Metal Removal and Secondary Contamination in a Passive Metal Mine Drainage Treatment System

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ABSTRACT

In March 2014, the UK's first full-scale passive treatment system for metal mine drainage was commissioned. The treatment system harnesses bacterial sulfate reduction (BSR) to immobilise the main contaminant metal, zinc, within the compost substrate of two parallel 'Vertical Flow Ponds' (VFPs), each of which has a treatment area of approximately 800 m^2. The final discharge from the treatment system enters a nutrient-sensitive upland river. Appropriate infrastructure was designed and installed to enable close control and monitoring of flow-rate and water quality. Such features include open channel flow with sharp-crested weirs for flow measurement, and an innovative penstock arrangement for fine adjustment of flow into the VFPs.

Effluent quality from the treatment system has evolved during early operation. Over the first 3 months of operation mean influent zinc concentration was 3.74 mg/L compared to 0.12 mg/L in the effluent (mean zinc removal of 97%; n = 15). Strongly reducing conditions are evident, with sharp decreases in sulfate concentration between influent (mean of 31.7 mg/L) and effluent (< 10 mg/L within approximately 2 months of commissioning) suggesting that BSR is an important metal attenuation mechanism. However, water first emerging from the VFPs had up to 82 mg/L ammonium, Biochemical Oxygen Demand (BOD) of up to 100 mg/L, and Chemical Oxygen Demand (COD) of up to 3084 mg/L, resulting in secondary contamination of the receiving watercourse. The issue was short-lived, with organics concentrations decreasing sharply. Within 4 months of commissioning the system the river was back to acceptable standards with respect to ammonium, BOD and COD concentrations. In this instance there were no downstream water users impacted by the secondary contamination. In other settings, mitigation measures may be required to address such issues during early operation of passive mine drainage treatment units of this type.

Keywords: passive treatment, secondary contamination, zinc, compost

INTRODUCTION

In March 2014 the UK's first full-scale passive treatment system for metal mine drainage treatment was commissioned, and at the time of writing has been operational for 6 months. The treatment system is located at the abandoned Force Crag mine in the Lake District National Park, north west England. The mine site lies at an elevation of 275 m.a.s.l. (above sea level), though the abandoned mine workings extend west by a horizontal distance of approximately 1 km, to an elevation of 600 m a.s.l. The mine operated intermittently for 157 years, but was finally abandoned in 1992 following a collapse in the lower workings. The mine is hosted in Ordovician-aged mudstone and lithic-wacke sediments (Kirk Stile Formation) (Barnes *et al.*, 2006). The vein-hosted mineralization present at Force Crag is dominated by galena (lead-ore) and sphalerite (zinc-ore) with barite and quartz gangue (Tyler, 2005). A series of nine individual levels form the workings at Force Crag, with Level 0 being the lowest level. Two adits currently drain the workings at Force Crag, namely Level 1 (the primary discharge) and Level 0.

Despite the occurrence of diffuse mining pollution, originating from the processing and mining waste located at the site, long-term monitoring demonstrated that the Level 1 discharge was the main point source of metal contamination to the receiving waters at Force Crag. Pollution from the mine site enters the Coledale Beck. Whilst the Coledale Beck is contaminated with metals due to both point and diffuse source pollution from the mine site, it is also a nutrient sensitive stream, with very low concentrations of both nutrients and organic compounds.

Table 1 illustrates that the main source of metals pollution to the Coledale Beck, the Level 1 discharge, is circum-neutral drainage (pH 5.6 – 7.7). The discharge is poorly mineralized, with low concentrations of all major ions, including sulfate, which has a concentration in the range 16.0 – 39.5 mg/L. The main metal of concern is zinc, which is present at concentrations in the range 1 730 – 4 660 μg/L. This concentration of zinc, and also the pH of the discharge, is typical of many discharges around England and Wales. The Level 1 discharge has a variable flow-rate (8.5 – 24.4 L/s) which is influenced by rainfall events (there is a clear inverse correlation between flow-rate and zinc concentration, indicating a dilution effect).

The installation of a treatment system for the Level 1 discharge was an initiative of the UK Coal Authority, the Environment Agency for England and Wales, the National Trust (the site owner) and Newcastle University. The treatment system was funded by the UK Department for Environment Food and Rural Affairs (Defra).

In this paper we discuss the design and early performance of the treatment system. However, whilst the main concern in relation to treatment performance is typically metal removal, an important consideration at the Force Crag site was the possibility of secondary contamination due to organic substances leached from the treatment media (see below). Therefore this paper focuses also on the evolution of treatment system effluent quality with respect to some of the more important organic constituents.

TREATMENT SYSTEM DESIGN AND LAYOUT

The passive treatment system at Force Crag is a downwards flow compost bioreactor, or Vertical Flow Pond (VFP). The treatment principle is to harness bacterial sulfate reduction (BSR) to attenuate divalent metals (Zn in particular) within the compost as their sulfides, as shown in Reactions (1) and (2).

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

$$H_2S + Zn^{2+} + 2HCO_3^- \rightarrow ZnS(s) + 2H_2O + 2CO_2 \tag{2}$$

This is a widely reported approach to passive mine water treatment (e.g. Mayes et al., 2011; Neculita et al., 2007; Sheoran and Sheoran, 2010). However, a key issue in the UK is to keep absolute system size to a minimum due to land constraints at many of the upland sites at which metal mine water discharges occur. On the basis of lab-scale (Mayes et al., 2011) and pilot-scale experiments (Gandy and Jarvis, 2012) the VFP units at Force Crag were therefore designed to have a hydraulic residence time of 15 – 20 hours, which is substantially shorter than typical designs.

As shown in Figure 1, the treatment system comprises two VFPs operating in parallel. Each VFP is lined with HDPE to prevent leakage. At the base of each VFP is a perforated pipe network. There are 4 separate perforated pipe networks in each VFP, each covering an equal area of the base of each VFP. There are also therefore 4 effluents from each VFP. Each pipe passes through the HDPE liner to a manhole chamber, where the pipes are raised to ensure that there is a 350 mm water cover over the compost substrate i.e. water level in the VFPs is controlled by the invert level of the effluent pipes in the manhole chambers. The pipe networks are overlain by a 200 mm layer of carboniferous limestone. Over the limestone is a 500 mm layer of compost substrate, which comprises 45% v/v PAS100 compost (see below), 45% v/v woodchips, and 10% v/v dried activated sewage sludge from a local municipal wastewater treatment plant. For this treatment system the limestone was used purely for the purposes of maintaining good permeability around the perforated pipe network, rather than being a requirement for generating alkalinity and elevating pH. BSI PAS100 compost meets certain agreed standards with respect to safety (British Standards Institute, 2011), and was therefore selected given that water draining through it would be entering a watercourse. The composition of the treatment media was based on successful pilot-scale trials reported by Gandy and Jarvis (2012).

Each VFP has a treatment substrate area of 760 m^2, and the volume of substrate in each VFP is 400 m^3 (each VFP is a trapezoidal basin, with internal slopes of 1:2.5). This volume of substrate was based on a design flow-rate of 6 L/s (3 L/s to each VFP, to give hydraulic residence time of 15 – 20 hours in each VFP). It will be apparent from the range of flow-rate for the Level 1 discharge (Table 1) that not all of the Level 1 discharge is treated by the system. This was due primarily to land constraints. As shown in Figure 1, excess water therefore discharges to the Coledale Beck untreated. However, during low flow conditions in the Coledale Beck, when the impact of the Level 1 discharge was historically greatest, the Level 1 flow-rate is typically at the lower end of the range reported in Table 1, and therefore the majority of the water is treated under such conditions.

Effluent from both VFPs drains to a small aerobic wetland, from where it is discharged back to the Coledale Beck (Figure 1).

Table 1 Summary water quality data for the Level 1 mine water discharge from the Force Crag mine, 2011 to 2014 (unpublished data of Environment Agency and Newcastle University)

Variable	Range	Mean	n[A]
Flow (L/s)	8.5 – 24.4	14.8	21
pH	5.6 – 7.7	6.8	25
HCO_3^- (mg/L)	8.5 – 26.8	16.7	28
Cl (mg/L)	4.7 – 7.6	5.7	28
SO_4 (mg/L)	16.0 – 39.5	26.6	28
Ca (mg/L)	5.1 – 14.5	9.5	28
Mg (mg/L)	1.95 – 5.00	3.30	28
Na (mg/L)	2.40 – 3.60	2.95	28
K (mg/L)	0.32 – 0.62	0.46	28[C]
Fe (mg/L)	0.26 – 1.08	0.52	28
Mn (mg/L)	0.29 – 0.76	0.51	28
Al (mg/L)	0.05 – 0.20	0.08	28
Zn (total) (μg/L)	1 730 – 4 660	2 997	28
Zn (filt.) (μg/L)[B]	1 710 – 4 550	2 950	28
Pb (μg/L)	25.0 – 87.9	43.6	28[D]
Cu (μg/L)	1.80 – 8.57	5.11	28[E]
Cd (μg/L)	5.00 – 20.00	14.24	28[F]
Ni (μg/L)	10.00 – 20.00	16.09	28

[A] number of samples

[B] Concentrations reported are after filtering through 0.45 μm filter

[C] 5 samples measured by ICP-OES below detection of 1.00 mg/L; value of 0.50 mg/L used for calculation of summary statistics

[D] 6 samples measured by ICP-OES below detection of 50 μg/L; value of 25 μg/L used for calculation of summary statistics

[E] 13 samples measured by ICP-OES below detection of 10 μg/L; value of 5 μg/L used for calculation of summary statistics

[F] 2 samples measured by ICP-OES below detection of 10 μg/L; value of 5 μg/L used for calculation of summary statistics

METHODS

Since commissioning of the treatment system flow and water quality monitoring has typically been undertaken on a weekly basis (fortnightly occasionally). The primary objective of monitoring has been to evaluate (a) the performance of the VFP system for Zn removal and (b) the improvement and / or impact of the treatment system effluent on the Coledale Beck downstream.

Flow-rate is measured via sharp-crested 20° V-notch weirs located at the influent of the system and the final effluent from the treatment system (at the effluent from the effluent from the aerobic wetland; see Figure 1). Flow-rate from the effluent pipes from the VFPs is measured by bucket-and-stopwatch (mean value of 3 measurements for each effluent pipe). Flow-rate in the Coledale Beck is measured with a flat V weir installed and operated by the England and Wales Environment Agency.

Because a primary objective of the Force Crag treatment system is to gain an improved understanding of the rate of removal of metals in the system, having the facility to accurately control flow-rate to the treatment units was a key consideration. For this system, a novel downwards-opening penstock arrangement was designed i.e. water is allowed to escape over the top of the penstock. Adjustment of the penstocks (one for each VFP) upwards or downwards controls water level in an open channel that is hydraulically connected to the penstock chamber. At the end of each channel is a sharp-crested 20° V-notch weir. Adjustment of the penstocks therefore controls depth of water over the V-notch weirs, and hence the flow-rate to the VFPs. This open channel arrangement is preferable to a system of pipes and valves, as the latter are prone to clogging where iron concentrations are even slightly elevated (Table 1).

Water quality samples are routinely collected and analysed by Newcastle University. Sampling and analysis is undertaken in strict accordance with methods documented in APHA (2005). Blanks and standards are run routinely, and triplicate samples are collected for analysis periodically.

There are 4 individual effluents from each of the VFPs. To evaluate overall performance of each VFP a composite sample is taken, as well as individual samples from each effluent pipe. The composite sample is made up of a volume of water from each individual pipe that is proportional to its contribution to the overall effluent flow-rate. For brevity, only composite analysis results are reported here.

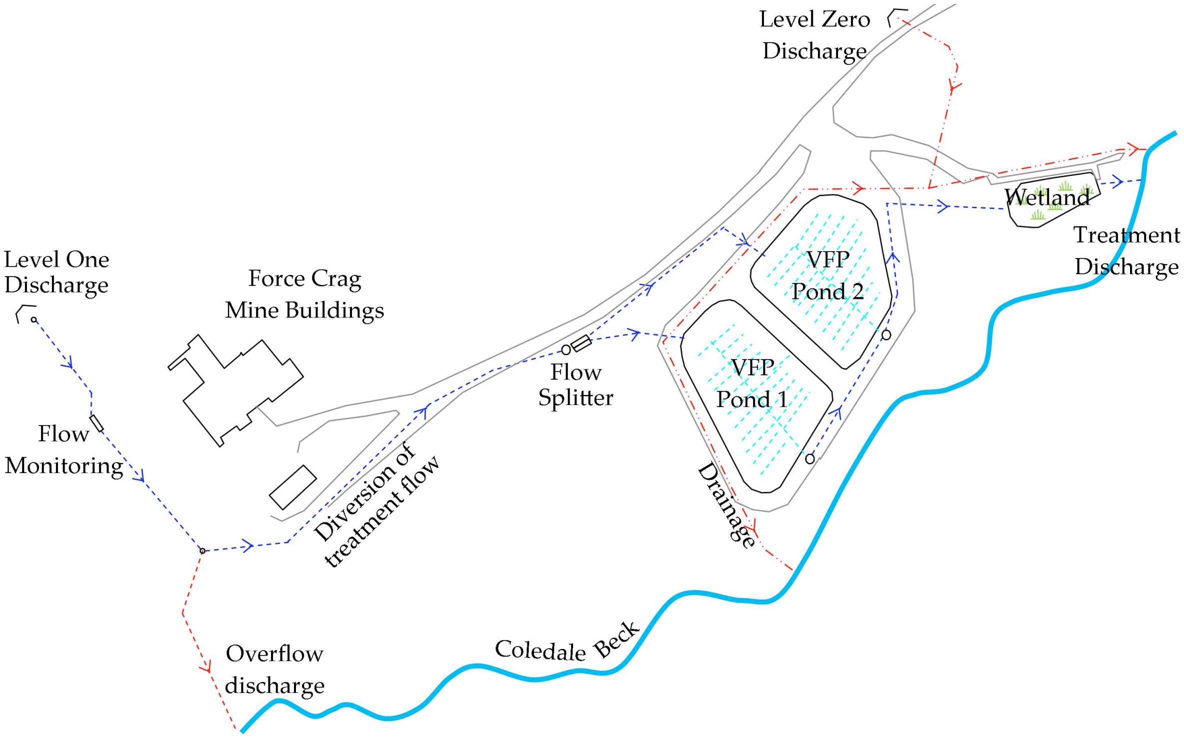

Figure 1 Layout of the Force Crag VFP passive treatment system (figure courtesy of the Coal Authority)

RESULTS AND DISCUSSION

Zinc removal

Figure 2 shows Zn removal by the treatment system for the first 6 months of its operation. Mean Zn removal efficiencies for VFP 1 and VFP 2 were 98.7% and 94.1% respectively for the period from 1 April 2014 to 23 September 2014. Overall treatment efficiency (Final effluent in Figure 2) was 96.8%. Sorption reactions, and precipitation of zinc as phases other than its sulfide, have been noted as possible sinks for zinc in previous investigations (e.g. Gibert et al., 2005; Neculita et al., 2008). At the Force Crag system it is too early to undertake detailed analyses of solid phases in the compost substrate. However, after elevated sulfate concentrations in the effluent waters for the first week of operation, sulfate concentrations decreased substantially between influent and effluent. Mean influent sulfate concentration to VFP 1 and VFP 2 was 30.4 mg/L (range: 19.3 – 38.2 mg/L) for the first 6 months of operation, whilst mean effluent concentrations were 10.1 mg/L for VFP1 (range: 0.4 – 27.8 mg/L) and 8.1 mg/L for VFP 2 (range 0.8 – 23.2 mg/L). Strong odours of hydrogen sulfide are also evident in the vicinity of the effluent manhole chambers.

Both total and filtered samples (0.45 μm) are collected for zinc analysis, and since June 2014 aliquots of both influent and VFP effluent waters have also been filtered through a 0.10 μm filter. For both VFPs, effluent filtered zinc concentrations were lower than effluent total zinc concentrations. For VFP 2 (which performed slightly less well than VFP 1), these data are illustrated in Figure 3. 0.45 μm filtered Zn concentration was, on average, 35.8% lower than total effluent concentration. 0.10 μm filtered Zn concentration was consistently below the 0.010 mg/L detection limit of the ICP-OES used for analysis (and are therefore shown as half this value – 0.005 mg/L – on Figure 3). The pattern was the same for VFP 1. This suggests that the zinc present in the VFP effluent waters is in colloidal phase. Future analyses will be undertaken to establish whether the colloidal zinc is sulfide or some other solid phase, with a view to investigating possible improvements to final water quality via additional treatment.

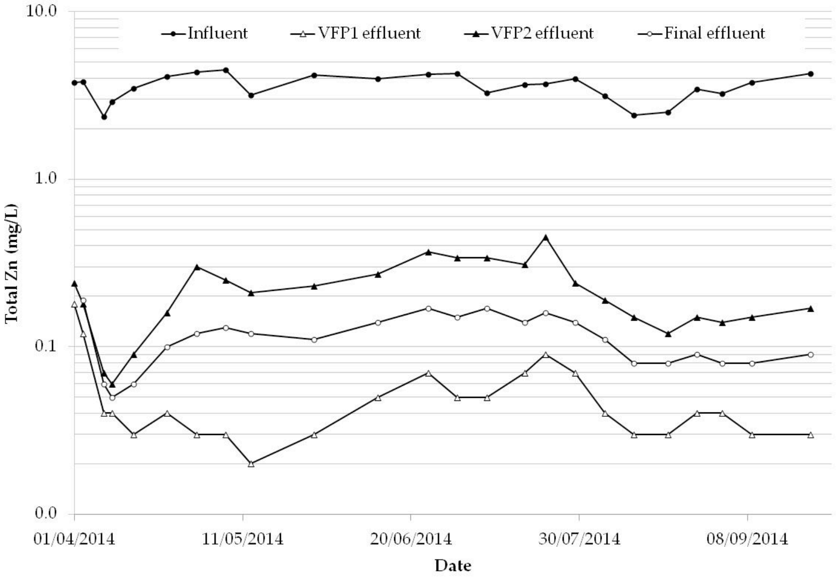

Figure 2 Zn removal at the Force Crag treatment system for the first 6 months of operation

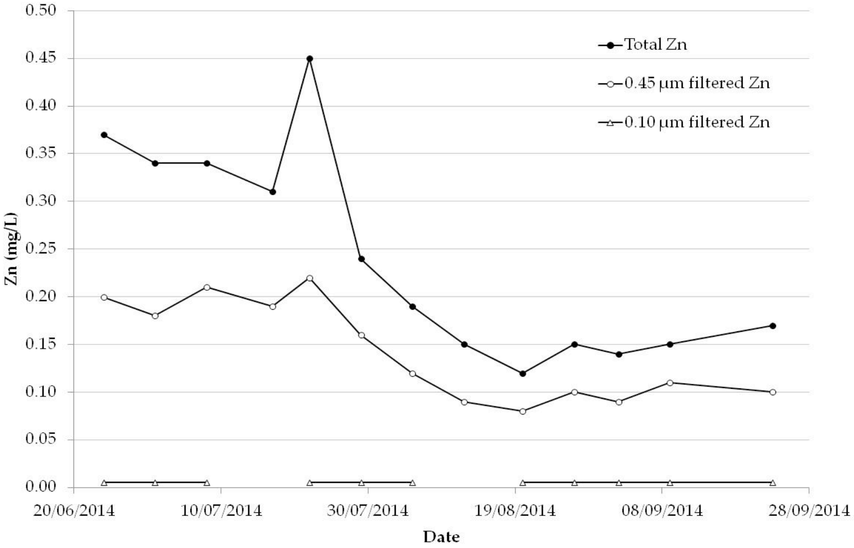

Figure 3 Differences in VFP 2 effluent total zinc concentration and effluent 0.45 μm and 0.10 μm filtered concentrations

Secondary contamination

The potential for secondary contamination from passive mine water treatment systems is rarely considered. As noted previously, the Coledale Beck is a nutrient-poor watercourse, with very limited organic enrichment. Concentrations of Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD), ammonium, nitrate and phosphate were therefore determined as part of the monitoring program for the Force Crag treatment system. A specific requirement of the environmental regulator, the Environment Agency, was that ammonium concentrations in the Coledale Beck should not exceed 0.2 mg/L on a long-term basis.

Concentrations of BOD, COD, ammonium and nutrients, for both the Level 1 discharge itself, and the Coledale Beck upstream of the treatment system, are shown in Table 2, and illustrate the low concentrations in both. Effluent water from the treatment system was initially monitored twice weekly following commissioning. Final effluent nutrient concentrations, BOD, COD and ammonium are shown in Figure 4. Concentrations for the same variables for the Coledale Beck downstream of the treatment system are shown in Figure 5 (nitrate concentration is not shown in Figures 4 and 5 as it was consistently < 0.2 mg/L in the treatment system effluent).

Table 2 Nutrient and organic concentrations in the Level 1 discharge and Coledale Beck upstream of the treatment system (all concentrations in mg/L; range shown where relevant; n = 9)

Variable	Level 1 discharge	Coledale Beck upstream of treatment system
COD	< 1.0	< 1.0
BOD	< 1.0	< 1.0
NH_4	< 0.01	< 0.01
NO_3	< 0.2 – 0.3	< 0.2 – 0.8
PO_4	< 0.2 – 5.9	< 0.2 – 3.4

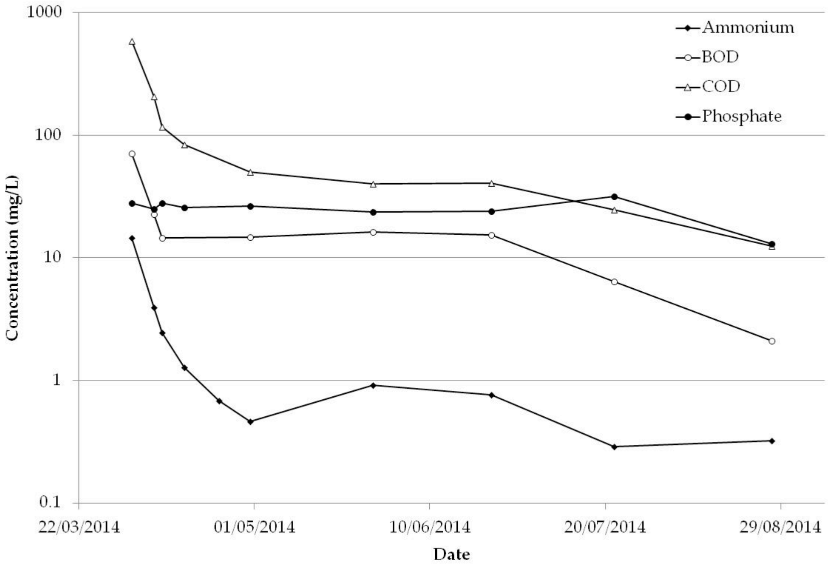

Figure 4 Concentrations of BOD, COD, NH4 and PO4 in the final effluent from the treatment system following commissioning in March 2014

There was a clear pattern of elevated concentrations of BOD, COD, PO_4 and NH_4 in the effluent water (Figure 4) compared to the Coledale Beck and Level 1 discharge (Table 2). In the final effluent water to the Coledale Beck initial concentrations of BOD, COD, PO_4 and NH_4 were 71 mg/L, 587 mg/L, 28 mg/L and 14.6 mg/L respectively. In the effluent directly from the VFPs concentrations were much higher: 82 mg/L NH_4, BOD of up to 100 mg/L, and COD of up to 3084 mg/L. However, these concentrations have dropped rapidly since water first emerged from the treatment system. These elevated concentrations were also reflected in the Coledale Beck downstream from the treatment system effluent (Figure 5), albeit absolute concentrations were lower due to dilution effects. Figure 4 illustrates that BOD, COD and NH_4 dropped rapidly within 5 – 10 days of commissioning, suggesting a ‘flushing’ effect through the compost substrate. NH_4

concentration in the Coledale Beck was also below the 0.2 mg/L value requested by the Environment Agency within 5 – 10 days.

The exception to this trend of rapidly decreasing concentrations was PO_4, which remained elevated in the effluent from the treatment system (Figure 4). Over the 6 month monitoring period, the mean PO_4 concentration was 4.3 mg/L in the Coledale Beck downstream of the treatment system effluent, compared to a mean of 1.8 mg/L upstream of the treatment system. The treatment system substrate therefore continues to act as a source of phosphate to the Coledale Beck. The downstream monitoring location on the Coledale Beck is only 70 m downstream from the final treatment system effluent point (this is below the mixing zone of treatment system effluent with the Coledale Beck). Additional dilution further downstream likely results in a decrease in PO_4 concentrations, and therefore in this instance the impact of elevated PO_4 is probably spatially limited. Nevertheless, the potential for elevated concentrations of nutrients, BOD, COD and NH_4 is an important consideration in the planning of passive, compost-based, treatment systems, especially where final discharge is to sensitive watercourses.

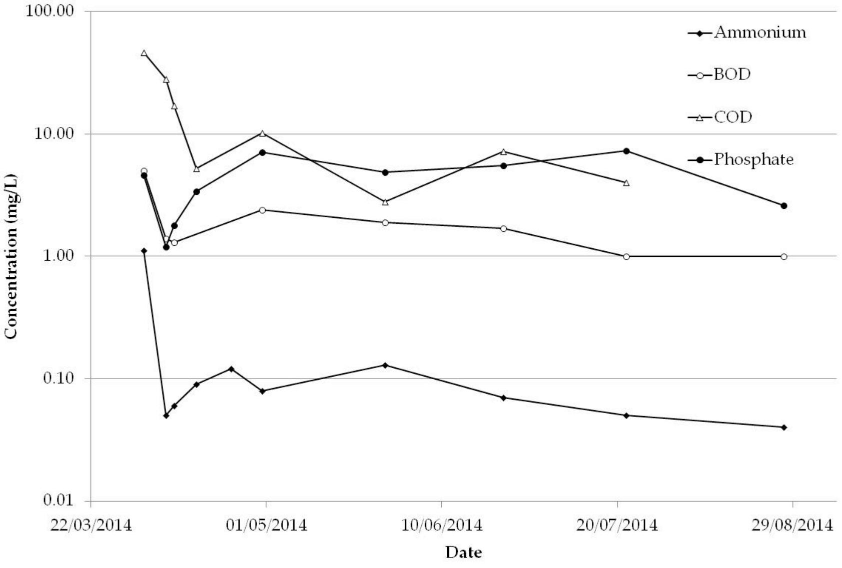

Figure 5 Concentrations of BOD, COD, NH4 and PO4 in the Coledale Beck downstream of the treatment system following commissioning in March 2014

CONCLUSIONS

The Force Crag mine water treatment system is the first full-scale passive treatment scheme for metal mine drainage in the UK. The system comprises two parallel Vertical Flow Ponds, which contain a compost substrate to encourage attenuation of zinc via bacterial sulfate reduction. The VFPs have a short hydraulic residence time for units of this type: 15 – 20 hours. For the first 6 months of operation the two VFPs consistently removed in excess of 90% of the zinc from the Level 1 discharge water at Force Crag, and overall treatment efficiency of the system for zinc removal was greater than 95%. Sulfate concentrations have consistently decreased across the treatment system, suggesting that bacterial sulfate reduction was an important attenuation mechanism. However, solid phase analyses of the compost substrate need to be undertaken to confirm this.

Over the first 6 months of operation secondary contamination was a concern. Concentrations of BOD, COD, NH_4, and PO_4 were initially elevated in the effluent water from the system, but rapidly decreased in all cases with the exception of PO_4. In the case of Force Crag, there are no downstream water users that could have been affected by these elevated concentrations, but in other situations measures may need to be put in place to deal with elevated organics / nutrients concentrations from passive mine water treatment systems, especially if there are abstractions in close proximity to the effluent point from the treatment system.

ACKNOWLEDGEMENTS

The Force Crag treatment system was funded by the UK Department for Environment Food and Rural Affairs (Defra), and was an initiative of a partnership comprising the UK Coal Authority, Environment Agency, National Trust and Newcastle University. Construction of the system was managed by the Coal Authority. The consulting firm Atkins undertook the civil engineering design of the scheme, and the construction contractor was Bentleys. The views expressed in this paper are those of the authors only, and not necessarily any of the organizations mentioned herein.

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