IRON AND TRACE METAL RETENTION IN NET ALKALINE CO$_2$-RICH MINE WATERS VIA AEROBIC PROCESSES[1]

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Abstract: Aerobic iron removal is a well-documented treatment process for net-alkaline mine waters. In this study, on-site field mesocosm experiments were conducted to evaluate effective oxidative removal of iron and trace metals from a lead-zinc mine discharge in the former Picher Mining Field in northeastern Oklahoma. Six *in situ* treatments (closed, closed with iron precipitate, open, open with iron precipitate, open and aerated, open and aerated with iron precipitate) were conducted in 40-L containers and water quality was analyzed over 24 hours to evaluate the effects of aeration and degassing on homogeneous and heterogeneous iron removal mechanisms. All treatments were established in triplicate. Iron concentrations decreased rapidly and significantly in the aerated treatments (180 mg/L to < 10 mg/L), with the addition of iron precipitate to the initial treatment having no significant impact on rates or final concentration. Iron concentrations also decreased significantly in the open buckets, but not as greatly (to ~170 mg/L), and decreased slightly (but not significantly) in the closed treatments (to ~190 mg/L). Zinc, nickel, arsenic, cadmium and lead concentrations also decreased significantly in the aerated treatments. Despite the production of proton acidity from iron hydrolysis, pH increased significantly in the aerated treatments (from ~6 to ~8) and slightly in the open treatments (~6 to ~6.1). The pH did not change in the closed treatments. Increased pH with increased iron removal indicates the major importance of CO$_2$ degassing by aeration, thus impacting both iron and trace metal concentration changes.

Additional Key Words: acid mine drainage, passive treatment, iron oxidation

Introduction

Aerobic iron removal is a well-documented passive treatment process for net-alkaline mine waters (e.g., Hedin et al. 1994, Watzlaf et al. 2004, Hedin 2008). In the presence of dissolved O_2, Fe^{2+} in mine water is oxidized to Fe^{3+} (Equation 1) which subsequently, and quite rapidly at circum-neutral pH, undergoes hydrolysis to form amorphous Fe oxyhydroxide solids and proton acidity (Equation 2). Retention of Fe solids is then driven by settling dynamics in appropriately-designed passive treatment system process units.

$$Fe^{2+} + 0.25O_2 + H^+ = Fe^{3+} + 0.5H_2O \qquad (1)$$
$$Fe^{3+} + 2H_2O = FeOOH + 3H^+ \qquad (2)$$

The overall reaction for Fe oxidation and hydrolysis with subsequent neutralization of proton acidity by bicarbonate alkalinity (whether due to natural bicarbonate concentrations or alkalinity produced in anoxic limestone drains) is described in Equation 3.

$$Fe^{+2} + 2HCO_3^- + 0.25O_2 = FeOOH(s) + 0.5H_2O + 2CO_2 \qquad (3)$$

Numerous studies have long-identified ferrous iron oxidation (Equation 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 Fe oxidation in natural waters, under net alkaline, circum-neutral pH conditions, abiotic Fe oxidation is the prevailing process (e.g., Hedin et al. 1994, Kirby et al. 1999, Athay et al. 2001).

Stumm and Morgan (1996) discussed limitations on the oxidation of dissolved Fe forms (Fe^{2+}, $FeOH^+$, $Fe(OH)_2$) as well as sorbed Fe(II). According to Dempsey et al. (2002), oxidation of $Fe(OH)_2$ dominates at pH > 5 (homogenous oxidation). Sung and Morgan (1980) identified ferric oxyhydroxide as a catalyst for abiotic Fe^{2+} oxidation. This oxidation of sorbed iron is described as heterogeneous. The overall rate at pH > 5 is therefore the sum of the homogenous and heterogeneous reactions. Both reactions are first order with respect to dissolved O_2. However, the heterogeneous reaction is first order with respect to pH, while the homogeneous reaction is second order with respect to pH (e.g., Hedin, 2008). Furthermore, Park and Dempsey (2005) found that rates of Fe(II) oxidation were proportional to dissolved O_2 concentrations and both dissolved and sorbed Fe(II) up to a given surface density.

From an operational perspective, passive diffusion of atmospheric O_2 into mine water is the actual rate limiting step for the entire Fe removal process (Hustwit et al., 1992). In passive treatment systems, aeration (e.g., via entrainment over structures, windmill or solar-powered aeration or other active mechanisms) has the potential to not only accelerate the process of oxygen diffusion, but also aid in the exsolution of elevated CO_2 commonly present in net alkaline mine waters, thus increasing pH as CO_2 is removed from solution (Cravotta 2007, Kirby et al. 2009). Bicarbonate alkalinity is exchanged for hydroxyl ions, thus increasing pH but not affecting alkalinity concentrations (Equation 4).

$$HCO_3^- = CO_2 \text{ (g)} + OH^- \qquad\qquad (4)$$

Because homogenous and heterogeneous Fe oxidation rates are second order and first order, respectively, with respect to pH, CO_2 degassing plays a vital role in Fe retention in aerobic passive treatment systems.

In addition, the trace metal sorptive capabilities of Fe solids are long well-documented (e.g., Benjamin and Leckie 1981, Dzombak and Morel 1990, Kairies et al 2005, Zeng et al. 2008, Neely 2010). Neely and Nairn (2011) describe iron oxides as prime candidates for mixed media filtration applications because of their large specific surface area and high affinity to form surface complexes with dissolved cations and anions (dependent upon the pH point of zero charge). When the pH of the ambient solution is above the pH_{pzc} of the iron oxide, the surface charge is negative and cation removal is favored (e.g., Ahmed and Maksimov 1968, Pechenyuk 1999, Dzombak and Morel 1990, Kairies et al. 2005). In the passive treatment of iron-rich mine water discharges containing elevated concentrations of ecotoxic trace metals, aerobic retention of Fe may result in significant trace metal removal via sorption and surface complexation.

Methods

Field mesocosm experiments were conducted at an uncontrolled 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 Rubbermaid plastic tubs) were filled with mine water pumped directly from the discharge. Mesocosms were incubated in standing water near the

discharge to maintain ambient temperature conditions throughout the experiment. Six treatments were examined to evaluate the effects of passive and active aeration on heterogeneous and homogenous 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 cm^3 of wet Fe solids collected on-site were added to the filled tubs and distributed through the water column. The relatively small initial solids volume was selected to evaluate the contribution of heterogeneous oxidation under system start-up conditions.

Table 1. Selected mean water quality data from the selected artesian discharge.

Constituent (units)	Value	Constituent (units)	Value
pH	5.97	Pb (mg/L)	0.069
Dissolved oxygen (mg/L)	1.04	Cd (mg/L)	0.016
Total alkalinity (mg/L CaCO$_3$)	371	Mn (mg/L)	1.51
Fe (mg/L)	178	As (mg/L)	0.064
Zn (mg/L)	8.15	Ni (mg/L)	0.94
SO$_4^{2-}$ (mg/L)	2264		

Temperature, pH, dissolved O_2, oxidation-reduction potential, total dissolved solids, conductivity, and specific conductance were determined *in situ* with a YSI 600QS multiparameter datasonde and YSI 650MDS display. Data were logged upon stability of dissolved oxygen readings. Water samples were collected using hand-held pumps, exercising caution to not entrain air into the sample. Total alkalinity and turbidity were measured immediately via titration with appropriate normality sulfuric acid using a Hach digital titrator (Method 8203) and via a Hach 2100P Turbidimeter, respectively. Samples for later analysis were collected in 250-mL HDPE bottles and preserved with trace metal grade HNO_3 to pH <1 for metals analyses. Samples were then transported to the Center for Restoration of Ecosystems and Watersheds (CREW) laboratories at the University of Oklahoma for analyses.

Preserved samples for metals analyses were first nitric acid digested in a CEM MARSXpress Digestion 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).

Results and Discussion

Over the 24 hours of the study, dissolved oxygen increased significantly as expected in the "Open Aerated" treatments to ~ 9 mg/L or 98% saturation (Fig. 1) and slightly in the "Open" treatments but still < 2 mg/L. In "Open Aerated" treatments, pH increased significantly to 7.5 - 8 as CO_2 was effectively degassed from the mine water solution (Fig. 2). In "Closed" and "Open" treatments, pH remained suppressed and only slightly greater than 6.
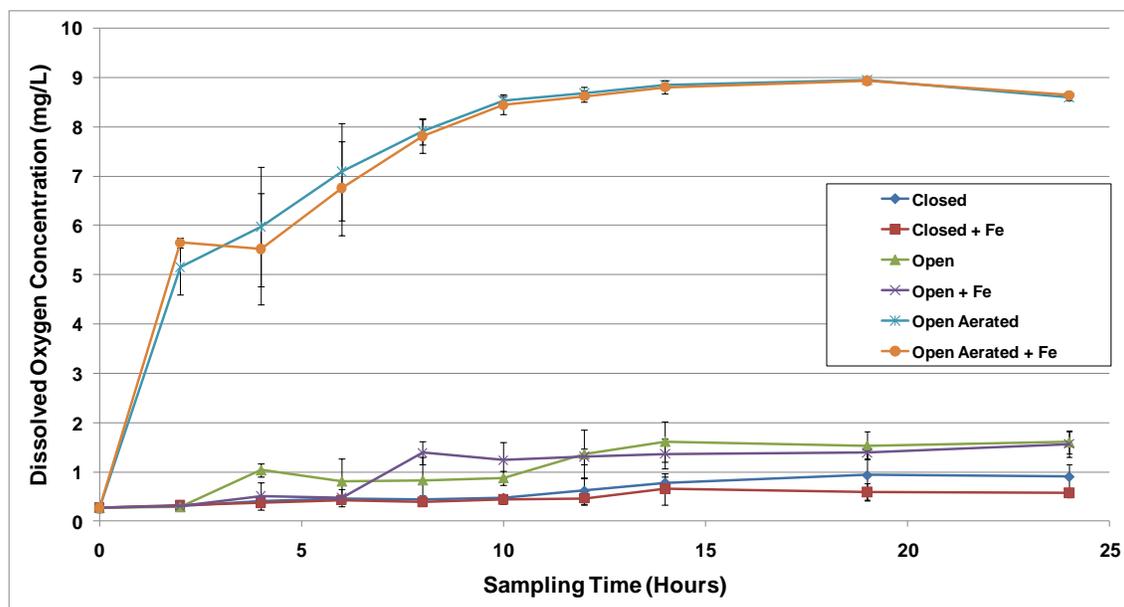
Figure 1. Dissolved oxygen concentrations for all treatments over the 24-hour study.

In examination of "Open Aerated" treatments only (Fig. 3), the addition of on-site iron particulates has no effect on dissolved oxygen concentrations, pH or total alkalinity. 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 CO_2 degassing. The greatest Fe removal was seen in the "Open Aerated" treatments (Fig. 4) which showed consistent and dramatic

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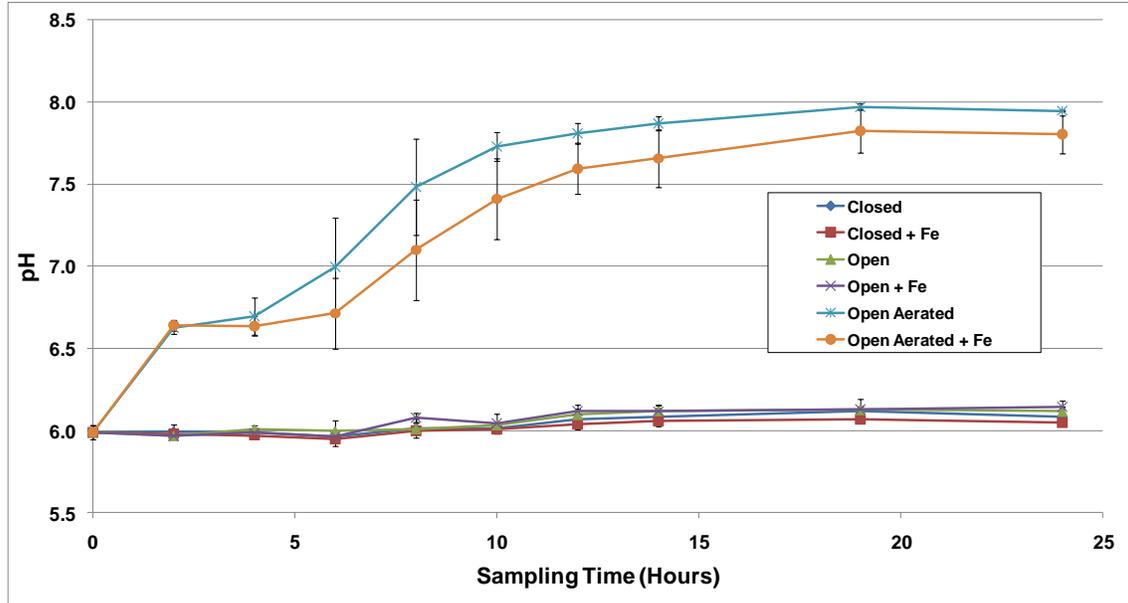
Figure 2. pH for all treatments over the 24-hour study.
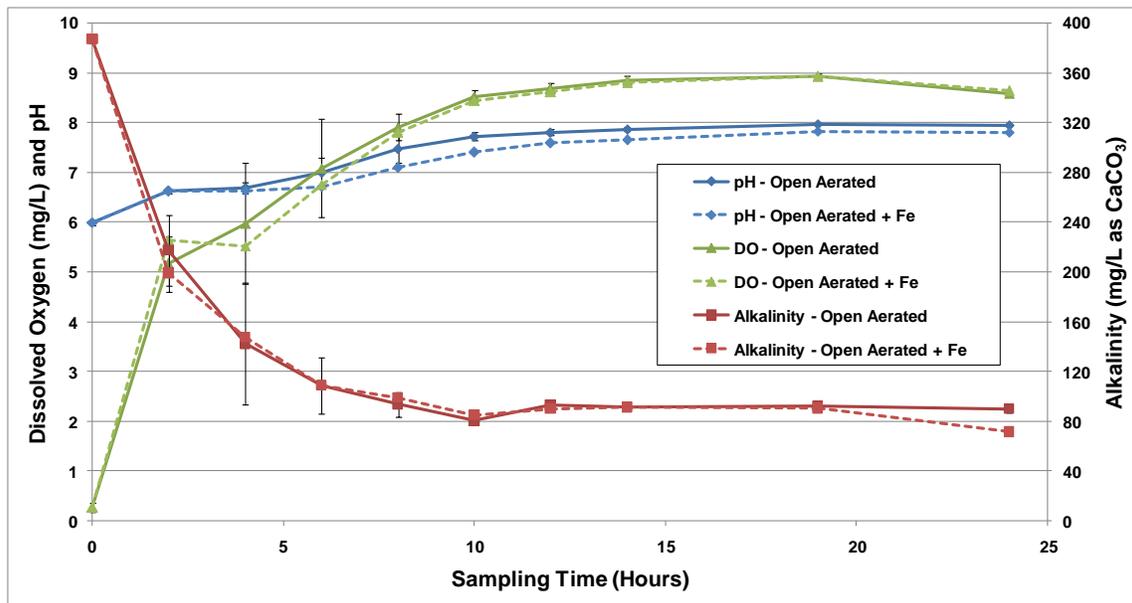
Figure 3. Alkalinity, pH, and dissolved oxygen concentrations in "Open Aerated" and "Open Aerated + Fe" treatments over the 24-hour study.
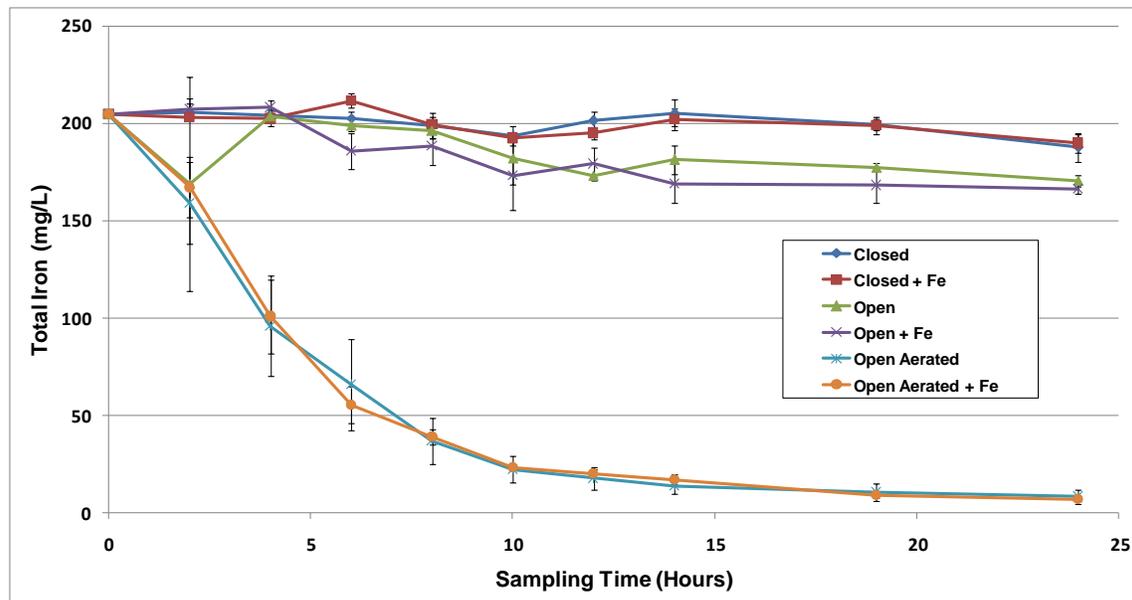
Figure 4. Iron concentrations in all containers over 24 hours.

concentration decreases to < 10 mg/L in 24 hours. "Open Aerated" and "Open Aerated + Fe" data were best fit by exponential models with resulting equations of $[Fe] = 150e^{-0.144t}$ ($r^2 = 0.91$) and $[Fe] = 159e^{-0.149t}$ ($r^2 = 0.94$), respectively, the slopes of which were not significantly different ($p < 0.05$). "Open" treatments demonstrated slightly greater final iron concentrations changes than closed treatments. However, no significant difference existed between treatments without added iron solids and those with added iron solids for any of the treatment pairs, unlike results from a similar preliminary experiment conducted with the same waters (Nairn et al. 2002).

Trace metals concentrations did not demonstrate significant decreases in "Closed" or "Open" treatments. In "Open Aerated" treatments, zinc concentrations demonstrated steady decreases to less than 2 mg/L, again with no difference between "Open Aerated" and "Open Aerated + Fe" treatments (Fig. 5). Nickel concentrations demonstrated similar decreases but only from ~1 to ~0.75 mg/L (Fig. 5). Arsenic, Cd and Pb concentrations decreased in a similar manner (Fig. 6), although As 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.
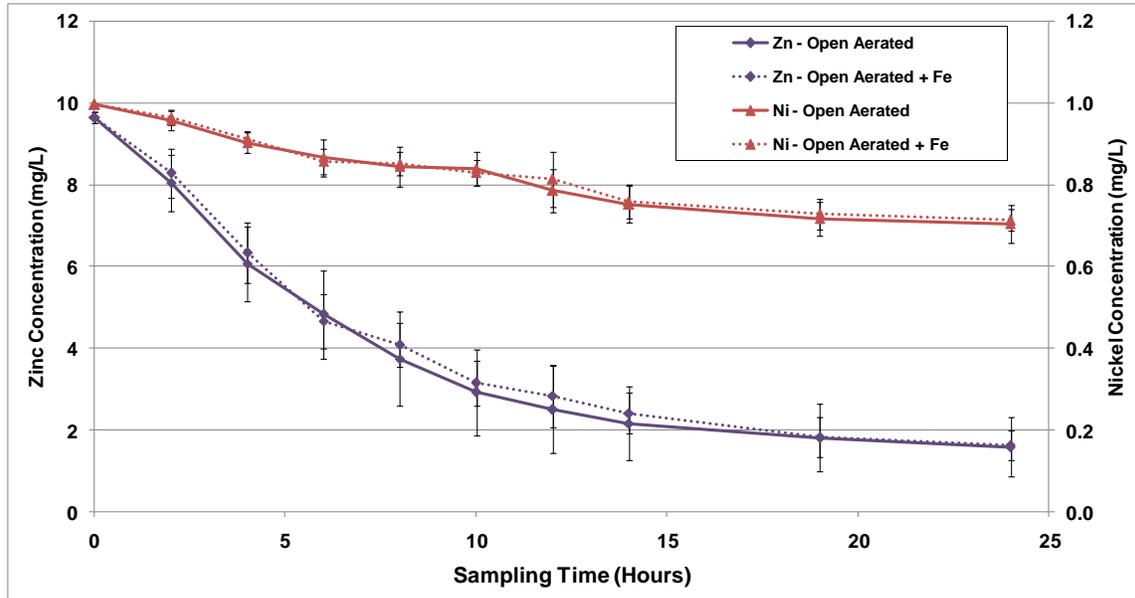
Figure 5. Zinc and nickel concentrations in "Open Aerated" and "Open Aerated + Fe" treatments over the 24-hour study.
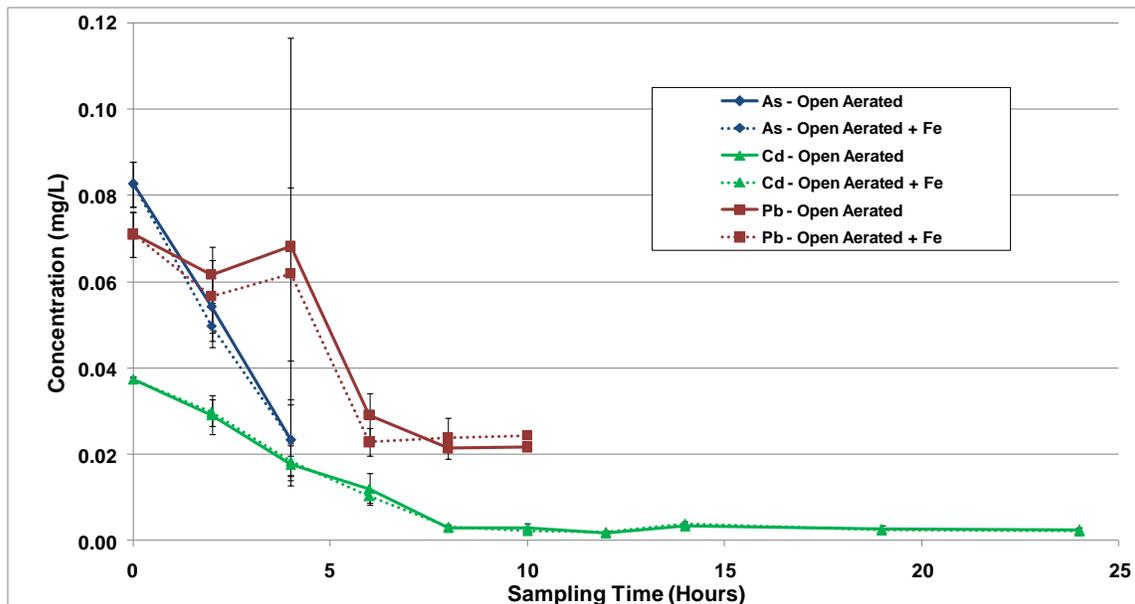
Figure 6. Arsenic, cadmium, and lead concentrations in "Open Aerated" and "Open Aerated + Fe" treatments over the 24-hour study. Arsenic and lead concentrations were below detectable limits by six hours and 12 hours, respectively.

Conclusions

This short-term field mesocosm study found that simple aeration had significant effects on pH (via CO_2 exsolution), and dissolved O_2, alkalinity, Fe and trace metal concentrations. Although significant decreases in Fe concentrations via oxidation, hydrolysis, precipitation and

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settling resulted in in-kind decreases in alkalinity due to proton acidity neutralization, pH increased as CO_2 degassed. The simple addition of field-collected Fe solids did not result in any significant difference in Fe, Zn, Ni, As, Cd or Pb concentrations over the period of study.

Iron removal, and concomitant trace metal sorption to the resulting solids, in passive treatment systems is a complex process with multiple factors affecting the rates of bulk treatment processes and ultimately final effluent water quality. This study found that active (as opposed to passive) diffusion of O_2 played a major role in Fe and trace metal removal. Full-scale passive treatment systems should include active entrainment of air into the water column, via flow over aeration structures (if elevation differences allow) or use of wind- or solar-powered aeration units, for maximum effectiveness. Addition of iron solids, hypothesized to facilitate heterogeneous iron oxidation, did not demonstrate any significant influence in this study.

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