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Metal removal mechanisms in a short hydraulic residence time subsurface flow compost wetland for mine drainage treatment

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ABSTRACT: The performance of an innovative pilot-scale subsurface flow compost wetland for the attenuation of zinc in mine drainage was investigated. The particular novelty of the system, which operated under ambient environmental conditions, was the short hydraulic residence time (HRT) of 7.5 – 14.5 hours. Short HRT is crucial because it reduces absolute wetland size and construction cost, which can be major impediments to use of wetlands. Over a 2 year period mean treatment efficiency was 67.5% (total Zn) and

84.4% (0.45 µm filtered Zn). Mean volume-adjusted removal rates for total and filtered Zn were 0.92 g/m^3/day and 1.05 g/m^3/day respectively. Both water and compost analyses showed bacterial sulfate reduction to be the most important Zn removal process within the subsurface flow wetland: water analyses showed consistent decreases in sulfate concentration through the system, whilst Acid Volatile Sulfide – Simultaneously Extracted Metals (AVS-SEM) analysis of the compost revealed concentrations of Zn up to 12 227 mg/kg and AVS up to 9 066 mg/kg. Geochemical modelling using PHREEQC also showed that biogeochemical conditions within the wetland favored Zn attenuation as its sulfide: ZnS was the only solid Zn phase that was super-saturated in the wetland effluent water (mean Saturation Index of +9.52). Preliminary investigation of the use of liquid waste carbon sources to further enhance performance were ambiguous, but the results of the research nevertheless show the potential of short hydraulic residence time subsurface flow compost wetlands as a low cost treatment option for metal-polluted abandoned mine drainage.

1.   Introduction

The combined flux of Zn from abandoned base metal mines across England and Wales is in excess of 250 tonnes / annum (Mayes et al., 2013), making abandoned metal mines the single most important source of aquatic Zn pollution in England and Wales. Internationally, Zn is commonly present at elevated concentrations in mine drainage (Nieto et al., 2007;

Taylor et al., 2013; Zhang et al., 2012). This is due primarily to the weathering of sphalerite (Younger et al., 2002). Zn is damaging to downstream ecological communities (de Jonge et al., 2013; Schmidt et al., 2011), resulting in failures of river systems to meet relevant national and international standards for water quality.

Passive technologies, which rely on naturally-occurring biogeochemical reactions and do not require energy inputs (Younger et al., 2002), are the preferred remedial option in many cases. This is mainly because (1) abandoned mine drainage is a long-running source of pollution (Younger, 1997) and therefore long-term operational costs of treatment are high, and (2) the locations of abandoned mine discharges in the UK are typically remote upland settings, which makes active chemical treatment costly and logistically difficult due to the need for an energy supply and regular chemical deliveries.

Immobilising metals as their sulfides, via dissimilatory bacterial sulfate reduction (BSR), has received considerable attention in recent years (Neculita et al., 2007; Sánchez-Andrea et al., 2014; Shubiao et al., 2013). The anoxic conditions required for BSR are achieved by passing mine water through an organic substrate such as compost (Neculita et al., 2007; Shubiao et al., 2013). The generation of sulfide via BSR, and precipitation of Zn sulfide, are represented in Reactions (1) and (2) respectively. Organic carbon sources can be added in an effort to enhance rates of BSR and therefore metal sulfide precipitation (i.e. driving Reaction (1) forwards) (Gibert et al., 2004; Tsukamoto et al., 2004).

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$$ (1)

$$H_2S + Zn^{2+} + 2HCO_3^- \rightarrow ZnS(s) + 2H_2O + 2CO_2$$ (2)
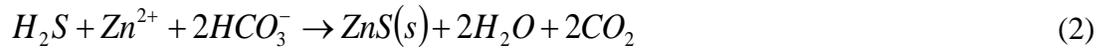
Many investigations of the potential for compost-based wetland systems to remove metals from mine drainage have focused on high strength, low pH mine drainage, in which iron is often the main pollutant (e.g. Biermann et al., 2014). Strosnider et al. (2011, 2013) investigated Zn removal in compost-based systems, but with Zn concentrations of 390 mg/L (Strosnider et al. 2011) and 550 mg/L (Strosnider et al., 2013). This is far higher than concentrations in abandoned mine drainage in the UK, where less than 10% of discharges have a Zn concentration greater than 10 mg/L (See Figure S1, Supplementary Information (SI)). Additionally, the pH of the waters investigated by Strosnider et al. (2011, 2013) was very low (pH 2.60 and 3.58), whereas the pH of UK mine water discharges is typically near-neutral (Jones et al., 2013). Cruz Viggi et al. (2010) used a water more typical of UK mine waters in lab-scale experiments (6.5 mg/L Zn and pH 5.5±0.1), but the nominal residence time of water in the system was 50 hours, over 3 times longer than the system discussed here. The investigations of Strosnider et al. (2011, 2013) and Song et al. (2012) also used systems in which hydraulic residence time was measurable in days. Biermann et al. (2014) calculated system HRT of at least a week for most operating conditions, and the dimensions and flow-rate of the large-scale free water surface wetland system for metal removal investigated by Di Luca et al. (2011) suggest that HRT was on the order of a week in that case also.

Near-neutral, moderately Zn-polluted, mine water discharges are common, but their treatment by short HRT wetland technologies has not been investigated. We address such gaps in understanding by reporting on the results of a 2 year pilot-scale investigation of a compost-based subsurface flow wetland for the attenuation of a Zn-polluted abandoned mine water in northern England. Specific objectives of the investigation were to:

1. Establish the Zn removal efficiency in the short HRT, compost-based subsurface flow wetland

2. Determine important mechanisms of metal removal within the wetland and, in particular, investigate the role of BSR

3. Evaluate the benefit of carbon amendments to metal immobilization, under ambient environmental conditions

2.   Materials and methods

2.1   Study Site

The Rampgill discharge, located in northern England, was selected for the pilot-scale wetland. Its geochemical characteristics are shown in Table S1; it has a mean Zn concentration of 2.32 mg/L, mean sulfate concentration of 134 mg/L and mean pH of 7.74. The discharge arises from a mine adit associated with abandoned Pb-Zn workings of the Alston Block of the North Pennine Orefield (Dunham, 1990; Raistrick and Jennings, 1965). It is located at an elevation of 450 m a.s.l. (Lat. N 54°47'10"N Long. W 2°20'28").

2.2   *Configuration of Pilot-Scale Bioreactor*

A pilot-scale vertical flow wetland (length 2 500 mm, width 1 500 mm, height 1 000 mm) received water directly from the Rampgill discharge. Mine water entered at the surface then flowed downwards, by gravity, through the reactive media and entered a pipe network at the base of the reactor. Effluent water was discharged via a variable height outlet pipe connected to the pipe network. The elevated outlet pipe ensured that the reactive media remained saturated, with a 200 mm cover of water above the compost media. Unlike conventional constructed wetlands, the compost media was not planted with reeds, as the introduction of oxygen via the rhizosphere is not desirable for this type of system, and neither is metal uptake by plants considered an important mechanism of metal attenuation (Wu et al., 2015). See Figure S2 for a schematic plan.

Limestone gravel (40 – 50 mm diameter) was placed on the base of the wetland, to a depth of approximately 200 mm, to cover the pipe network and prevent clogging with particulate matter from the overlying substrate. The reactive wetland substrate comprised BSI PAS 100 compost (45% v/v), wood chips (45% v/v) and activated sludge from a municipal wastewater treatment plant (10%), together with a small amount of limestone gravel to aid permeability. This was mixed and placed on top of the limestone gravel to a depth of 400 mm. The activated sludge provided an initial source of available carbon for metabolism of Sulfate Reducing Bacteria (SRB) but the critical medium- to long-term source of carbon was the BSI PAS 100 compost. British Standards Institution (BSI) Publicly Available

Specification (PAS) 100 compost meets certain UK standards of quality with respect to its safety and performance (British Standards Institution, 2011).

2.3   Operation of Pilot-Scale Bioreactor

A Watson Marlow 300 series peristaltic pump transferred mine water to the wetland at a design flow rate of 1.1 L/min. Tracer tests, using sodium fluorescein, were undertaken during the 2 year trial to determine variations in HRT. A Seapoint fluorimeter in the effluent water recorded fluorescence at 15 minute intervals.

The influence of organic carbon additions on the performance of the wetland was undertaken via both slug and semi-continuous additions of liquid carbon, in the following chronological sequence (see Figure 1):

- After 256 days of operation a 13 L slug of brewery waste was added to the water surface at the influent end of the reactor.
- After 278 days of operation semi-continuous addition of brewery waste commenced, in the form of 34 ml daily.
- After 411 days of operation the volume of brewery waste added was reduced to approximately 15 ml daily
- After 691 days of operation brewery waste additions ceased

The volume of the initial slug and the subsequent semi-continuous carbon additions was determined from previous trials (Mayes et al., 2011).

2.4 Water Sampling and Analysis

Water samples from the wetland were collected, according to standard sampling protocols (see SI), on a weekly basis over a 2 year period. Cation analysis was undertaken using a Varian Vista-MPX inductively coupled plasma-optical emission spectrometer (ICP-OES) and anion concentrations were determined using a Dionex DX320 ion chromatograph. A Merck Microquant colorimetric sulfide field test kit was used for direct analysis of sulfide concentration in the influent and effluent waters to the wetland for the final 295 days of the investigation (27 influent and effluent measurements).

2.5 Sediment Sampling and Analysis

24 sediment samples were collected at the end of the investigation, comprising 12 samples from each of an upper layer (0 to 50 mm) and a lower layer (200 - 250 mm) of substrate. The sampling locations were regularly spaced across the reactor in the form of a grid arrangement to ensure complete spatial coverage (Figure S3). Full details of sediment sampling and preparation are given in the SI. The samples were subjected to Acid Volatile Sulfide – Simultaneously Extracted Metals (AVS-SEM) analysis, using the method of Allen et al. (1991), except that H_2S was purged from the samples for 3 hours to ensure that all AVS was recovered, as recommended by Standard Method 4500-S^{2-} J (APHA, 2005). Metals analysis was undertaken as for water samples. Control samples of the original substrate mixture were subjected to the same analysis.

3.   Results and discussion

3.1   Effectiveness of Zn removal

Total and filtered (0.45 µm filter) Zn concentrations in the influent and effluent waters are shown in Figure 1. Influent Zn was predominantly in its filtered form (mean of 95.7% of the total concentration). Results were disregarded when influent particulate Zn concentrations were uncharacteristically high due to known disturbances of sediment within the mine by explorers.
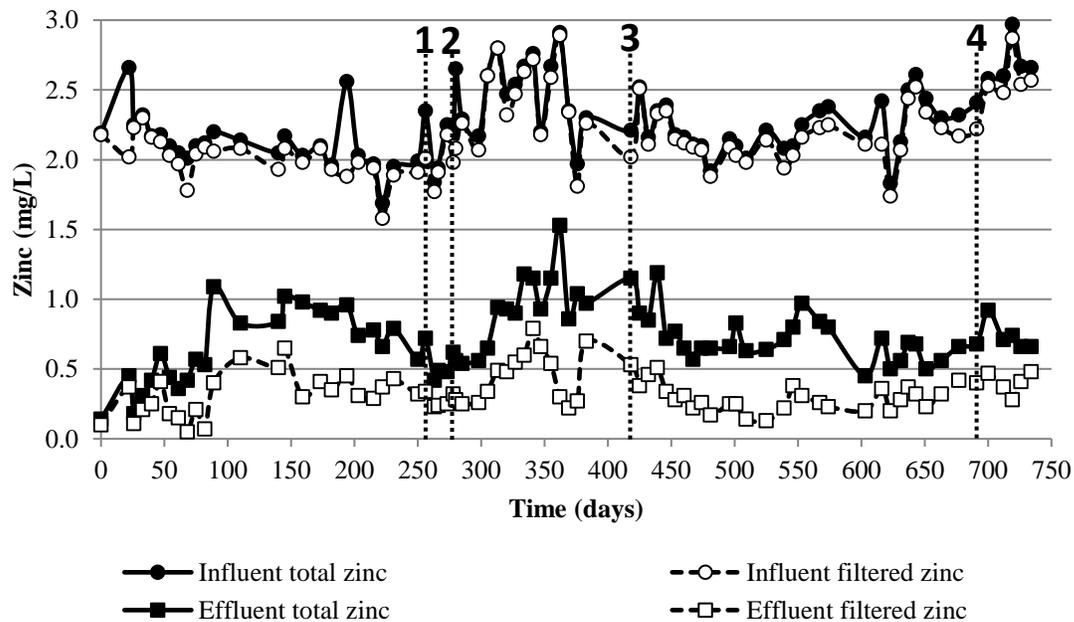

Figure 1. Influent and effluent Zn concentrations in the pilot-scale wetland (adapted from Environment Agency (2014)).Vertical dashed lines refer to: (1) slug liquid brewery waste addition (13 L); (2) commencement of semi-continuous liquid brewery waste addition (34 mL/day); (3) semi-continuous liquid brewery waste addition reduced to 15 mL/day; (4) semi-continuous liquid brewery waste addition stopped.

The wetland had a mean Zn removal efficiency of 67.5% total Zn and 84.4% filtered Zn, where removal efficiency is the percentage reduction in contaminant concentration between influent and effluent waters. The use of removal efficiency to assess system performance neglects to take account of flow rate, and therefore HRT. Higher Zn removal efficiencies have been reported for laboratory-scale trials of similar compost-based systems, but these are typically associated with significantly longer hydraulic residence times (Mayes et al., 2009). Volume-adjusted removal rate (VARR) was therefore calculated using the equation:

$$Volume-adjusted\ removal\ rate\ (g\ /\ m^3\ /\ d) = \frac{Q_{in}C_{in} - Q_{out}C_{out}}{V} \qquad (3)$$

where Q_{in} = influent flow-rate (m^3/d), Q_{out} = effluent flow-rate (m^3/d), C_{in} = influent Zn concentration (mg/L), C_{out} = effluent Zn concentration (mg/L), and V = substrate volume (m^3).

Mean VARR for total and filtered Zn was 0.92 g/m^3/day (SD = ±0.31) and 1.05 g/m^3/day (SD = ±0.36) respectively. These figures compare favorably to VARR for passive treatment technologies reported elsewhere, some of which are 1 or 2 orders of magnitude lower (Mayes et al., 2009). Four tracer tests showed that peak residence time in the reactor varied from 7.5 – 14.5 hours, which is very short for a wetland of this type (Environment Agency, 2014). Flow-rate appears to be the most important influence on VARR. There is a strong positive Spearman's rank correlation (r_s) between influent and effluent flow-rate and VARR ($r_s = 0.822$ for influent flow-rate and $r_s = 0.779$ for effluent flow-rate; $p < 0.001$ and

$n = 79$), whereas there is only a weak statistical relationship between VARR and effluent Zn concentration ($r_s = -0.247$; $p < 0.05$) and no relationship between VARR and influent Zn concentration ($r_s = 0.196$; $p > 0.05$). There may be scope to increase flow-rate further, to maximize the rate of attenuation of Zn, but it is not clear whether this would compromise treatment efficiency.

The slug addition of liquid organic carbon to the bioreactor after 265 days (Figure 1) resulted in an immediate decrease in effluent Zn concentration, from 0.72 mg/L to 0.42 mg/L total Zn and 0.34 mg/L to 0.23 mg/L filtered Zn. This decrease in concentration was short-lived (approximately 7 days), after which Zn concentrations increased (Figure 1). Upon commencement of semi-continuous 34 mL carbon additions performance generally deteriorated. The subsequent reduction in volume of carbon added to 15 mL, after 411 days, resulted in a decreasing trend of effluent Zn concentration over the remainder of the trial (Figure 1). Further discussion of the influence of organic carbon additions on the performance of the wetland is provided below.

3.2   *Metal Removal Mechanisms*

BSR is frequently identified as the principal mechanism for removal of divalent metals within compost-based bioreactors (Johnson and Hallberg, 2005), but it may not always be the dominant process (Matthies et al., 2009). Several studies have attributed divalent metal removal to a combination of metal (oxy)hydroxide precipitation, co-precipitation with (oxy)hydroxides and sorption of metals onto the compost surface (Gibert et al. 2005;

Neculita et al., 2008). Others have reported BSR to be taking place alongside these additional processes (Song et al., 2001).

For the wetland discussed here all evidence pointed to BSR as the primary removal mechanism for Zn, as presented and discussed below.

3.2.1 Water Quality

Reaction (1) shows that sulfate is consumed during the BSR process resulting in a decrease in aqueous sulfate concentration. Figure S4 shows that a quantitative decrease in sulfate occurred across the wetland, with a measured decrease in sulfate concentration on 74 of 84 sampling occasions (mean decrease 17.4 mg/L (181.1 µmol/L)). On 10 occasions effluent sulfate concentration was higher than influent concentration (Figure S4), which is an artefact of variable influent water quality rather than actual generation of sulfate within the wetland. The Rampgill discharge is subject to dilution by rainfall, resulting in lower influent sulfate concentrations. The hydraulic residence time within the bioreactor was 7.5 – 14.5 hours, but influent and effluent samples were collected almost simultaneously. Consequently a sample of effluent water may have entered the bioreactor when influent sulfate concentration was high, but the simultaneously collected influent water sample may have a comparatively low sulfate concentration due to dilution effects. 8 of the 10 occasions on which effluent sulfate was higher than influent concentration fall within the lowest 10 influent sulfate concentrations recorded throughout the investigation.

The mass of sulfate and Zn retained within the wetland, calculated by summing the differences between individual influent and effluent mass flux, was 10.17 kg (106 moles) and 1.42 kg (21.8 moles), respectively. This equates to a molar ratio of sulfate to Zn of 4.9:1. Reactions (1) and (2) indicate that, in the reduction of sulfate to sulfide and precipitation of ZnS, the molar ratio of sulfate to Zn is 1:1. This strong molar excess of sulfate retained within the compost substrate (also evident in Figure S4) favored the attenuation of Zn as a monosulfide.

If the 106 moles of sulfate retained within the substrate was entirely due to reaction (2), then this would result in the generation of 212 moles bicarbonate. A second bicarbonate generating reaction is the dissolution of the calcite layer beneath the compost at pH > 5 (Younger et al., 2002):

$$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2HCO_3^- \tag{4}$$

Over the trial duration there was a net release of 0.88 kg (21.9 moles) of calcium from the wetland, which is equivalent to 43.8 moles of bicarbonate (reaction (4)). The total quantity of bicarbonate generated, using the figures for sulfate retention and calcium release provided above, would therefore be 255.8 moles. The formation of ZnS consumes bicarbonate (Reaction (2)). 21.8 moles of Zn were retained within the bioreactor, which is equivalent to 43.6 moles bicarbonate. The calculated net production of bicarbonate is therefore 212.2 moles, which is very close to the measured molar mass of bicarbonate

released from the system: 202 moles. Whilst recognizing that these simplified stoichiometric calculations neglect other reactions that may influence the flux of bicarbonate, they nevertheless demonstrate the apparent importance of BSR in both attenuating Zn and generating bicarbonate alkalinity.

pH (mean pH = 7.33; n = 56) and redox (mean Eh = -262 mV; n = 56) values for the wetland effluent over the last 468 days of the trial (Figure 2) were optimal for SRB activity (Cohen, 1996). The pH and Eh recorded during this period plot directly within the centre of the ZnS phase of the pH-Eh diagram for Zn (Hem, 1972), showing that ZnS(s) precipitation was favoured. Geochemical modelling with PHREEQC (Parkhurst and Appelo, 1999), using data from the same period, indicated that the influent water was either at equilibrium, or slightly under-saturated, with respect to the solid Zn phases $ZnCO_3$, $Zn(OH)_2$ and Zn_2SiO_4. The effluent water was also under-saturated with respect to these phases, but was super-saturated with respect to ZnS (mean Saturation Index = 9.52; n = 27; Figure 3), showing ZnS to be the main sink for Zn within the wetland.
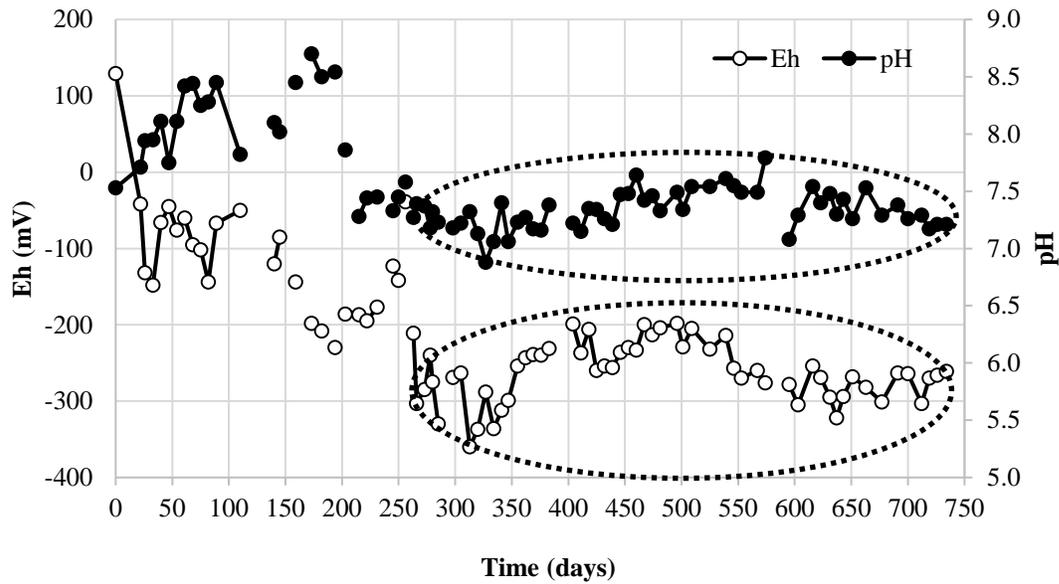
Figure 2. Wetland effluent pH and Eh (adapted from Environment Agency, 2014).
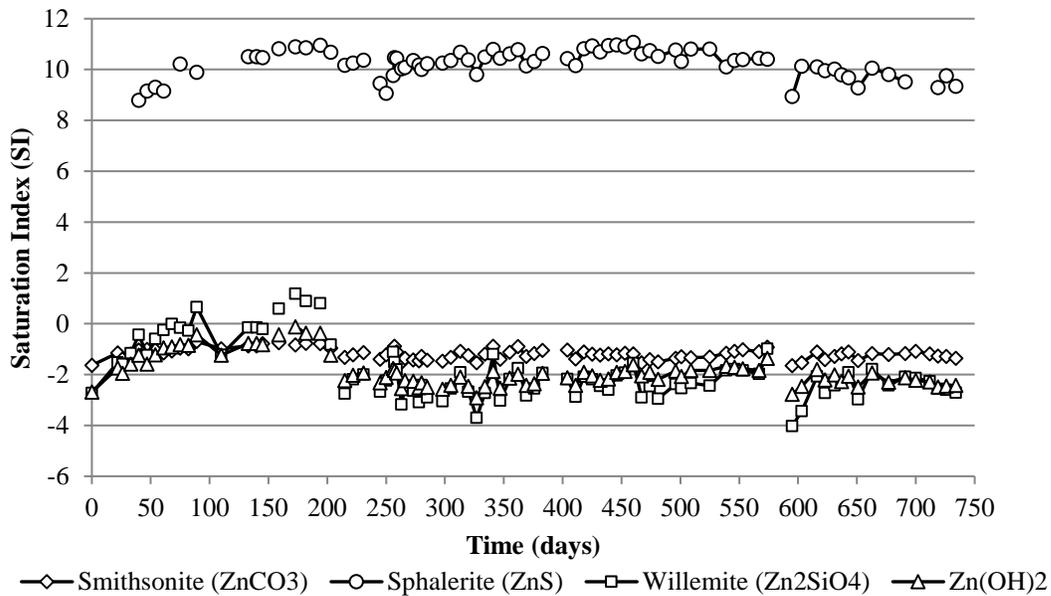

Figure 3. Saturation Indices for Zn phases for bioreactor effluent waters, modelled using

PHREEQC

3.2.2   Sediment Analysis

Sampling and analysis of the compost substrate at the end of the investigation provided further evidence for the important role of BSR as a Zn removal mechanism. The determination of acid volatile sulfides (AVS) and simultaneous extracted metals (SEM) has proved to be an effective technique to assess metal attenuation processes (Jong and Parry, 2004). AVS is defined as the amount of sulfide released as hydrogen sulfide gas by the addition of cold hydrochloric acid to sediments (Rickard and Morse, 2005) The metal sulfides are a major component of AVS and, as such, SEM is defined as the metals simultaneously released during the AVS procedure (Jong and Parry, 2004).

The concentrations of AVS and SEM at 2 different depths within the compost substrate are shown in Table 1. The samples were regularly spaced across the wetland in the form of a grid arrangement, with sample IDs containing the prefix 'A' collected from the influent end of the reactor, those containing the prefix 'D' collected from the effluent end of the reactor, and 'B' and 'C' samples collected at evenly spaced longitudinal intervals between (see Figure S3 for sampling locations). The original compost substrate mix had low concentrations of AVS (13.1 mg/kg) and Zn (by SEM: 163 mg/kg). Table 1 demonstrates the substantial accumulation of both AVS and Zn within the wetland during the investigation. This is entirely consistent with observed decreases in Zn and sulfate concentration between influent and effluent waters shown in Figures 1 and S4, and again illustrates that ZnS was the main sink for aqueous Zn.

Zn concentrations in the upper layer of the compost substrate were higher than those in the lower layer with the exception of sample B2 (Table 1; upper layer mean Zn concentration of 9 146 mg/kg (SD = ± 2 595 mg/kg); lower layer mean Zn concentration of 1 961 mg/kg (SD = ± 980 mg/kg)). The AVS concentrations in the upper and lower layers were similar, with mean values of 4 388 mg/kg and 5 215 mg/kg respectively, but there was greater heterogeneity in the upper layer (SD = ± 2 464 mg/kg) compared to the lower layer (SD = ± 1 541 mg/kg). Furthermore, in the upper layer, there were higher concentrations of both AVS and Zn close to the influent end of the wetland and high Zn but low AVS concentrations near to the effluent end of the system. This is ascribed to vigorous BSR at and immediately below the water-sediment interface, particularly close to the influent end of the wetland, where Zn and sulfate concentrations were relatively high. Other Zn attenuation mechanisms may have been significant in the upper layer, towards the effluent end of the wetland, where there were high Zn but low AVS concentrations. Processes such as adsorption and binding to organic matter have previously been observed in the upper substrate layers of such systems (Neculita et al., 2008), and may have been important here too.

Table 1. Acid Volatile Sulfide (AVS) concentration and Zn concentration by Simultaneously Extracted Metals (SEM), together with the molar ratio of AVS:Zn, at two different depths in the compost substrate

Sample ID	Upper layer: 0-50 mm				Lower layer: 200 - 250 mm			
	AVS (mg/kg)	Zn (mg/kg)	Molar ratio AVS:Zn	Molar ratio AVS:$\sum M^{2+}$ [a]	AVS (mg/kg)	Zn (mg/kg)	Molar ratio AVS:Zn	Molar ratio AVS: $\sum M^{2+}$ [a]
A1	5 587	10 031	1.14	0.61	5 042	2 391	4.30	0.62
A2	6 761	12 227	1.13	0.57	5 968	1 182	10.30	0.92
A3	9 066	11 141	1.66	0.75	7 173	1 717	8.52	0.81
B1	5 472	8 732	1.28	0.55	5 716	738	15.79	1.34
B2	5 957	2 664	4.56	0.66	4 236	584	14.79	1.02
B3	3 376	10 673	0.65	0.33	3 974	1 053	7.70	0.85
C1	5 547	7 491	1.51	0.53	6 575	2 033	6.60	0.92
C2	4 038	10 098	0.82	0.34	3 397	2 395	2.89	0.73
C3	2 927	11 597	0.51	0.35	4 364	3 870	2.30	0.73
D1	2 152	9 156	0.48	0.23	2 458	1 960	2.56	0.38
D2	813	9 165	0.18	0.10	7 148	3 139	4.64	0.94
D3	955	6 771	0.29	0.13	6 525	2 475	5.38	1.02
Blank [b]	13.1	163	-	-	-	-	-	-

[a] $\sum M^{2+}$ represents the sum of the molar concentrations of Fe, Mn, Zn, Ni, Pb, Cd

[b] Blank was unused substrate; results shown are mean values of analysis of quadruplicate subsamples (range for AVS was 8.5 − 17.8 mg/kg, and range for Zn was 85 - 237 mg/kg)

Table 1 shows the variation of AVS:Zn molar ratio across the wetland and between the upper and lower layers. In most samples, and in all samples collected from the lower layer of substrate, the molar ratio of AVS:Zn is > 1. In the process of ZnS precipitation via BSR (reactions (1) and (2)) the AVS:Zn molar ratio is 1:1, and therefore the ratios in Table 1 demonstrate that there was an excess of sulfide present in the substrate. The only exception is in the area towards the effluent end of the bioreactor in the upper layer of substrate, where AVS:Zn ratios < 1 were recorded. Therefore additional Zn immobilization processes, such as adsorption, must also have taken place, at least in some parts of the wetland, which is consistent with previous findings (Neculita et al., 2008). The predominance of ratios substantially greater than unity in the lower layer of substrate indicates that sufficient sulfide was available to immobilize all of the Zn present as a sulfide.

The high concentrations of AVS and SEM in the substrate illustrate the successful attenuation of Zn, but the potential for elevated concentrations of metals and / or sulfide to become toxic to, or inhibit, SRB activity (Utgikar et al., 2003) may limit system performance over the longer term. It is not possible to conclude whether such toxicity / inhibitory effects might have compromised the performance of this wetland if it had continued to operate. Certainly, for the many compost-based systems that receive low pH, high sulfate and metal concentration mine drainage (Rose, 2006), these issues would likely impact on performance far more quickly than for the lower strength wastewaters that are more prevalent in the UK.

Other divalent metals also form sulfides within wetlands and hence may be released by the SEM analysis. These metals are accounted for in Table 1, which shows the molar ratio of AVS to the sum of the moles of Fe, Mn, Zn, Ni, Pb and Cd (termed AVS:$\sum M^{2+}$). With the exception of Fe, other metals present within both the Rampgill discharge (Table S1) and the compost substrate (Pb, Cd, Ni, Mn) have significantly lower concentrations than Zn and consequently contribute very little to the total AVS:$\sum M^{2+}$ ratio, which is dominated by Zn.

Fe concentrations in the Rampgill discharge are somewhat lower than Zn (Table S1), but Fe contributes significantly to the $\sum M^{2+}$, and consequently to the AVS:$\sum M^{2+}$ ratio, as shown in Table 1. When Fe is accounted for, the AVS: $\sum M^{2+}$ ratio in the majority of samples is < 1. The mean AVS: $\sum M^{2+}$ ratio in the upper layer of substrate is 0.43 (SD = ± 0.21), whilst in the lower layer the mean ratio is 0.86 (SD = ± 0.24). Other metal attenuation mechanisms must also have been important in the upper layers of the substrate, as noted previously. In contrast, in the lower layers of substrate, sufficient AVS was present to account for the attenuation of the majority of all metals present.

Uncertainty remains regarding the exact role of Fe cycling in governing the removal of Zn in the wetland. Initially there was a net release of Fe, after which the general trend was of limited Fe attenuation (Figure S5). *Aqua regia* digestions of unused and used substrate showed that Fe concentrations in the substrate increased slightly over the 2 year investigation, from 19 345 mg/kg in the unused substrate to 25 796 mg/kg in the used substrate (mean values; unpublished data). SEM analyses indicated that SEM-extractable

Fe concentration was significantly higher in the used substrate (mean 8 036 mg/kg; unpublished data) than in the unused substrate (2 424 mg/kg). Thus, the proportion of the total Fe present as SEM-extractable Fe increased over time. It is postulated that oxidized Fe phases in the unused substrate, and recalcitrant solid Fe phases not released during the SEM analysis, are mobilized over time, and transformed to FeS. The presence of FeS may in turn influence the removal of Zn. Zn forms a more insoluble sulfide than Fe according to the solubility products of these two metal sulfides (Di Toro et al., 1992). Because of this, Zn may displace the Fe according to reaction (5) (Di Toro et al., 1992).

$$Zn^{2+} + FeS \rightarrow ZnS(s) + Fe^{2+} \tag{5}$$

An equivalent reaction has previously been shown for cadmium (Di Toro et al., 1992), and this may be an alternate, or additional, mechanism for Zn attenuation to that shown in reaction (2). The nature of Fe cycling in this type of wetland, and its role in attenuation of other metals, is an area for future research.

3.3 Carbon Amendments

The influence of organic carbon amendments on system performance was assessed initially by the addition of a slug of liquid brewery waste. A decrease in total and filtered effluent Zn concentrations was apparent immediately after the carbon addition (Figure 1), before concentrations returned to their former levels after a period of around 7 days. The effect of the carbon was therefore short-lived.

The commencement of semi-continuous addition of liquid brewery waste 22 days later

(Figure 1), in the form of 34 ml added daily, was followed by a small decrease in both total

and filtered Zn concentrations in the effluent water for a period of approximately 7 days,

but effluent Zn concentrations subsequently showed a gradual increase and treatment

efficiency reduced to 47% (total Zn) and 70% (filtered Zn), which was significantly lower

than that prior to carbon additions (Figure 1). Again, it is not certain why this occurred,

though it is possible that the volume of carbon added was still too great, particularly given

the relatively low influent sulfate concentration in the Rampgill mine water, compared to

the higher influent sulfate concentration used in successful laboratory trials adding similar

volumes of carbon (Mayes et al., 2011). Martins et al. (2011) observed the same

phenomenon when doubling the amount of carbon, in the form of wine wastes, added to

laboratory columns, which resulted in an instant deterioration in performance. This was

attributed either to compounds within the wine wastes affecting the SRB activity when

added in large amounts, or to the excess of nutrients promoting changes in the bacterial

community (Martins et al., 2011). To make an empirical assessment of whether this was the

case, the volume of brewery waste added was reduced to 15 ml daily (Figure 1). Once

again, there was no obvious improvement in water quality in terms of decreases in effluent

Zn and sulfate concentrations.

Whilst the results of this preliminary evaluation of the benefits of carbon addition to the

performance of the system appear ambiguous, nevertheless from the onset of carbon

additions, until the end of the investigation, pH and redox conditions were ideal for the

precipitation of ZnS and far more constant than prior to carbon additions (mean pH = 7.33, SD = ± 0.17; mean Eh = -262, SD = ± 38.5; circled pH and Eh data in Figure 2). It is possible that the benefits of carbon additions for metal attenuation are difficult to discern in a relatively dilute waste stream such as the mine water used here, and / or that other variables mask any influence of carbon addition. Further research is required to determine the benefits of carbon additions to such systems, and the optimum volumes of such additions, under ambient conditions.

4.   Conclusions

- A short hydraulic residence time (7.5 – 14.5 hours) pilot-scale compost wetland effectively removed Zn from a mine water discharge for the 2 years during which it operated, with no evidence of a deterioration in performance. Mean treatment efficiency for total Zn removal was 67.5%, and mean volume-adjusted removal rate was 0.92 g/m^3/d.

- Water quality data indicate that bacterial sulfate reduction (BSR) was an important mechanism of Zn attenuation: sulfate concentrations decreased between influent and effluent, and PhreeqC modelling indicated that the wetland effluent water was strongly over-saturated with respect to ZnS (mean Saturation Index of 9.52), but no other solid Zn phase.

- Analysis of the wetland substrate after the 734 days of operation indicated very high concentrations of both Acid Volatile Sulfide and Zn. There was a strong molar excess of AVS to Zn, indicating that there was sufficient sulfide to immobilize all Zn in the mine

water. Accounting for other divalent metals, mean $AVS : \sum M^{2+}$ ratios were 0.43 in the upper layer of the substrate and 0.82 in the lower layer. This suggests that BSR was a more important mechanism of Zn removal in the lower layers of the substrate than in the upper layers. The nature of Fe cycling in the substrate, and especially its influence on Zn removal, requires further investigation.

- Organic carbon additions were made to investigate whether such amendments improved performance by increasing rates of BSR. Despite the impact of carbon additions being somewhat ambiguous in the short term, an evaluation of system performance over the entire period in which semi-continuous, low feed-rate additions were made showed that performance both improved and became more consistent during this time. Nevertheless, further work is necessary to demonstrate the effectiveness of organic carbon additions under ambient environmental conditions, firstly to evaluate the benefits of such amendments and, secondly, to determine optimum carbon dose rates.

- Mine drainage such as that described here may cause significant downstream water quality problems if unabated, but is amenable to passive treatment using compost-based wetland systems. Further research still needs to be undertaken, particularly to enable better forecasts of overall system lifetime in light of concerns regarding deterioration in performance due to exhaustion of carbon sources and possible toxic / inhibitory effects of elevated metal and AVS concentrations in the wetland substrate. Without such information it is not possible to calculate the full life cycle costs of such units, which is a key consideration for the owners / operators of such water treatment facilities.

Appendix A. Supplementary data

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SUPPORTING INFORMATION

Field sample and data collection

Water samples were collected in polypropylene bottles from the influent and effluent to the pilot-scale treatment system. One 30 mL sample was acidified with 1% v/v trace analysis grade concentrated nitric acid for cations analysis, whilst another 30 mL sample was passed through a 0.45 μm cellulose acetate filter, prior to acidification, for filtered cations analysis. Finally, a 30 mL sample was left unacidified for anions analysis. All samples were stored at 4°C prior to analysis.

Field measurements of water temperature, pH, Eh and electrical conductivity were made at the time of sample collection using a pre-calibrated Myron L 6P Ultrameter. Total alkalinity was also assessed in the field using a Hach digital titrator with 1.6N sulphuric acid and a bromcresol - green methyl - red indicator, with results expressed in units of mg/L as $CaCO_3$. The influent and effluent flow rates were assessed on each sampling occasion using a 500 mL measuring cylinder and stopwatch.

Sediment sample collection and preparation

Sediment samples were collected in pre-washed polypropylene bottles which were submerged at all times during sample collection to prevent exposure to atmospheric oxygen. The water level in the treatment system was lowered to a point just above the sample location, a grab sample of sediment was taken, and then the bottles were filled with water from within the treatment system. The samples were frozen at minus 20°C upon return to the laboratory to minimise any biogeochemical changes in the sediment. Before being subjected to AVS-SEM analysis, the samples were allowed to defrost in an anaerobic cabinet to prevent exposure to oxygen.

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Table S1. Summary chemistry data for the Rampgill Horse Level mine water discharge (metal concentrations are total concentrations) (adapted from Environment Agency (2014))

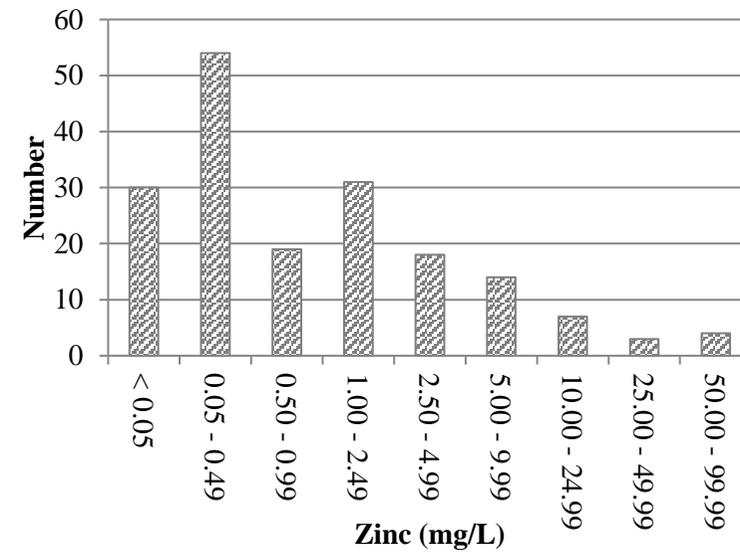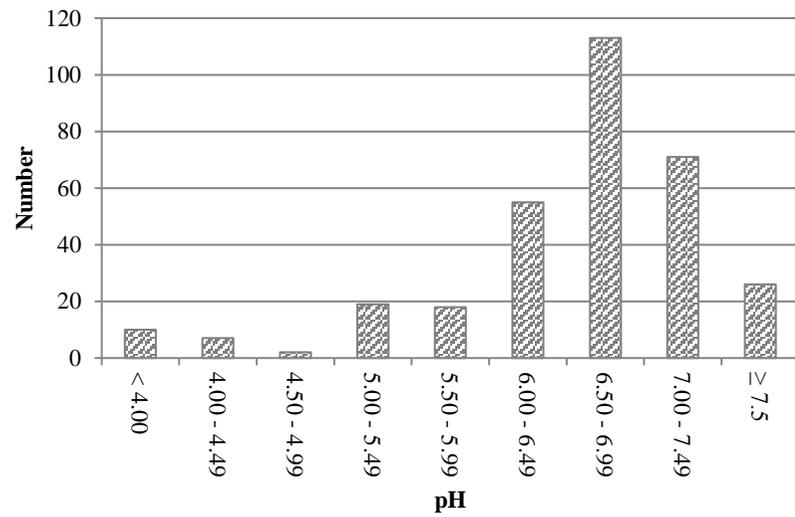| Parameter	Unit	Mean	Range	n
pH	pH units	7.74	6.88-8.62	85
Temperature	°C	8.89	5.8-12.5	84
Conductivity	μS/cm	589.5	389-681.4	85
Eh	mV	139	28-276	84
Alkalinity	mg/L CaCO$_3$	156	103-238	84
Sulphate	mg/L	134	87-164	84
Zinc	mg/L	2.32	1.69-4.5	83
Lead	mg/L	< 0.05	-	85
Cadmium	mg/L	< 0.01	-	85
Iron	mg/L	0.33	0.1-2.72	83
Manganese	mg/L	0.15	0.08-0.56	82

Figure S1. Frequency distributions of pH (n = 321) and zinc concentration (n = 180) of dicharges across England and Wales (data from Mayes et al. (2010) updated with additional data from the Environment Agency)
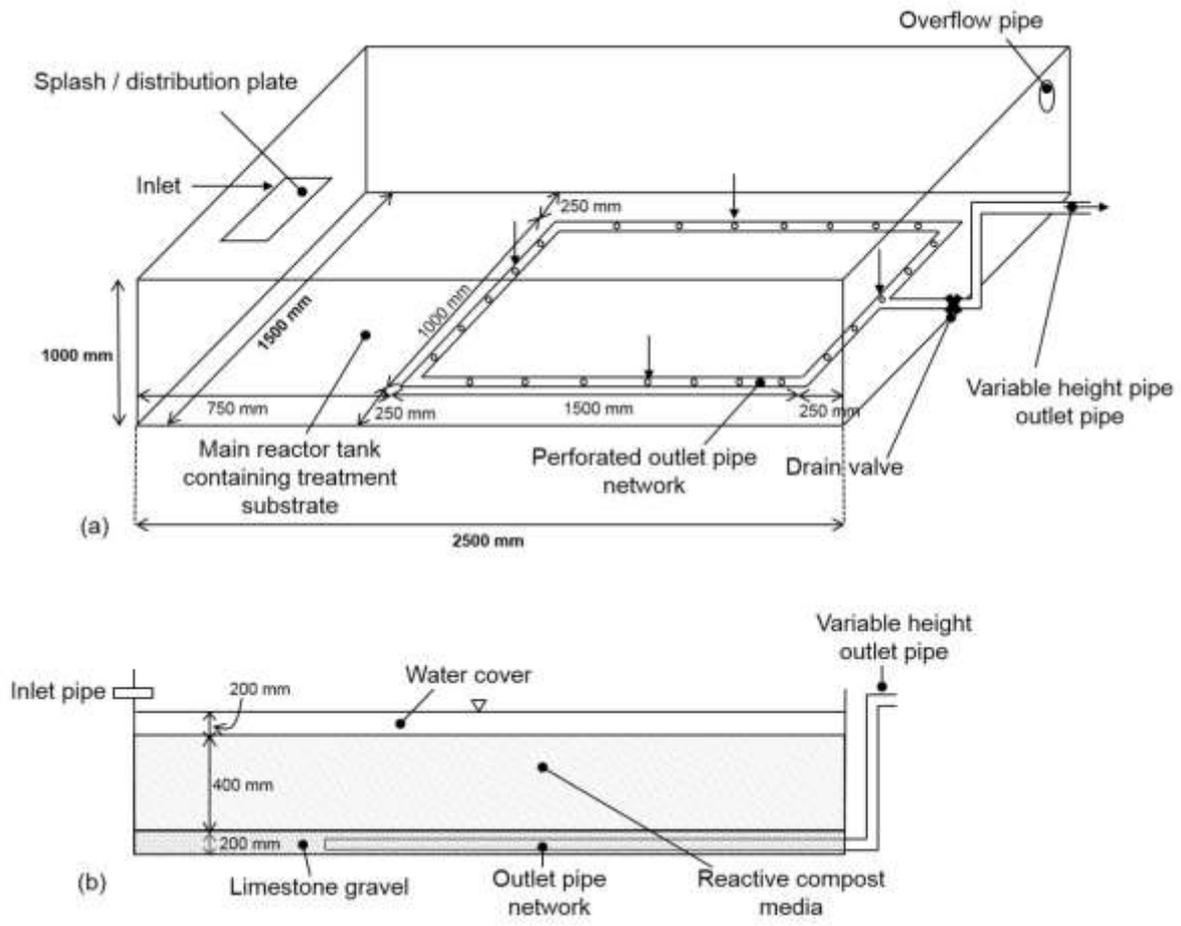
Figure S2. Schematic plan (a) and cross-section (b) of pilot-scale wetland treatment system (adapted from Environment Agency (2014))
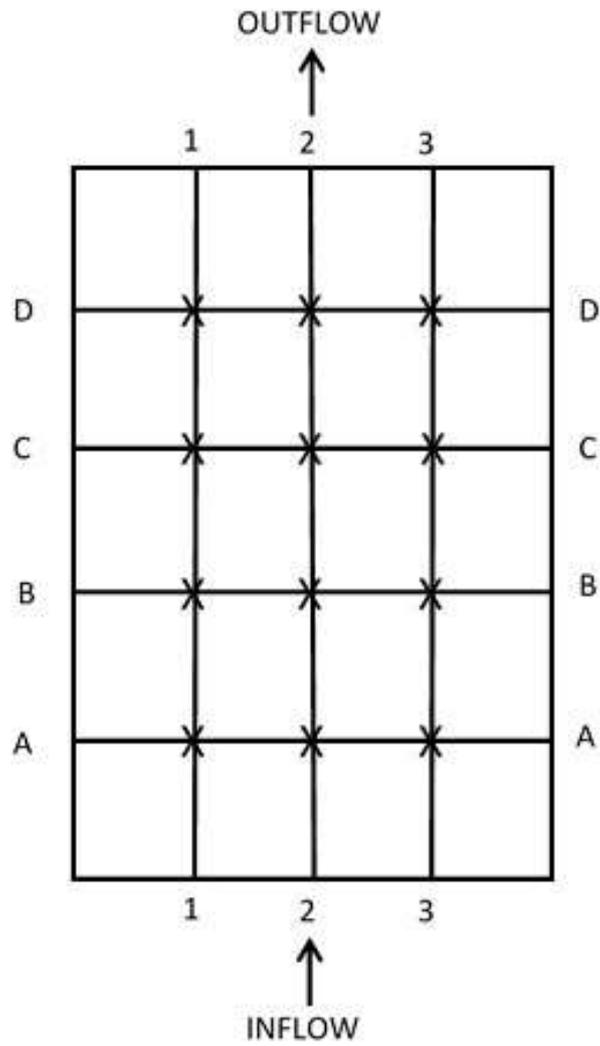
OUTFLOW

Figure S3. Schematic plan view of treatment system showing the locations (X) and identifiers for the wetland substrate sample locations
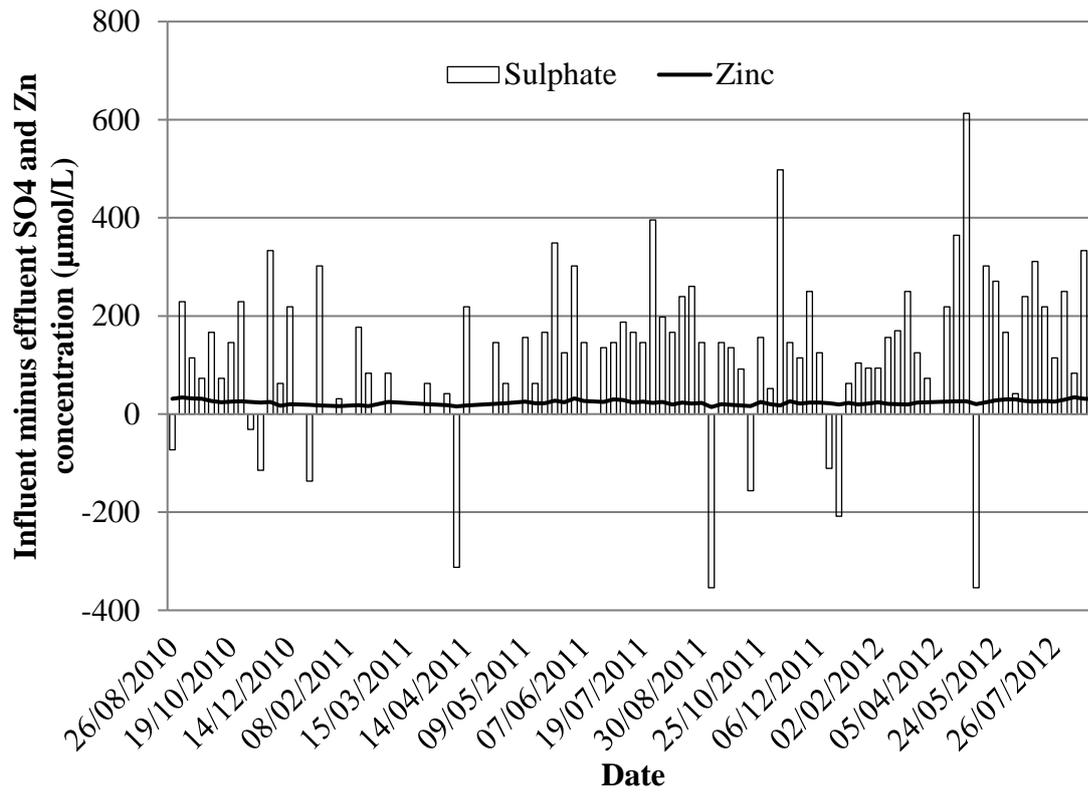
Figure S4. The decrease in sulfate and zinc concentrations between influent and effluent waters of the pilot-scale treatment system, shown by plotting influent minus effluent concentrations

Figure S5. Net change in iron concentration between the influent and effluent waters of the treatment system throughout its operation