

Carbon dioxide impacts both passive treatment system effectiveness and carbon footprint

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Abstract Artesian discharges of net-alkaline, ferruginous waters from abandoned underground lead-zinc mines were examined in field mesocosms and a full-scale passive treatment system. Influent waters were calculated to contain ≈ 290 mg/L dissolved CO_2 ($p\text{CO}_2$ of 0.16 atm). Degassing of CO_2 improved iron and trace metal removal performance. Despite proton acidity produced by oxidative iron removal, pH values increased to >6.5 , thus enhancing the rate of iron removal. Degassing resulted in return of $\approx 84,000$ kg of CO_2 to the atmosphere on an annual basis, while maximum biological productivity would result in carbon sequestration of $\approx 4,500$ kg a^{-1} in the full-scale system.

Keywords passive treatment, carbon dioxide, exsolution, sequestration, carbon footprint

Introduction

Over the past three decades, hundreds of passive treatment systems have been designed and constructed for coal and metal mining impacted waters (e.g. Hedin *et al.* 1994, Younger *et al.* 2002). Properly operating passive systems are often viewed as sustainable "green" alternatives to energy- and resource-intensive active chemical treatment technologies. Long-term operation in gravity-driven passive systems typically requires no direct fossil fuel consumption and process units which include algae or macrophytic vegetation contribute to temporal carbon sequestration through photosynthetic primary production. These ecologically engineered ecosystems are considered to have a low to neutral carbon footprint, while providing direct benefits to society (e.g. water quality improvement and contaminant retention) and the natural environment (e.g. habitat provision and receiving stream ecological recovery).

In addition to problematic metals, sulfate and acidity concentrations, many mine water discharges also contain elevated concentrations of dissolved carbon dioxide (CO_2) depending on geological and environmental

conditions. In treatment design scenarios, CO_2 concentrations may be examined for their contribution to acidity as carbonic acid (H_2CO_3), however that role is typically viewed as temporary because CO_2 -rich mine waters readily degas when exposed to atmospheric conditions (e.g. Kirby *et al.* 2009). Dissolved CO_2 may also be considered for its implications on effective treatment, either due to the fact elevated concentrations constrain the performance of some alkaline additions due to carbonate solid formation, or, in anoxic limestone drain applications closed to the atmosphere, the role they play in enhancing equilibrium alkalinity concentrations (e.g. Cravotta 2007). In each case, the role of elevated CO_2 concentrations in mine water treatment is typically assessed from a water quality perspective, and not from a more holistic systems point of view.

In this study, the role of dissolved CO_2 in passive treatment system performance for circum-neutral pH, net-alkaline mine waters was analyzed using a simple ecosystems-driven carbon-balance approach. Influences of CO_2 on water quality improvement mechanisms were the driving force for the field studies. Com-

pared to traditional active treatment technologies, the system may certainly be considered a more sustainable "green" technology, however, initial evaluation of the contributions to atmospheric CO₂ by the passive treatment system questions the low to neutral carbon footprint of at least some of these technologies.

Methods

Field mesocosm experiments were conducted at a mine drainage discharge in the Tar Creek Superfund Site, part of the historic Tri-State Lead-Zinc Mining District. Water quality at the discharge has been well-documented (Nairn *et al.* 2009, Nairn *et al.* 2010a; Nairn *et al.* 2010b; Table 1). Eighteen field mesocosms (40-L plastic tubs) were filled with untreated mine water and were incubated in standing water near the discharge to maintain ambient temperature conditions throughout the 24-hr experiment. Six treatments were examined to evaluate the effects of passive and active oxygenation/CO₂ degassing on heterogeneous and homogeneous iron retention and trace metal sorption. Treatments included: i) Closed, ii) Closed + Fe, iii) Open, iv) Open + Fe, v) Open Aerated and vi) Open Aerated + Fe. All "Closed" treatments included a properly fitted plastic lid, fitted with a sampling line (so water samples could be drawn without exposing the water surface) and a stoppered hole allowing placement of a water quality data sonde for *in situ* measurements. "Open" systems remained uncovered. Each "Aerated" treatment was mechanically aerated with two standard aquarium aeration stones and aquarium pumps. In all "+Fe" treatments, approximately 50 cm³ of iron solids collected on-site were added to the already

water-filled tubs.

Design and construction of the full-scale Mayer Ranch passive treatment system for this discharge was reported by Nairn *et al.* (2009) and initial evaluation documented by Nairn *et al.* (2010a, 2010b, 2011, 2012). The system was designed for 1000 L/minute of flow and consists of ten distinct process units including two parallel treatment trains (Fig. 1). Waters from three discharges flow into an initial oxidation pond (1), followed by parallel surface-flow aerobic wetlands/ponds (2N and 2S), vertical-flow bioreactors (3N and 3S), re-aeration ponds (4N and 4S), horizontal-flow limestone beds (5N and 5S), and are recombined in a single polishing pond/wetland (6). Each process unit is designed to carry out specific functions as described in Table 2 (Nairn *et al.* 2009). Construction was completed in late 2008 and the full system has been sampled regularly (n=28 sampling events)

Temperature, pH, dissolved oxygen, oxidation-reduction potential, total dissolved solids, conductivity, and specific conductance were determined *in situ* with a YSI 600QS multiparameter datasonde and YSI 650MDS display. Total alkalinity and turbidity were measured immediately upon sample collection via titration with appropriate normality sulfuric acid using a Hach digital titrator (Method 8203) and via a Hach 2100P turbidimeter, respectively. Samples were collected in 250-mL HDPE bottles and preserved with trace metal grade HNO₃ to pH <1 for metals analyses at the Center for Restoration of Ecosystems and Watersheds (CREW) laboratories at the University of Oklahoma. Preserved samples were first nitric acid digested in a CEM MARSXpress Diges-

Constituent	Mean	Constituent	Mean
pH	5.95	Fe (mg/L)	177
Temperature (°C)	18	Zn (mg/L)	8.3
Salinity (ppK)	1.9	Pb (mg/L)	0.07
Total alkalinity (mg/L CaCO ₃)	393	Cd (mg/L)	0.02
Calculated dissolved CO ₂ (mg/L)	283	As (mg/L)	0.06
Calculated pCO ₂ (atm)	0.16	Ni (mg/L)	0.95

Table 1 Selected water quality data for artesian discharges used in full system design.

Process unit	Targeted parameter	Function
Oxidation pond	Fe	Oxidation, hydrolysis and settling of iron oxyhydroxide solids; Trace metal sorption
Surface-flow wetlands/ponds	Fe	Solids settling
Vertical-flow bioreactors	Zn, Pb, and Cd	Retention of trace metal sulfides via reducing mechanisms
Re-aeration ponds	Oxygen demand and odor	Wind- and solar-powered re-aeration; Oxygen demand and H ₂ S stripping; Addition of O ₂
Horizontal-flow limestone beds	Zn, Mn and hardness	Final polishing of Zn as ZnCO ₃ and of Mn as MnO ₂ ; Hardness addition to offset bioavailability of remaining trace metals
Polishing pond/wetland	Residual solids	Solids settling; Photosynthetic oxygenation; Ecological buffering

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



Fig. 1 Mayer Ranch passive treatment system, Tar Creek Superfund Site, Oklahoma, USA.

tion System following EPA Method 3015 (EPA 2006). Digested samples were then analyzed with a Varian Vista-PRO simultaneous axial Inductively Coupled Plasma-Optical Emission Spectrometer following EPA Method 6010b (EPA 2006) for 15 analytes (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, and Zn). Dissolved carbon dioxide concentrations and partial pressures were calculated from field measurements of pH, temperature, salinity and total alkalinity using appropriate reference equations from Harned and Owen (1958), Millero (1995), Stumm and Morgan (1996) and Weiss (1974).

Results

In the mesocosm experiment, degassing of CO₂ in the "Open Aerated" treatments led to rapid pH increases to \approx pH 8 despite concomitant proton production by iron hydrolysis (Fig. 2). In "Closed" and "Open" treatments, pH remained suppressed and only slightly greater than 6. Total alkalinity showed a dramatic initial decrease (in the first ten hours) as proton acidity produced by iron hydrolysis was neutralized. Note that pH increased or remained constant as alkalinity decreased, again indicative of the important role of CO₂ degassing. The greatest iron removal was seen in the "Open Aerated" treatment which showed consistent and dramatic concentration decreases to < 10 mg/L in 24 hours. "Open Aerated" and "Open Aerated + Fe" data were best fit by exponential models of $[\text{Fe}] = 150e^{-0.144t}$ ($r^2 = 0.91$) and $[\text{Fe}] = 159e^{-0.149t}$ ($r^2 = 0.94$), respectively, the slopes of which were not significantly different ($p < 0.05$). "Open" treatments demonstrated slightly lower final iron concentration changes than closed treatments. Trace metals concentrations did not demonstrate significant decreases in "Closed" or "Open" treatments (data not shown). In "Open Aerated" treatments, zinc concentrations demonstrated steady decreases to less than 2 mg/L, again with no dif-

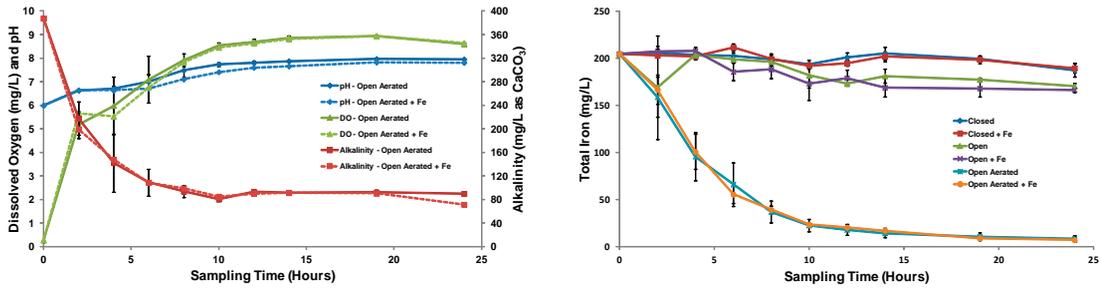


Fig. 2 Selected water quality changes in 24-hr mesocosm experiment.

ference between “Open Aerated” and “Open Aerated + Fe” treatments. Nickel concentrations demonstrated similar decreases but only from ≈ 1 to ≈ 0.75 mg/L. Arsenic, cadmium and lead concentrations decreased in a similar manner, although arsenic and lead concentrations were below analytical detection limits by six hours and 12 hours, respectively. Cadmium concentrations decreased steadily to 12 hours, after which they became asymptotic. Trace metal sorptive capabilities of iron solids are long well-documented (e.g. Dzombak and Morel 1990, Kairies *et al.* 2005, Neely 2010). The critical effects of CO₂ degassing in effective mine water treatment was demonstrated by this short-term mesocosm experiment.

The full-scale passive treatment system has been operational for over four years. From

a water quality improvement perspective, the system has performed as designed, maintaining a net alkaline nature throughout the system as target metals were removed from solution. Due in part to degassing of elevated CO₂ concentrations in the artesian discharges, pH increased from less than 6 to >7 at final discharge. Table 3 shows typical changes in selected measured and calculated constituents for a single sampling event.

Iron was predominately retained in the oxidation pond and surface flow wetlands. Arsenic, lead, and cadmium concentrations also demonstrated significant decreases in these units via sorption to iron solids. Degassing of CO₂, and subsequent increases in pH, directly influenced iron, and thus trace metal, removal in these initial process units. Zinc and nickel

	System influent	System effluent		System influent	System effluent
pH	5.96	7.36	Fe (mg/L)	183	0.096
Temperature (°C)	17.87	28.02	Zn (mg/L)	8.1	0.005
Salinity (ppK)	1.89	1.80	Pb (mg/L)	0.058	<PQL
Total alkalinity (mg/L CaCO ₃)	374	288	Cd (mg/L)	0.025	<PQL
Dissolved CO ₂ (mg/L)	262	6.56	As (mg/L)	0.062	<PQL
pCO ₂ (atm)	0.14	0.005	Ni (mg/L)	0.968	0.040

Table 3 Typical water quality performance of full-scale passive treatment system. Data are from August 2009 sampling event. PQL is practical quantification limit.

were primarily removed in the vertical flow bioreactors.

Dissolved CO₂ concentrations dramatically decreased with flow through the passive treatment system. For the data presented in Table 3 for a typical mid-summer day (representing the most extreme water temperature changes with flow through the system as well as a period of peak biomass production and thus photosynthetic rates), the system received approximately 213 kg d⁻¹ of dissolved CO₂ from the artesian mine water sources and discharged slightly more than 5 kg d⁻¹ in the final effluent, resulting in a loss of 208 kg of CO₂ on this summer day.

Few authors have systematically examined the carbon footprint of passive treatment systems, although some initial efforts have been made (*e.g.* Gusek *et al.* 2011, Jordahl *et al.* 2009). On an annual basis, the studied system is estimated to have lost approximately 84,000 kg a⁻¹ of dissolved CO₂ from the water column. An assumption of peak primary production rates for the vegetated units of the system results in a potential carbon utilization of approximately 4,500 kg a⁻¹. Therefore, it may be projected that the system loses the great majority of CO₂ (around 79,500 kg a⁻¹) to the atmosphere. These estimated CO₂ emissions are equivalent to approximately 17 passenger vehicles for one year or 34,000 L of gasoline (EPA 2013).

Conclusions

Dissolved carbon dioxide is a common constituent in many mine waters and plays an important role in many passive treatment processes. Degassing of elevated concentrations of CO₂ can lead to increased pH, thus having a positive impact on oxidative iron removal rates, which may also lead to trace metal removals via sorption. Despite this critical contribution to contaminant removals, the role of CO₂ is often neglected or misunderstood. In the mesocosm and full-scale passive treatment system studies described herein, CO₂ degassing from net alkaline mine waters played

a critical and influential role in several water quality improvement processes (*e.g.* oxidative iron removal, subsequent trace metal sorption, pH increase, etc.) and contributed considerably to overall system performance. Enhancement of the rates of water column aeration and CO₂ degassing in the primary oxidation pond, perhaps through solar- and wind-powered devices, is a potential line of additional research necessitating further inquiry and could decrease passive treatment system sizing requirements.

This initial analysis focused on carbon dynamics during passive treatment system operation. It neglects to include carbon inputs during system construction, tradeoffs between passive treatment system operation and other alternatives (*e.g.* either no action or active chemical treatment) and does not delve into individual process unit carbon balances. However, it does indicate that comprehensive analysis of "green" technologies requires an understanding of mine water geochemistry and should be performed using a whole ecosystem approach.

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