceedings of the 26th National Conference of the American Society of Mining and Reclamation*, Billings, MT, pp. 871-892.
- Oklahoma Climatological Survey. 2009. http://climate.mesonet.org/county_climate/Products/CountyPages/latimer.html
- Park, B., and B.A. Dempsey. 2005. Mechanisms of Heterogeneous Oxidation of Fe(II) on Ferric Oxide at Neutral pH. *Environmental Science and Technology* 39(17):6494-6500
- Pennsylvania Department of Environmental Protection and Office of Surface Mining Reclamation and Enforcement. 2008. Mine Drainage Treatability and Project Selection Guidelines, 42 pp.
- Porter, C.M. 2004. Impacts of treated and untreated coal mine drainage on biological organization and evaluation of ecosystem functions in a constructed treatment wetland, Masters of Environmental Science thesis, University of Oklahoma, Norman, OK, 191 pp.
- Porter, C.M. and R.W. Nairn. 2008. Ecosystem Functions within a Mine Drainage Passive Treatment System. *Ecological Engineering: The Journal of Ecosystem Restoration*. 32(4): 337-346.
- Porter, C.M. and R.W. Nairn. 2010. Fluidized Bed Ash and Passive Treatment Reduce the Adverse Effects of Acid Mine Drainage on Aquatic Organisms. In review at *Science of the Total Environment*, 9/2009
- Sabatini, D. and Austin, T.A. 1991. Characteristics of Rhodamine WT and Fluorescein as Adsorbing Ground-Water Tracers. *Ground Water* 29(3): 341-349
- Sabatini, D., Kasnavia, T., and Vu, D. 1999. Fluorescent Dye and Media Properties Affecting Sorption and Tracer Selection. *Ground Water* 37(3): 376-381
- Schmidt, T.W. 2004. Evaluation of Aeration Techniques for Mine Water Treatment in Passive Systems. *In: Proceedings, 2004 National Meeting, American Society of Mining and Reclamation and 25th West Virginia Surface Coal Mine Drainage Task Force*, Morgantown, WV, pp. 1619-1627.
- Schnaitman, C.A., M.S Korczynski and D. Lundgren. 1969. Kinetic studies of iron oxidation by whole cells of *Ferrobacillus ferrooxidans*. *Journal of Bacteriology* 9: 552-557.
- Singer, P.C, and W. Stumm. 1970. Acidic mine drainage: The rate determining step. *Science* 167:1121-1123
- Skelly and Loy 2004. The Importance of Aeration in Coal Mine Drainage Treatment. *Progress and the Environment*, 3 pp.
- Skousen, J.G. and P.F. Ziemkiewicz. 1996. Acid mine drainage control and treatment. 2nd Edition. National Research Center for Coal and Energy, West Virginia University, 56 pp.
- Smart, P.L. and Laidlaw, I.M.S. 1977. An Evaluation of Some Fluorescent Dyes for Water Tracing. *Water Resources Research* 13(1): 15-33
- Solar Aerators. 2009. <http://www.solaraerator.com/>

- Sung, W. and J. Morgan. 1980. Kinetics and product of ferrous iron oxygenation in aqueous systems. *Environmental Science and Technology* 14: 561-568
- Superior Windmill Aeration Systems. 2009. <http://www.windmillaeration.com/>
- U.S. Environmental Protection Agency. 1993. Determination of Inorganic Anions by Ion Chromatography. USEPA Method 300.0, Environmental Monitoring Systems Laboratory, Office of Research and Development.
- U.S. Environmental Protection Agency. 2006. Test Methods for Evaluating Solid Wastes, Physical and Chemical Methods. USEPA SW-846, Office of Solid Waste, Washington, D.C. <http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm>
- U.S. Geological Survey. 2003. National Field Manual for the Collection of Water Quality Data. <http://water.usgs.gov/owq/FieldManual/>
- Watzlaf, G.R., K.T Schroeder, R.L.P. Kleinmann, C.L. Kairies and R.W. Nairn. 2004. The Passive Treatment of Coal Mine Drainage. DOE/NETL-2004/1202. National Technical Information Service, Springfield, VA, 72 pp.
- Westerman, P.W. and R.H. Zhang. 1997. Aeration of livestock manure slurry and lagoon liquid for odor control: a review. *Applied Engineering in Agriculture* 13(2): 245-249.
- Wildeman, T., J. Gusek, J. Dietz and S. Morea. 1991. Handbook for constructed wetlands receiving acid mine drainage. Environmental Protection Agency, Cincinnati, OH.
- Willow, M., R.R.H. Cohen, and L. Thompson. 1998. Factors affecting the efficiency of passive mine drainage treatment systems. *Tailings and Mine Waste* 98: 899-907.
- Yepez, S.A. and R.W. Nairn. 2012. Nutrient and Sulfide Export from a Mine Drainage Passive Treatment System. *Proceedings of the 29th National Conference of the American Society of Mining and Reclamation*, Tupelo, MS, pp. 539-556.
- Younger, P.L., S.A. Banwart and R.S. Hedin. 2002. Mine Water: Hydrology, Pollution, Remediation. Kluwer Academic Publishers, Dordrecht, 442 pp.

Appendices

1. Published abstract for 2012 National Meeting of the American Society of Mining and Reclamation
2. Presentation for 2012 National Meeting of the American Society of Mining and Reclamation
3. Published abstract for 2013 National Meeting of the American Society of Mining and Reclamation
4. Presentation for 2013 National Meeting of the American Society of Mining and Reclamation

Re-Aerating Off the Grid: Improving Passive Treatment Success with Solar and Wind Energies¹

R.W Nairn, K.A. Strevett and B.M. Callies²

Abstract: Hundreds of passive treatment systems have been constructed to address abandoned mine water quality problems. In some cases, system performance has been less than adequate due to lack of understanding of site-specific water quality or quantity characteristics, required treatment mechanisms or the limited maintenance necessary to sustain operation, all of which may result in poor performance. In this study, passive treatment effectiveness was evaluated by examining, understanding and improving aeration in both oxidation (designed for oxidative iron retention) and re-aeration (designed to re-aerate waters after passage through anaerobic conditions in vertical flow bioreactors) ponds. Methods to enhance aerobic treatment are necessary to not only improve performance, but to decrease passive treatment system size and thus reduce construction and maintenance costs. Relatively simple, renewable energy-driven re-aeration devices requiring limited operation and maintenance may effectively enhance aerobic passive treatment processes by re-oxygenating and mixing the water column, thus positively affecting iron oxidation and retention rates and/or sulfide and biochemical oxygen demand (BOD) removal. The efficacy of two different re-aeration devices (wind- and solar-powered) were evaluated specifically as to their effect on oxygen mass transfer, carbon dioxide exsolution, and the kinetics of both iron oxidation, hydrolysis and settling, and sulfide/BOD removal. Water quality changes and hydraulic performance of two passive treatment systems both with and without additional aeration were comprehensively evaluated. Both enhanced iron retention performance of oxidation ponds and oxygenation performance of re-aeration ponds was assessed through design, installation and monitoring of sustainable aeration devices. In addition to enhancement of water quality improvement performance, operation and maintenance concerns were also evaluated.

Additional Key Words: Aeration, iron oxidation, sulfide removal, biochemical oxygen demand removal, renewable energy

¹Paper was presented at the 2012 National Meeting of the American Society of Mining and Reclamation, Tupelo, MS, *Sustainable Reclamation*, June 8 - 15, 2012. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

²Robert W. Nairn, Professor, Keith A. Strevett, Professor, and Bryce M. Callies, Graduate Research Assistant, Center for Restoration of Ecosystems and Watersheds, School of Civil Engineering and Environmental Science, University of Oklahoma, 202 West Boyd Street, Norman, OK, 73019.

Re-Aerating Off the Grid: Improving Passive Treatment Success with Solar and Wind Energies

R.W Nairn, K.A. Strevett and B.M. Callies
Center for Restoration of Ecosystems and Watersheds
School of Civil Engineering and Environmental Science
The University of Oklahoma, Norman, OK

Funding provided through OSMRE
Applied Science Program
Cooperative Agreement S11AC20000





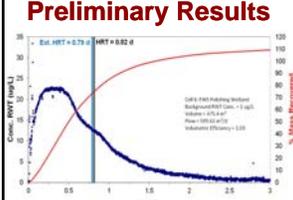
Why Aerate



Study Objectives and Sites



Preliminary Results



Conclusions

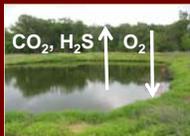




Aeration in Passive Treatment

- Oxidative iron removal in net alkaline waters
- Re-aeration of vertical flow bioreactor effluents

- Mass transfer gas-water interface processes

Aeration in Passive Treatment

- Oxidative iron removal in net alkaline waters

$$\text{Fe}^{+2} + 2\text{HCO}_3^- + 0.25\text{O}_2 \rightarrow \text{FeOOH(s)} + 0.5\text{H}_2\text{O} + 2\text{CO}_2$$

- Oxidation rate limiting
- Hydrolysis rapid
- Adequate solids settling critical for effective iron retention

Iron Oxidation Kinetics

- Homogenous and heterogenous mechanisms

– Sung and Morgan 1980, Tufecki and Sarikaya 1996, Dempsey et al. 2002, Park and Dempsey 2005, Hedin 2008

$$\text{rate}_{\text{homogenous}} = \frac{k_1[\text{Fe}^{+2}][\text{O}_2]}{\{\text{H}^+\}^2}$$

$$\text{rate}_{\text{heterogenous}} = \frac{k_2[\text{Fe(III)}][\text{Fe}^{+2}][\text{O}_2]}{\{\text{H}^+\}}$$

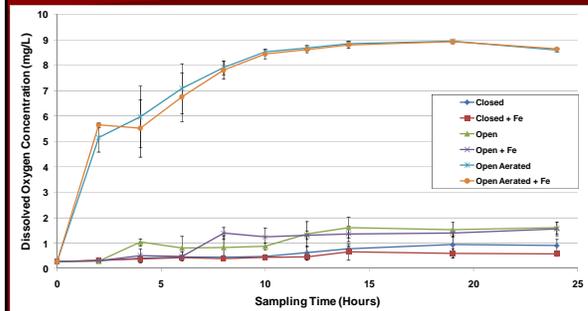
O₂ Addition and CO₂ Exsolution

- Operationally, diffusion or entrainment of atmospheric O₂ critical
- Exsolution of elevated CO₂ in net alkaline waters also important
 - Cravotta 2007, Hedin 2008, Kirby et al 2009

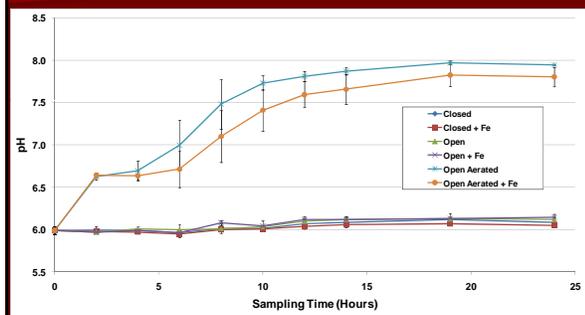


- Increases pH; does not effect alkalinity

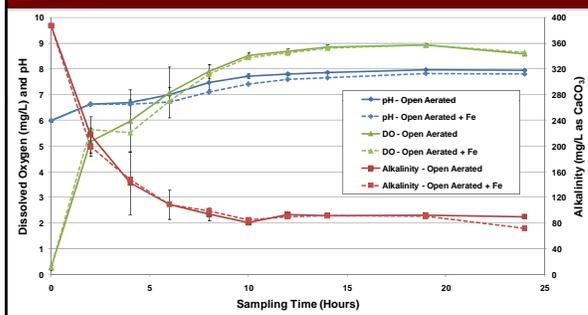
Aeration increases DO!



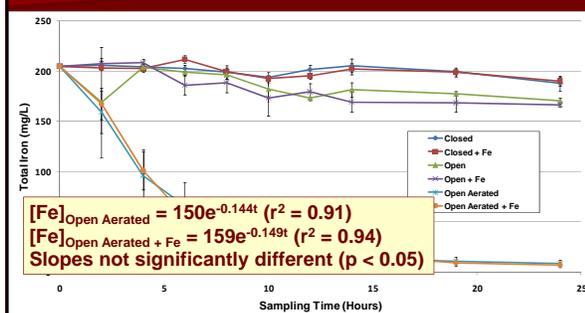
Aeration increases pH as CO₂ degasses



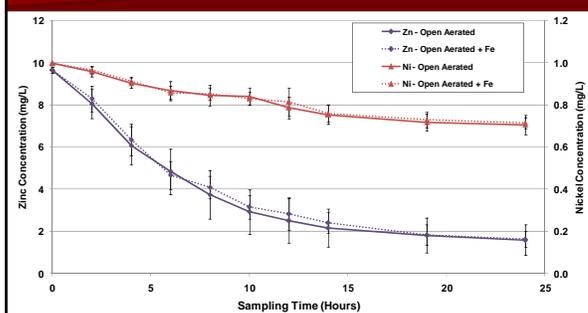
Added Fe showed no effect in Open Aerated treatments



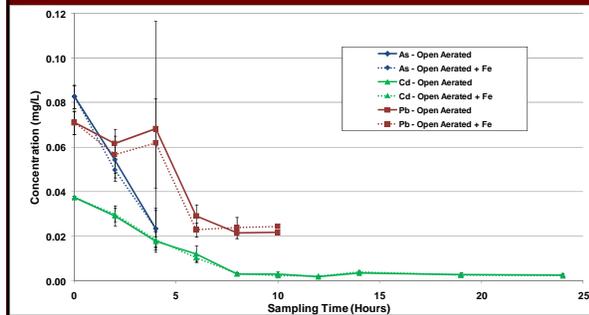
Iron removal greatest in Open Aerated treatments



Zn and Ni removal nil in Closed and Open treatments but significant in Open Aerated treatments



As, Cd and Pb removal nil in Closed and Open treatments but significant in Open Aerated treatments



Aeration in Passive Treatment

2. Re-aeration of vertical flow bioreactor effluent



- $[\text{H}_2\text{S}]$ often at nuisance odor levels; can reach ecotoxic levels
- $[\text{BOD}_5]$ and nutrient concentrations can be problematic for receiving streams

Aeration in Passive Treatment

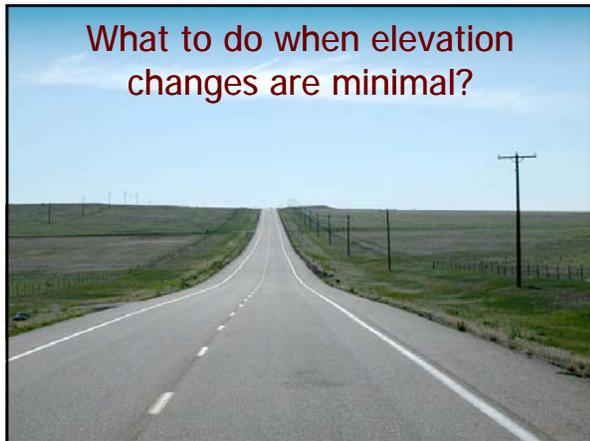
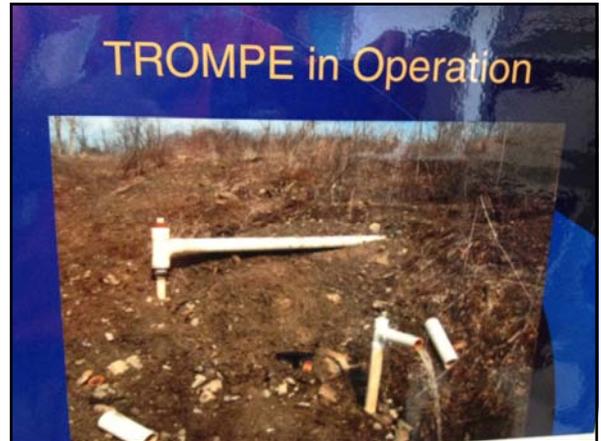
- Especially problematic during initial start up
- One problem (elevated metals) "traded" for another (elevated oxygen demand and sulfide).



Common Aeration Techniques

- Utilize elevation changes/head pressure differences
- Physically entrain air via turbulent flow
- Well-studied for iron oxidation; less so for VFBR re-aeration



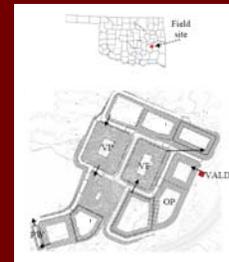


Objectives

- Evaluate baseline water quality changes and hydraulic performance of two passive treatment systems
- Enhance iron retention performance of oxidation ponds
- Enhance oxygenation performance of re-aeration ponds
- Assess operation and maintenance concerns

Hartshorne Study Site

- Abandoned Rock Island underground coal mine
- Constructed late 2005
 - Vertical anoxic limestone drain
 - Two VFBRs
 - Three OPs
 - Polishing wetland
- Flows: <1 to 75 LPM
- Cooperative effort by OSMRE, OCC and OU

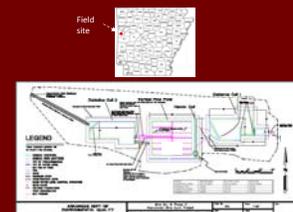


Hartshorne Water Quality

	Minimum	Maximum	Median	n
Temperature (°C)	17.4	22.3	20.9	18
pH	5.25	5.64	5.36	18
DO (mg/L)	0.1	0.8	0.2	17
Specific conductance (mS/cm)	2960	17100	11800	18
Alkalinity (mg/L)	95	214	117	18
Acidity (mg/L)	419	2402	1405	15
Iron (mg/L)	215	1311	765	15
Manganese (mg/L)	14	29	18	15
Sodium (mg/L)	1400	3437	1893	4
Calcium (mg/L)	259	380	320	9
Magnesium (mg/L)	170	361	230	8
Chloride (mg/L)	197	381	225	9
Sulfate (mg/L)	5456	13620	7842	12

Mine #6 Site

- Abandoned Central Coal and Coke Mine #6 Complex
- Constructed 2008
 - Vertical anoxic limestone drain
 - OP
 - VFBR
 - Re-aeration pond
- Cooperative effort by ADEQ and OSMRE

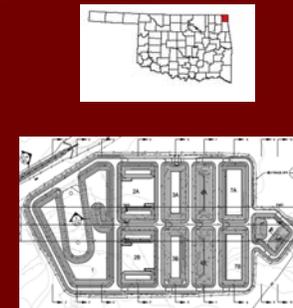


Mine #6 Site

- Water quality
 - 39 mg/L Fe
 - 2 mg/L Mn
- Designed for nominal 700 LPM flow
- Complete loss of water in summer 2011 eliminated site from further study

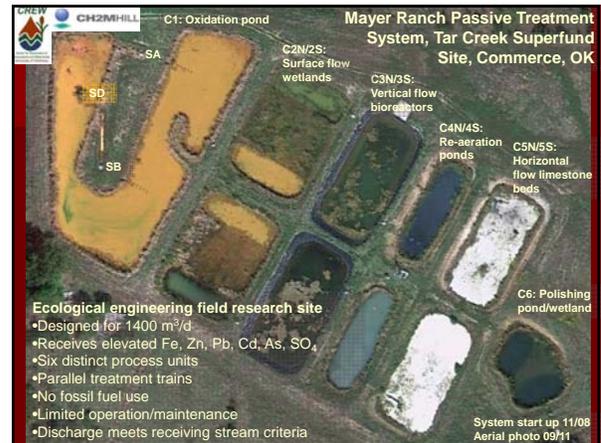
Mayer Ranch Site

- Abandoned Tri-State Lead-Zinc Mining District
- 1000 LPM
- Represent ~ 20% contaminant mass load in watershed

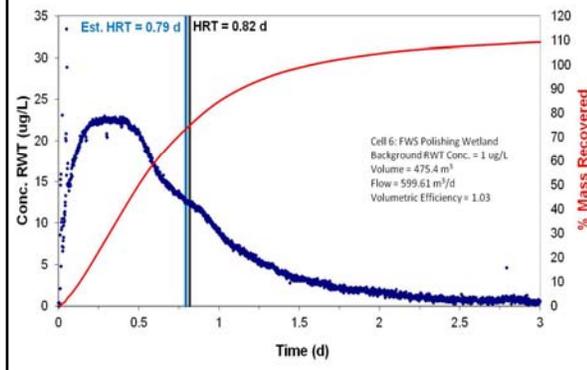


Mayer Ranch Water Quality

pH	5.95 ± 0.06
Alk. (net)	393 ± 18 (29) mg/L
Fe	192 ± 3 mg/L
Zn	11 ± 0.07 mg/L
Ni	0.97 ± 0.02 mg/L
Cd	17 ± 4 µg/L
Pb	60 ± 13 µg/L
As	64 ± 2 µg/L
SO ₄ ⁻²	2239 ± 26 mg/L



Preliminary Results



Hartshorne Site



Hartshorne Site

- Windmill aeration in initial oxidation pond
 - No significant change in overall iron removal rates
 - Fluctuating flow rates/water quality compromise data analyses
- Solar aeration in secondary re-aeration pond
 - Significant air stone fouling problems
- Other O & M issues



Mayer Ranch Site

- Data collection began early 2012
- Parallel evaluation of wind- and solar-units for VFBR effluent
- Airstone configuration important
 - VFBR below-grade discharge
 - Airstone on bottom effectively mixes anaerobic waters
 - Limited stripping of H₂S

Mayer Ranch Site

- Suspended airstone in water column
- Effectively decrease H₂S concentrations



Mayer Ranch Site

- Sulfide removed
- Seasonal patterns could be critical

Sulfide (mg/L)				
	4N in	4S in	4N Out	4S Out
February	1.22	1.41	0.35	0.53
March	5.97	12.84	0.78	0.10
April	8.71	12.92	0.26	1.46
May	13.52	16.81	1.67	1.81

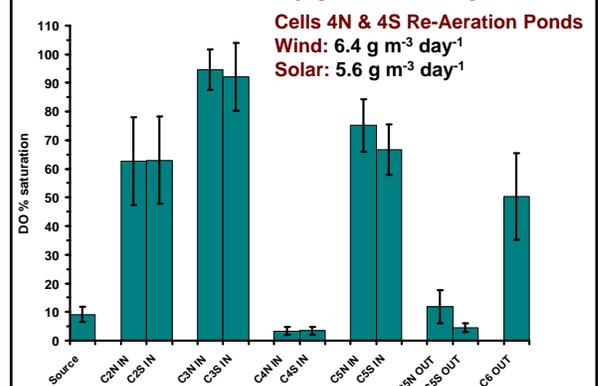


Conclusions

Conclusions

- On limited-relief sites, aeration is critical to effective water quality improvement
- Wind- and solar-powered re-aeration units may provide effective means to strip sulfide from VFBR effluents
- More work needed on enhanced iron oxidation and O&M issues

Dissolved Oxygen Changes





Questions?

<http://crew.ou.edu>

nairn@ou.edu

Off-the-Grid Aeration to Address Nuisance Constituent Production from Specific Passive Treatment System Process Units¹

R.W Nairn and K.A. Strevett²

Abstract: Data from hundreds of passive treatment systems demonstrate successful improvement of abandoned mine water quality by decreasing ecotoxic metals concentrations, and increasing alkalinity concentrations and pH. However, certain biologically-based process units may produce excessive concentrations of atypical, non-mine drainage related constituents. These predominately anaerobic units (e.g., vertical flow bioreactors, sulfate-reducing bioreactors, biochemical reactors, vertical flow ponds, etc.) are designed to promote reductive microbial mechanisms (e.g., fermentation and sulfate reduction). Therefore, even if functioning properly from a mine water quality improvement perspective, effluent waters may contain excessive concentrations of biochemical oxygen demand (BOD), sulfide, and nutrients, have low dissolved oxygen concentrations and oxidation-reduction potential, and cause nuisance odor problems. Compounding a general lack of understanding of these issues, these non-mine drainage related water quality constituents are not typically included in most monitoring schemes and system performance evaluations. In this study, nuisance constituent concentrations and mass balances were developed for re-aeration ponds which were enhanced with renewable energy-driven (solar- and wind-powered) re-aeration devices. The devices were evaluated for their ability to effectively enhance re-oxygenation and mixing of the water column downstream of anaerobic process units. The efficacy of two different re-aeration devices (wind- and solar-powered) were evaluated specifically as to their effect on oxygen mass transfer and the rates of sulfide and BOD removal. Both with and without re-aeration, sulfide, BOD and nutrient concentrations exceeded water quality criteria for most sampling location-event pairs. System effluent dissolved oxygen and oxidation-reduction potential data displayed a distinct seasonality based on the biological nature of production. Nuisance constituent production demonstrated an overall decrease as systems aged, and is likely most problematic in the first few growing seasons. However, more robust monitoring schemes, including constituents beyond the typical mine water parameter suite, may be appropriate when anaerobic process units are included in passive treatment systems.

Additional Key Words: Solar power, wind power, renewable energy, hydrogen sulfide, biochemical oxygen demand, nuisance parameters

¹ Oral paper was presented at the 2013 National Meeting of the American Society of Mining and Reclamation, Laramie, WY, *Reclamation Across Industries*, June 1 – 6, 2013. R.I. Barnhisel (Ed.) Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

² R.W. Nairn and K.A. Strevett are Professors, Center for Restoration of Ecosystems and Watersheds, School of Civil Engineering and Environmental Science, University of Oklahoma, 202 West Boyd St. Norman, OK.

Off-the-Grid Aeration to Address Nuisance Constituent Production in Passive Treatment Systems

R.W. Nairn and K.A. Strevett

Center for Restoration of Ecosystems and Watersheds
School of Civil Engineering and Environmental Science
The University of Oklahoma, Norman, OK



OSMRE Applied Science Program
Cooperative Agreement S11AC20000



Nuisance Constituents

Re-aeration Options

Performance

Conclusions



What do we consider a nuisance?

- Excessive concentrations of atypical, non-mine drainage related constituents
- Produced by predominately anaerobic, biologically-based process units
 - Vertical flow bioreactors (VFBRs)
- Are we simply trading one water quality problem for another?

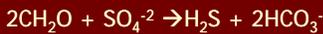
Common Nuisance Constituents

- Elevated nutrient concentrations
 - Nitrogen
 - Phosphorus

- Oxygen demanding substances



- Sulfide at ecotoxic levels



Typical Performance Data

Mayer Ranch Passive Treatment System, Tar Creek Superfund Site, Ottawa County, OK

Targeted Contaminants of Concern Mass Retention

	-----Mass Loadings (g/d)-----				
	As*	Cd*	Fe	Pb*	Zn
Total inflow	57	10	105,000	73	6,770
System outflow	7.3	0.25	479	12	88
Retention	51	9.94	105,000	61	6,690

*Effluent concentrations below detection limit; 1/2 value of practical quantification limit used for mass balance calculations

Data from S. Yepez MS thesis 2012

Typical Performance Data

Mayer Ranch Passive Treatment System, Tar Creek Superfund Site, Ottawa County, OK

Major Nutrients Mass Retention

	-----TP (g/d)-----			-----TN (g/d)-----		
	Fall	Spring	Summer	Fall	Spring	Summer
Influent	1,180	1,890	1,060	491	565	456
OX	-1,160	-1,830	-1,010	-344	-163	-286
SF	-10	-19	-33	-49	40	-78
VF	38	46	62	54	-123	77
RA	-7	-24	11	77	-127	20
LB	-19	-11	52	31	-16	50
PW	-26	-13	-2	-64	55	30
Effluent	21	72	283	195	232	509
Export	-1,160	-1,810	-777	-296	-333	53

Data from S. Yepez MS thesis 2012

Typical Performance Data

Mayer Ranch Passive Treatment System, Tar Creek Superfund Site, Ottawa County, OK

Major Nutrients Mass Retention

	-----TP (g/d)-----			-----TN (g/d)-----		
	Fall	Spring	Summer	Fall	Spring	Summer
Influent	1,180	1,890	1,060	491	565	456
OX	-1,160	-1,830	-1,010	-344	-163	-286
SF	-10	-19	-33	-49	40	-78
VF	38	46	62	54	-123	77
RA	-7	-24	11	77	-127	20
LB	-19	-11	52	31	-16	50
PW	-26	-13	-2	-64	55	30
Effluent	21	72	283	195	232	509
Export	-1,160	-1,810	-777	-296	-333	53

Data from S. Yepez MS thesis 2012

Typical Performance Data

Mayer Ranch Passive Treatment System, Tar Creek Superfund Site, Ottawa County, OK

Total Sulfide Mass Retention

	-----Total Sulfide (g/d)-----		
	Fall	Spring	Summer
Influent	---	---	---
OX	---	---	---
SF	---	---	---
VF	1,460	1,670	6,020
RA	-1,380	-1,620	-2,430
LB	-83	-53	-214
PW	---	---	-5,860
Effluent	---	---	1,000
Export	---	---	868

Data from S. Yepez MS thesis 2012

Typical Performance Data

Mayer Ranch Passive Treatment System, Tar Creek Superfund Site, Ottawa County, OK

Total Sulfide Mass Retention

	-----Total Sulfide (g/d)-----		
	Fall	Spring	Summer
Influent	---	---	---
OX	---	---	---
SF	---	---	---
VF	1,460	1,670	6,020
RA	-1,380	-1,620	-2,430
LB	-83	-53	-214
PW	---	---	-5,860
Effluent	---	---	1,000
Export	---	---	868

Data from S. Yepez MS thesis 2012

Typical Performance Data



Mayer Ranch Passive Treatment System, Tar Creek Superfund Site, Ottawa County, OK

Oxygen Demand Mass Retention

	-----CBOD ₅ (g/d)-----			-----COD (g/d)-----		
	Fall	Spring	Summer	Fall	Spring	Summer
Influent	9,030	4,160	5,020	25,600	21,200	14,800
OX	-8,310	-3,070	-3,550	-19,900	-14,700	-8,970
SF	-351	-678	-1,250	-1,420	-874	-2,860
VF	638	945	4,690	786	-4,470	7,870
RA	244	-737	-2,690	-157	1,290	-3,140
LB	1,270	107	-785	-629	-308	-1,630
PW	293	315	-1,500	-314	2,160	-2,470
Effluent	5,340	1,770	1,400	8,170	6,380	9,620
Export	-3,690	-2,390	-3,630	-17,400	-14,800	-5,130

Data from S. Yenez MS thesis 2012

Typical Performance Data



Mayer Ranch Passive Treatment System, Tar Creek Superfund Site, Ottawa County, OK

Oxygen Demand Mass Retention

	-----CBOD ₅ (g/d)-----			-----COD (g/d)-----		
	Fall	Spring	Summer	Fall	Spring	Summer
Influent	9,030	4,160	5,020	25,600	21,200	14,800
OX	-8,310	-3,070	-3,550	-19,900	-14,700	-8,970
SF	-351	-678	-1,250	-1,420	-874	-2,860
VF	638	945	4,690	786	-4,470	7,870
RA	244	-737	-2,690	-157	1,290	-3,140
LB	1,270	107	-785	-629	-308	-1,630
PW	293	315	-1,500	-314	2,160	-2,470
Effluent	5,340	1,770	1,400	8,170	6,380	9,620
Export	-3,690	-2,390	-3,630	-17,400	-14,800	-5,130

Data from S. Yenez MS thesis 2012

Effluent Criteria



	System Effluent (mg/L)	Effluent Criteria (mg/L)	Source
TN	1.01 ± 0.26	0.36 (lakes) 0.69 (streams)	EPA, 2000
TP	0.59 ± 0.14	0.020 (lakes) 0.037 (streams)	EPA, 2000
Sulfide	<0.5 - 3.4	0.002 as H ₂ S	EPA, 1986
CBOD ₅	2.3 - 8.5	25	EPA, 1984
COD	8 - 21	NA	NA

Re-aeration Options



Common Aeration Techniques



- Utilize elevation changes/head pressure differences
- Physically entrain air via turbulent flow
- Well-studied for iron oxidation
- Much less so for VFBR effluent re-aeration





What to do when elevation changes are minimal?

Hartshorne Study Site

- Abandoned Rock Island underground coal mine
- Constructed late 2005
 - Vertical anoxic limestone drain
 - Two VFBRs
 - Three oxidation ponds
 - Polishing wetland
- Flows: <1 to 75 LPM
- Cooperative effort by OSMRE, OCC and OU



Hartshorne Water Quality

	Minimum	Maximum	Median	n
pH	5.25	5.84	5.36	18
SC (mS/cm)	2960	17100	11800	18
T. Alk. (mg/L)	95	214	117	18
Fe (mg/L)	215	1311	765	15
Mn (mg/L)	14	29	18	15
Na (mg/L)	1400	3437	1893	4
Cl (mg/L)	197	381	225	9
SO ₄ ⁻² (mg/L)	5456	13620	7842	12

Hartshorne Re-aeration

- Windmill aeration in initial oxidation pond
 - Examining iron removal rates
- Solar aeration in re-aeration pond after first VFBR
- No side-by-side comparison




Hartshorne VFBR Re-aeration

- Pennington EKBS-15 Solar Aerator
- 15 W Solar Panel
- 14.5 v output
- 12 v marine battery
- PEC 45 pump (0.6 amp-hour)
- Single rubber diaphragm bubble diffuser
- Cost: \$2300

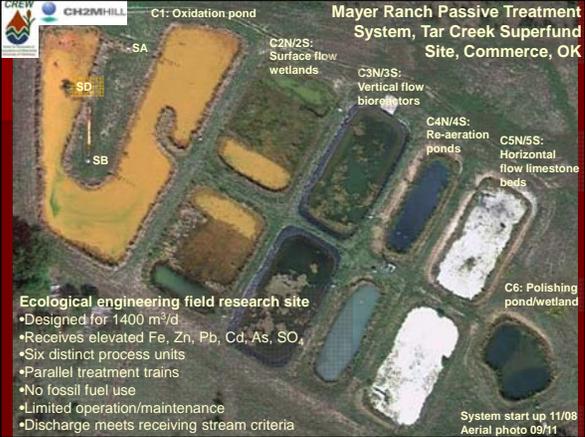


Mayer Ranch Study Site

- Abandoned Tri-State Lead-Zinc Mining District
- Constructed 2008
 - 10 process units
 - Parallel trains
- Design flow: 1000 LPM
- USEPA and USGS funding



Mayer Ranch Passive Treatment System, Tar Creek Superfund Site, Commerce, OK



Ecological engineering field research site

- Designed for 1400 m³/d
- Receives elevated Fe, Zn, Pb, Cd, As, SO₄
- Six distinct process units
- Parallel treatment trains
- No fossil fuel use
- Limited operation/maintenance
- Discharge meets receiving stream criteria

System start up 11/08
Aerial photo 09/11

Mayer Ranch Water Quality

pH	5.95 ± 0.06
Alk. (net)	393 ± 18 (29) mg/L
Fe	192 ± 3 mg/L
Zn	11 ± 0.07 mg/L
Ni	0.97 ± 0.02 mg/L
Cd	17 ± 4 µg/L
Pb	60 ± 13 µg/L
As	64 ± 2 µg/L
SO ₄ ⁻²	2239 ± 26 mg/L




Mayer Ranch VFBR Re-aeration

- North - windmill aeration
- South - solar aeration
- Allows side-by-side comparison





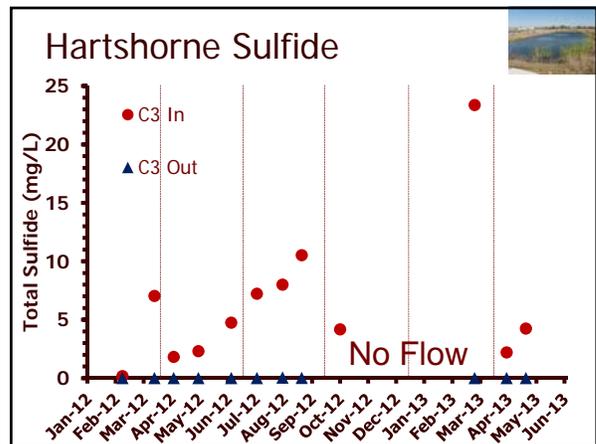
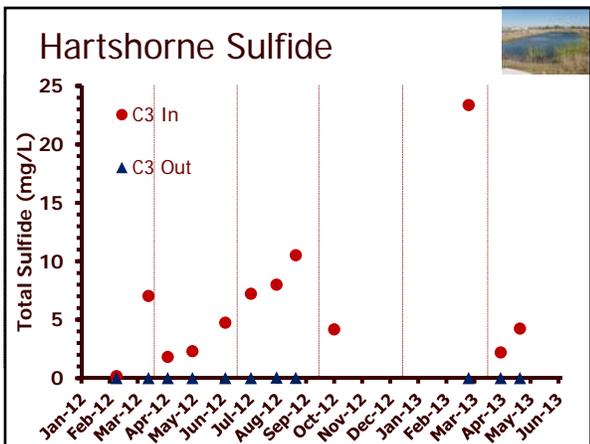
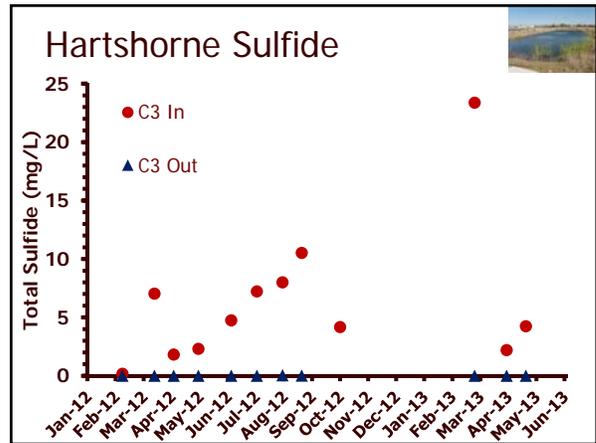
Mayer Ranch VFBR Re-aeration: Windmill

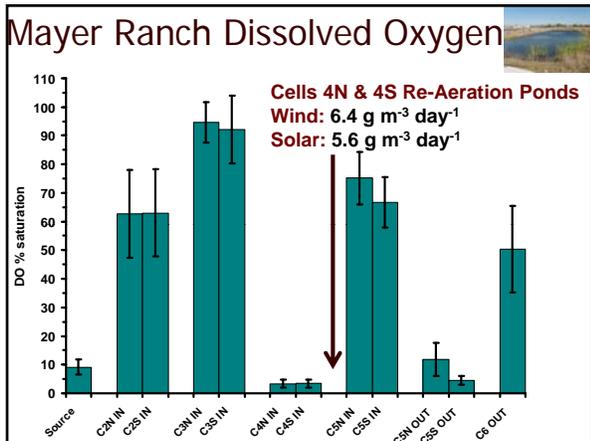
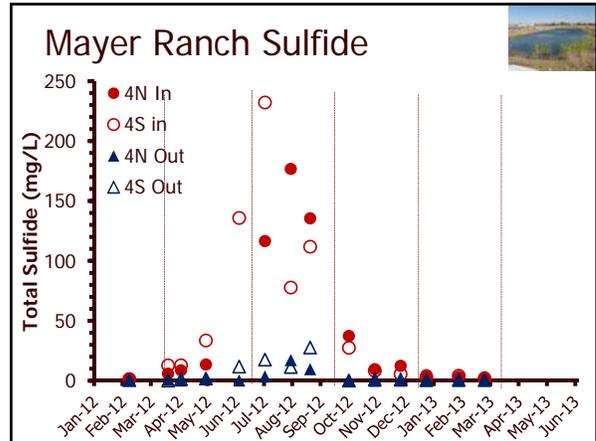
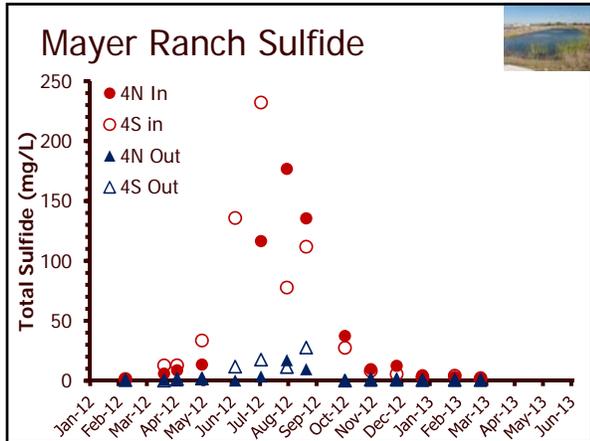
- Superior Windmill Aeration System
- 20-foot tower
- 70" upwind turbine
- Jet Stream direct drive compressor
- 30 psi produced
- 90 cfh at 9 mph
- Operates at 3.9 mph
- Dual rubber diaphragm bubble diffusers
- Cost: \$2100



Mayer Ranch VFBR Re-aeration: Solar panel

- Keeton Industries SB-1 Solear Lake Bed Aeration System
- 120 W Solar panel
- High volume compressor
- 30-amp charge control center
- 210 amp-hour deep cycle solar battery
- 12/24 volt smart box convertor
- Dual rubber diaphragm bubble diffusers
- Cost: \$5200





Nutrients and Oxygen Demand

- Nutrient concentrations elevated in VFBR effluents
 - Nitrogen and phosphorus show seasonality
 - Blue-green algae blooms documented in final units
- Biochemical and chemical oxygen demand levels not of substantial concern

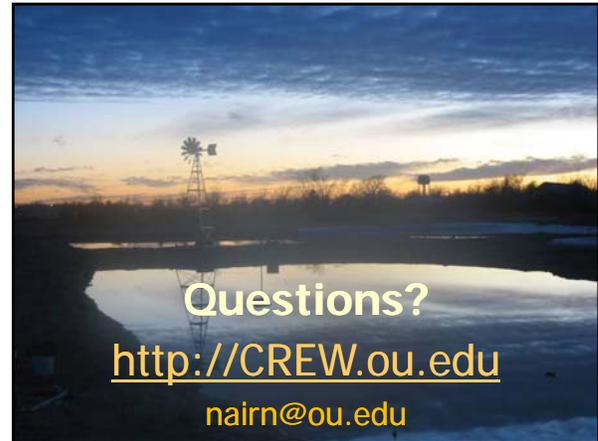


Conclusions

- Non-mine drainage water quality constituents should be included in monitoring schemes and system performance evaluations
- Off-the-grid solar- and wind-powered aeration systems can effectively address these constituents

Conclusions

- Comparative evaluation of performance is ongoing
 - Direct drive wind-powered re-aeration impacted by time of day and time of year
 - Solar-powered units can operate 20 hours/day and store energy in battery for operation on cloudy days
- Operation and maintenance appear to be minimal





ASMR '14 OKLAHOMA CITY WIN FREE STUFF CONTEST



31st National Meeting, Oklahoma City Renaissance Convention Center Hotel, June 14-19, 2014

**Do you like to win free stuff?
Then play to win at ASMR '14 in OKC!**

Contest Rules:

1. Take a free ASMR '14 OKC koozie.
2. Use your ASMR '14 OKC koozie to keep your favorite beverage ice cold.
3. **Take a digital photo of you and your ASMR '14 OKC koozie at the most unusual or exotic place possible.**
4. Send that photo to nairn@ou.edu before June 1, 2014.
5. Sender of the best photo will win free stuff at ASMR '14 OKC!

