Predicting the benefits of mine water treatment under varying hydrological conditions using a synoptic mass balance approach

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ABSTRACT

Geochemical and hydrological data from abandoned mine watersheds demonstrated that: (1) point sources of pollution fail to account for total receiving watercourse metal load at higher flows and (2) an inverse relationship exists between river flow and pH due to peatland runoff. Quantifying the varying importance of point and diffuse pollution sources enabled prediction of treatment benefits for a major point source of pollution in one watershed. Instream zinc load increases with river flow ($\approx$ 3 kg Zn/d to 14 kg Zn/d) due to diffuse groundwater and surface runoff pollution sources at higher flows. Lab tests demonstrated that metal release from the streambed, driven by pH decreases at higher flows, also contribute to increased downstream metal loads. Predicting point source treatment benefits demonstrates major instream improvements at low flow (zinc decreases from > 800 μg Zn/L to 120 μg Zn/L). At higher flows treatment benefits diminish (Zn decreases from 240 μg Zn/L to only 200 μg Zn/L) due to the greater influence of diffuse sources. A quantitative understanding of the variable importance of point and diffuse sources of pollution, and instream processes of metal

attenuation and release, is crucial to evaluating the benefits of treatment to downstream water quality.

GRAPHICAL ABSTRACT
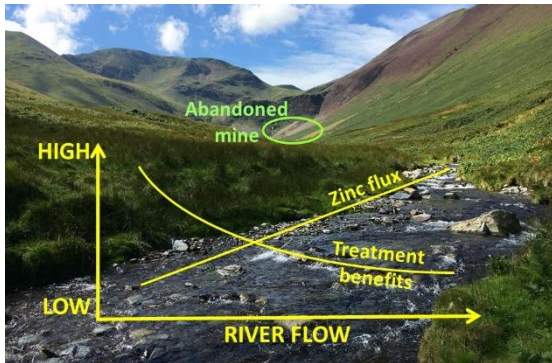
INTRODUCTION

Pollution from operational and abandoned mines is a significant, and pervasive, cause of degradation of freshwater chemical and ecological quality.[1,2] More than 50% of the total zinc and cadmium burden of watercourses in England and Wales is due to discharges from such abandoned mines.[3,4] Many of these pollution problems have their source in the headwaters of larger UK watersheds, and therefore have impacts for many kilometres downstream. Estimates of the cost of remediation of abandoned metal mine water pollution are substantial: £372 million in England and Wales,[5] and an upper estimate of US$ 72 billion in the USA.[6]

Approximately 260 individual point source discharges have been identified across England and Wales to date.[7] These are typified by elevated trace metal and sulphate concentrations.

Although some are strongly acidic, the majority in the UK have circum-neutral pH. In northern England the rivers receiving this pollution are commonly in upland locations. These rivers are often poorly mineralised, with low electrical conductivities and low concentrations of major ions.

Point sources of mine water pollution have been the primary targets for remedial efforts since they are recognised as a key source of chemical pollution of rivers[8]. However, total pollutant loadings in impacted watercourses may vary considerably with changing hydrological conditions, both in coal[9,10] and metal[11-14] mining watersheds. The diffuse sources of pollution that result in this increased pollutant load, typically during higher flow conditions, include direct inputs of contaminated groundwater into surface waters via the hyporheic zone,[15,16] and runoff from mine waste heaps.[13,17]

These findings have important implications for the design of remediation schemes that primarily target point source discharges. Passive remediation options have been favoured in the UK since the majority of abandoned metal mines are located in upland areas with steep topography and hence are unsuitable for active treatment. Given the substantial costs of constructing these extensive passive remediation systems, it is essential that the long-term benefits of point source treatment are considered.

The aim of this research was therefore to make a quantitative assessment of the potential long-term benefits of mine water treatment. This necessitates longer-term data that captures variations in hydrological conditions and aqueous geochemistry, both spatially and temporally. A synoptic mass balance approach was adopted to meet this aim. This entails

detailed spatial sampling combined with synchronous flow measurements. It has been applied previously to mining-impacted watersheds to quantify the spatial variation in metal load,[14,18-21] and, in combination with reactive solute transport models, to evaluate different remediation options.[22-24] However, use of a mass balance approach to both predict the comparative benefits of remedial interventions, and discern the nature of diffuse inputs, across different hydrological conditions has not previously been investigated.

A comprehensive evaluation of the relative importance of point sources to instream metal concentration and flux, across hydrological conditions, is challenging since many of these watercourses are turbulent upland streams with no permanent flow gauging infrastructure. An exception is the Coledale Beck, Cumbria, where an array of monitoring equipment has been installed, enabling a more detailed exploration of metal dynamics and the potential benefits of point source treatment. Water quality and flow data, from multiple locations in the Coledale Beck, were combined to produce spatial profiles of metal load across the watershed. The relative contributions of all point and diffuse sources to the instream metal load could then be discerned. Using a mass balance approach, potential benefits to water quality from remediation of a major point source are predicted, in an approach that can be applied to other mining-impacted watersheds.

MATERIALS AND METHODS

Study area: Methods used for interrogation of Environment Agency data from metal mining impacted watersheds in upland areas of northern England (Figure S1) are provided in Supporting Information (SI). More intensive monitoring was undertaken on the Coledale Beck,

which drains an upland area of 10 km^2 in Cumbria, north-west England (Figure 1 and Figure S2). Elevation within the watershed ranges from 840 m AOD (Above Ordnance Datum) to 80 m AOD and a steep gradient (550 m AOD to 100 m AOD over a distance of approximately 4 km) results in a dynamic, turbulent stream that responds rapidly to rainfall events. The underlying bedrock geology comprises siltstones and mudstones of the Ordovician-age Skiddaw Group,[25] whilst overlying superficial deposits consist largely of glacial boulder clay, with alluvial sediments and small lenses of river terrace deposits along the river channel and riparian zone.

Force Crag mine is at the head of the watershed. It was mined for barytes, lead and zinc from 1835 until 1991. The primary point source of mine water is the Level 1 discharge (Figure 1). Additional point sources (Level 0, Channels A, B and C), together with a tributary, Pudding Beck, are shown in Figure 1. Activities at Force Crag have also left a legacy of mine waste around the workings (Figure S2). The Coledale Beck remains polluted for at least 10 km downstream of the mine.
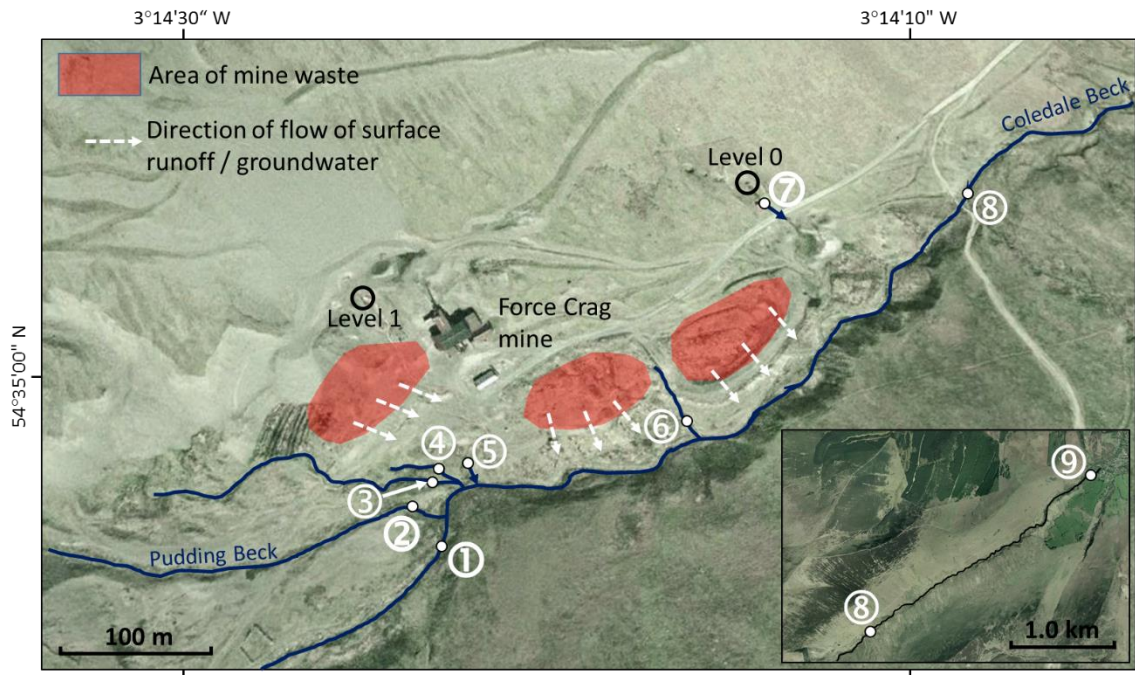
Figure 1. The Force Crag mine and Coledale Beck. Monitoring locations are (1) Coledale Beck upstream mine site (2) Pudding Beck (3) Channel A (4) Channel B (5) Level 1 discharge point (6) Channel C (7) Level 0 discharge (8) Coledale Beck downstream mine site (shown on main map and inset) and (9) Coledale Beck at Braithwaite (aerial image from GoogleEarth)

Time constraints of the synoptic mass balance approach means choice of monitoring locations is critical. For comparative purposes all sites must be monitored under consistent hydrological conditions, and therefore in a single day. Diel cycling of zinc is a well-known phenomenon in mining-impacted streams of near-neutral to alkaline pH, with higher concentrations evident at night.[26,27] To assess the extent to which this phenomenon may influence metal loads a targeted campaign of high frequency monitoring over 24 hours was undertaken on the Coledale Beck.

The sampling network (Figure 1) incorporated point sources, Pudding Beck and instream locations upstream and downstream of point sources on the Coledale Beck . Additional

instream monitoring locations were included to provide useful insight into the fate and transport of metals beyond the mine site. Diffuse sources were operationally defined for this research as the following:

a) Volumetrically very small inflows, the inclusion of which would have made it impractical to sample from all locations in a single day

b) Inputs for which it was not possible to measure flow-rate due to their dispersed nature.

c) Ephemeral flows to the Coledale Beck

Water and sediment sampling and analysis: 25 rounds of water quality and flow monitoring were completed between December 2011 and February 2014, with synchronous flow and quality measurements at all 5 point source discharges and 4 instream locations (Figure 1) on 14 of these occasions. This includes 4 occasions when data was collected by the Environment Agency. Targeted sampling campaigns captured a wide range of flow conditions.

At each site, field measurements of water temperature, pH, oxidation-reduction potential (ORP) and electrical conductivity were recorded using a pre-calibrated Myron L 6P Ultrameter. Total alkalinity was determined using a Hach digital titrator with 0.16 N sulphuric acid and bromcresol-green methyl-red indicator. Three 30 mL water samples were collected in polypropylene bottles for cation (total and filtered) and anion (filtered) analyses. Filtration was performed using 0.45 µm cellulose nitrate filters. Samples for cation analysis were acidified with 1% v/v concentrated nitric acid. All samples were stored at 4°C prior to analysis. Cation analysis was undertaken using a Varian Vista-MPX Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) or a Thermo Scientific Thermo X-series 2 Inductively

Coupled Plasma – Mass Spectrometer (ICP-MS). Anion concentrations were determined using a Dionex DX320 Ion Chromatograph (IC). The major and trace ions determined are shown in Tables S1 to S4.

Samples of river bed sediment and mine waste, from multiple locations, were collected on a single occasion. Samples were oven-dried at 105°C and passed through a 2 mm sieve. A 10g sub-sample of the < 2 mm fraction was then ground to a fine powder (< 125 μm) and analysed by X-Ray Fluorescence (XRF) using a Niton XLt 700 Series Environmental Analyser to determine metal concentrations. Subsequently triplicate river bed sediment samples were collected from below the mine site (location 8, Figure 1). These were analysed using the BCR sequential extraction technique, following the method of Rauret et al.[28]

Measurement of flow rates: Flow rates of the point source discharges and instream locations shown in Figure 1 were determined using a suite of methods. These comprised sharp-crested V-notch weirs (locations 3 – 7), a flat V weir (location 8) and salt gulp-injection dilution gauging (locations 1, 2 and 9).[29] The latter method (see SI for further details) is particularly effective in steep, turbulent streams, such as the Coledale Beck, where traditional current metering would be inaccurate.[24] To check the method accuracy, on two occasions salt gulp-injection dilution gauging was also employed at location 8, where there is a flat V weir. On both occasions the flows were comparable (37.3 L/s flat V weir, 36.0 L/s salt dilution gauging; 225.2 L/s flat V weir, 216.4 L/s salt dilution gauging).

The synoptic mass balance approach is based on the assumption that sampling is conducted under steady-state conditions in which flows are temporally constant.[21] River stage was

recorded at the most downstream location on the Coledale Beck (location 9, Figure 1) at the beginning and end of a day to check that no measurable change in flow had occurred during the course of sampling.

Synoptic mass balance analysis: Synoptic sampling combined with synchronous flow measurements enabled the quantification of metal load at each monitoring location. Metal load (in kg/d) is the product of metal concentration and flow rate. The change in instream load between locations 1 and 8 (Figure 1) was compared to the cumulative point source load to allow quantification of diffuse sources under varying hydrological conditions.

The synoptic mass balance approach was also used to predict zinc concentrations in the Coledale Beck, under varying hydrological conditions, following remediation of the Level 1 point source. A zinc removal efficiency of 70% was assumed, based on the results of pilot-scale investigations of a suitable passive treatment option.[30] Predicted concentrations were calculated according to the following equation (where 0.7 indicates treatment efficiency):

$$C_i^{Pred.} = \frac{(C_i^{Meas.} \times Q_i^{Meas.}) - (0.7 C_{ps}^{Meas.} \times Q_{ps}^{Meas.})}{Q_i^{Meas.}}$$

(1)

$C_i^{Pred.}$ =   Predicted concentration at location i

$C_i^{Meas.}$ =   Measured concentration at location i

$Q_i^{Meas.}$ =   Measured flow at location i

$C_{ps}^{Meas.}$ =   Measured concentration of point source

$Q_{ps}^{Meas.}$ =   Measured flow of point source

Laboratory batch studies: Riverbed sediment, together with Coledale Beck water, was collected at monitoring location 8 (Figure 1) for laboratory-based batch experiments to establish the importance of pH on sediment metal release. Triplicate experiments, comprising 75 g of sieved sediment (< 10 mm fraction) and 300 ml of Coledale Beck water, were placed on a reciprocal shaker and the pH adjusted periodically by addition of 0.1M HCl. Samples were collected for filtered metals and anion analysis prior to each pH adjustment. A control test received no HCl additions. The determination of filtered metals and anions was undertaken as above for river water samples. Further details on the methods used in these experiments are included in the SI.

RESULTS

Water chemistry: Table 1 shows summary hydrochemistry data for the point sources and all instream sampling locations (see Tables S1 to S4 for more details). Point source mine water discharges to the Coledale Beck are characterised by high Zn concentrations compared to upstream locations. Zinc, which is predominantly in the < 0.45 μm fraction (Table 1), is the main contaminant metal of concern. Level 1 has the highest total zinc concentration (mean 2 947 μg/L; maximum 4 660 μg/L; Table S2). Cadmium and lead are also present at elevated concentrations. A high proportion of lead occurs in its particulate form (i.e. total concentration exceeds < 0.45 μm concentration), likely due to sorption or the low solubility of lead sulphate.[31] Cadmium is predominantly in the < 0.45 μm fraction in all the point source discharges. Sulphate is present at relatively low concentrations[12] in the Force Crag mine waters (maximum 39.5 mg/L in Level 1), though still elevated relative to upstream

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concentrations. All point sources are net-alkaline[2] and poorly mineralised, with low electrical conductivity and low concentrations of major ions (Table S1). Although there is some variability, with the exception of Channel A the pH of the point sources is typically circum-neutral and there is no clear relationship between flow and pH for any of the point discharges.

The Coledale Beck is poorly mineralised and buffered, with low concentrations of major ions (Table S3). Zinc is the most important contaminant metal, although cadmium and lead concentrations are elevated also (Table 1 and S4). Zinc is present almost exclusively in the < 0.45 μm fraction. Concentrations are above regulatory standards in the Coledale Beck,[32] even upstream of the mine. Immediately downstream of the mine site zinc concentrations increase, before decreasing again further downstream due to dilution. Maximum zinc concentrations occur during low flow conditions when there is less dilution. Cadmium and lead exceed the regulatory standards at all instream sampling locations over the full range of flow conditions. Unlike the point source mine water discharges, low pH conditions are common in the Coledale Beck upstream of Pudding Beck and the Pudding Beck (Table 1 and Table S3). Downstream of the mine site pH of the Coledale Beck tends to be higher, partly due to the inputs of circum-neutral point discharges, but is still subject to periodic low pH. There is a strong inverse relationship between flow-rate and pH at all locations on the Coledale Beck and in the Pudding Beck (r = -0.820; p < 0.001 for location 8). pH decreases from 7.34 during the lowest flow conditions to 4.98 at high flow.

A high frequency monitoring campaign showed that zinc concentrations increased at night (Figure S3), due to the well-known phenomenon of diel cycling of metals[26,27]. For that reason all other data reported here are for samples collected during daylight hours. The key objective

of the research was to gather data across as wide a range of hydrological conditions as possible, irrespective of when in the year they occurred, and therefore no seasonal trends were evident in the data.

Table 1. Summary flow and water chemistry data for point source mine discharges and Coledale Beck (all values are means; values in parentheses are percentage of total concentration in filtered (0.45 µm) fraction; n = number of samples; u/s = upstream, d/s = downstream; see SI for additional data)

Point source	Flow (L/s)	pH	E.C. (µS/cm)	SO_4^{2-} (mg/L)	Total Zn (µg/L)	Total Pb (µg/L)	Total Cd (µg/L)
Level 1 (*Point source*)	**15.3** n=18	**6.74** n=22	**108.1** n=24	**26.1** n=24	**2 947** (98.2%) n=25	**48.4** (36.8%) n=25	**15.6** (95.5%) n=18
Level 0 (*Point source*)	**2.0** n=18	**6.71** n=22	**57.4** n=24	**9.0** n=11	**59.0** (91.9%) n=24	**7.66** (56.4%) n=14	**0.17** (88.2%) n=14
Channel A (*Point source*)	**10.6** n=17	**5.09** n=22	**41.2** n=24	**6.7** n=10	**643** (98.9%) n=24	**97.2** (95.7%) n=16	**3.18** (99.7%) n=14
Channel B (*Point source*)	**10.1** n=18	**6.15** n=22	**58.5** n=24	**12.1** n=19	**899** (79.3%) n=24	**20.9** (29.7%) n=14	**6.65** (90.1%) n=13
Channel C (*Point source*)	**4.0** n=21	**6.49** n=19	**72.6** n=21	**17.4** n=22	**1 693** (97.1%) n=22	**4.73** (53.1%) n=13	**8.98** (98.3%) n=8
Pudding Beck	**30.1** n=20	**4.80** n=23	**33.6** n=25	**3.7** n=10	**51.8** (100%) n=25	**58.2** (99.5%) n=21	**0.31** (96.8%) n=12
Coledale Beck u/s Pudding Beck	**140.5** n=11	**4.89** n=11	**33.3** n=11	**2.9** n=11	**21.0** (100%) n=11	**nd**	**nd**
Coledale Beck d/s Level 0	**225.5** n=19	**6.17** n=23	**43.6** n=25	**7.7** n=13	**449** (99.1%) n=25	**13.0** (50.6%) n=13	**1.96** (100%) n=7
Coledale Beck at Braithwaite	**591.1** n=18	**6.21** n=22	**37.3** n=25	**4.4** n=10	**170** (96.5%) n=25	**7.17** (46.2%) n=13	**0.73** (95.9%) n=13

Terrestrial and stream bed sediment metals: Analysis of mine waste around Force Crag mine, using XRF, reveals zinc concentrations up to ≈ 20,000 mg/kg (Figure S4(A)). Equivalent

analyses of stream bed sediments indicates zinc concentrations of up to 874 mg/kg. At location 8 (Figure 1), immediately downstream of the mine site, a concentration of 478 mg/kg was determined (Figure S4(B)). Subsequent analysis of these sediments, in triplicate, by the BCR sequential extraction procedure[28] determined a total concentration of 443 mg/kg. Of this total, and using the operational definitions of the BCR procedure, 20.9% was determined to be acetic acid extractable, 20.6% reducible, 8.8% oxidizable, and 49.7% in the residual fraction (see Table S5 for full results).

The results of batch experiments to assess sediment metal release under varying pH conditions are shown in Figure 2. A clear inverse relationship between pH and zinc concentration is evident; zinc concentration increased from 160 µg/L at a pH of 7.42 to 5530 µg/L at a pH of 4.66. A similar pattern of desorption was observed for lead and cadmium (Figure S5), albeit concentrations were below the level of detection for the analytical method used at all but the lowest pH values.
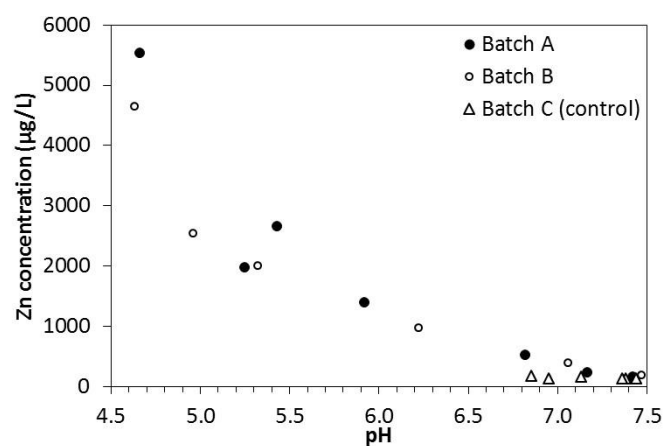
Figure 2. Variation in zinc concentration (µg/L) with pH in laboratory-based batch experiments in which Coledale Beck water was mixed with river bed sediment (Batch C represents a control test in which no pH adjustments were made). Note that the pH was

incrementally lowered over the course of the experiment, which thus proceeded from high pH to low pH.

Influence of point and diffuse sources on instream zinc load under varying hydrological conditions: Figure 3(A) shows the effect of hydrological conditions on instream zinc load in the Coledale Beck, downstream of Force Crag mine (location 8, Figure 1). Zinc load increases markedly, from around 3 kg/day (excepting one outlier) under low flow conditions (< 100 L/s) to a maximum of 14 kg/day at the highest flow (670 L/s). Concurrently, the relative contribution of point and diffuse sources of mine water to the overall zinc load varies. At low flow, instream attenuation of zinc is apparent since the cumulative point source and upstream zinc load exceeds instream zinc load below the mine site by up to 41%. As flow increases, a gradual rise in the cumulative point source and upstream zinc load is evident (Figure 3(A)) but the proportionate influence of point mine water sources on instream zinc load diminishes. Under the highest flow conditions, the total point source zinc load contribution to the Coledale Beck reduces to 57% as the role of diffuse zinc inputs becomes increasingly important.

Level 1 contributes up to 88% of the cumulative point source and upstream zinc load to the Coledale Beck under low flow conditions, (Figure 3(A)). Although the flow of Level 1 varies from 8.5 to 24.4 L/s (Table S1), the zinc load remains relatively constant (2.64 to 4.03 kg/day) over all hydrological conditions. Consequently, as the Coledale Beck flow increases, the importance of Level 1 decreases (Figure 3(A)). At high flows the contribution of Level 1 to the absolute zinc load in the Coledale Beck reduces to 26%. This is partly due to a greater contribution from other point sources so that, at high flow, the Level 1 zinc load is responsible

for just 46% of the cumulative point source and upstream zinc load. However, despite this increased point source contribution, it is the diffuse sources of zinc that begin to dominate the zinc load in the Coledale Beck as flow increases (Figure 3(A)).

Lead and cadmium show a similar pattern to zinc (Figure S6). Whilst the Level 1 lead and cadmium loads remain relatively constant (Pb 0.01 to 0.11 kg/day; Cd 0.01 to 0.02 kg/day), as the Coledale Beck flow increases the importance of Level 1 to instream lead and cadmium loads diminishes.
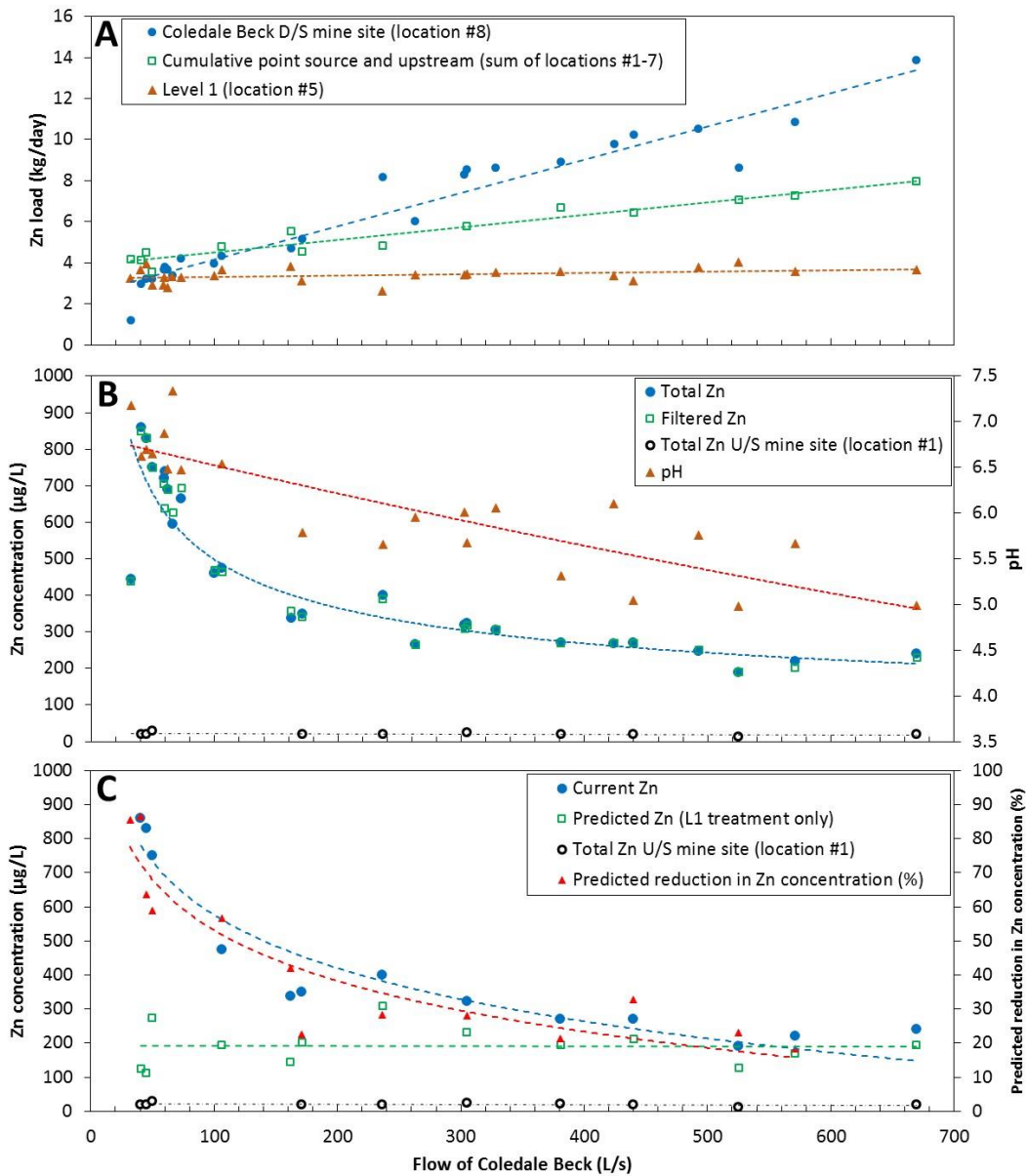
Figure 3. Variation in zinc source and downstream water quality with increasing stream flow-rate (flow at location 8 on Figure 1); (A) Comparison of Coledale Beck zinc load downstream of the mine site (location 8), the sum of measured upstream zinc loads, and the Level 1 discharge zinc load, (B) the relationship between stream flow-rate, zinc concentration and pH at location 8, and (C) the predicted downstream (location 8) zinc concentration if the Level 1 discharge is remediated (70% removal).

DISCUSSION

Identification of diffuse sources of pollution: Increased metal loads during high flows are often attributed to a lumped diffuse inputs component[12] since it is difficult to quantify the contribution of individual diffuse sources. In the Coledale Beck watershed zinc-rich mine waste material (Figure S4(A)) may be susceptible to entrainment during surface runoff following heavy rainfall, a process which has previously been identified as a cause of increased metal burden in other rivers.[17,33,34] There is visible evidence of flow pathways through the mine waste (Figures 1 and S2) during storm events. However, particulate zinc concentrations in the Coledale Beck are consistently low (filtered concentration ≥ 90% of the total concentration, Tables 1 and S4). One possible mechanism for release of (filterable fraction) metals from the mine waste is the rewetting of evaporative salts formed on, and within, the mine wastes during dry antecedent conditions[14] but further investigation would be needed to establish the role of this process for the Coledale Beck watershed. Nevertheless, metal associated with sediment suspended in the water column clearly does not account for the observed increases in metal load at high flows.

Groundwater discharge under high flow conditions is commonly observed in mining-impacted catchments[12,14,16] and can represent an important diffuse source of metals, particularly in areas where substantial fracturing of bedrock occurs.[18,35] As the Coledale Beck flow-rate increases during rainfall events an increasing discrepancy occurs between the sum of all measurable upstream flows and the Coledale Beck downstream of the mine site (Figure S7), indicating the presence of additional, unmeasured, flows. These are likely shallow subsurface flows and surface runoff. They may be an important diffuse source of metals pollution, but their quantification is challenging, requiring detailed reach-scale investigations.

Efforts to apportion diffuse inputs to specific surface water and groundwater pathways are confounded by instream physico-chemical processes. Attenuation of zinc is evident in the Coledale Beck under low flow conditions ($\leq$ 100 L/s at location 8; Figure 3(A)), and streambed sediment of the main Coledale Beck channel has zinc concentrations up to almost 900 mg/kg (Figure S4(B)). Physical mobilisation and transport of these contaminated sediment particles during high flow is of limited importance since zinc is present within the Coledale Beck primarily in the < 0.45 μm fraction (Table 1). A far more important cause of increased metal load during high flows (Figure 3(A)) is release of sediment-associated metals into the water column due to changes in river chemistry. This has been observed in other abandoned mine watersheds,[36,37] including specifically due to pH changes,[38] but the close relationship between flow, pH and metal load has not previously been illustrated. Although groundwater inflows have been shown to lower instream pH in some instances,[14] monitoring of a subsurface drain to the Coledale Beck indicates that the local groundwater has a pH of 6.0 to 6.7 (n = 22). The decreases in pH, and resulting release of metals, appear therefore to be associated with the increasing proportion of peat runoff during high flow, albeit the quantitative influence of circum-neutral groundwater on absolute metal loads requires further investigation to distinguish the relative roles of groundwater and in-stream geochemical processes. Nevertheless, variations in pH are an important control on the absolute metal load in the Coledale Beck (Figure 3(A) and 3(B)).

In other abandoned mine watersheds of northern England significant quantities of metals were shown to be transported in weakly bound fractions, suggesting that changes in chemical properties of the river water will result in the release of these metals into solution.[37] The

results of BCR sequential extraction of Coledale Beck sediment revealed that 21% of the zinc associated with sediment was acetic acid extractable i.e. weakly bound. Batch experiments undertaken to directly assess sediment metal release under varying pH conditions illustrate the important role of stream sediments as a source of zinc (Figure 2). A clear inverse relationship between pH and zinc concentration is evident; with zinc concentration increasing to 5 530 µg/L as pH decreased to 4.66, likely due to release of the weakly bound fraction of the metal. A similar pattern was observed for lead and cadmium (Figure S5). Previous investigations have identified desorption of zinc from ferrihydrite and other hydrous oxides as the most likely cause of such increases in aqueous metal concentrations, which is encouraged by lower pH conditions.[39] Conversely, during low flow, when pH is comparatively high, sorption of zinc to such hydrous oxides on the streambed could account for attenuation of zinc. Such adsorption / desorption cycles of metals to ferrihydrite have previously been observed experimentally.[40] More detailed research is required to confirm the role of hydrous oxides in the attenuation and release of metals in the Coledale Beck, such as that undertaken for other watersheds internationally[41] (such work was not a specific aim of the current research).

Potential benefits of point source remediation: The Level 1 discharge is the single greatest point source contributor to zinc load in the Coledale Beck under all flow conditions and is therefore an obvious target for remediation. To quantify the water quality benefits of remediation of the Level 1 discharge, a mass balance approach is used to predict zinc concentrations in the Coledale Beck under varying hydrological conditions.

Figure 3(C) shows the predicted zinc concentration downstream of the mine (location 8, Figure 1), following a scenario in which Level 1 is treated (removal of 70% of the zinc). Under low flow conditions (< 100 L/s) zinc concentration is predicted to reduce by 87%, from over 800 µg/L to around 120 µg/L. In contrast, under high flow conditions (> 400 L/s), the predicted improvement to instream zinc concentration is less marked as diffuse sources of zinc have a much greater influence on the instream zinc load under these conditions; ≈ 20% decrease in zinc concentration, from around 240 µg/L to 200 µg/L at the highest flow conditions. Between these extremes the benefits of treatment to downstream water quality diminish proportionally to the increase in flow. Diffuse sources of zinc may therefore limit the benefits of point source treatment at high flows.

In many abandoned mine watersheds of the UK reliable long-term mean daily flow records do not exist. However, for rivers where such data do exist, or could be derived from a stage-discharge relationship, it would be possible to use the flow-duration curve to estimate the percentage of time in a year that any specified improvement from treatment would likely be evident, and to what extent. Thus, improving understanding of the long-term hydrological regime in abandoned mine watersheds will strengthen efforts to predict the water quality benefits of mine water treatment.

Implications: From a watershed management perspective, decreasing the severity of pollution is desirable since this will lower the risks to aquatic life, and so remediating the Level 1 point source discharge should deliver substantial environmental benefits, at least under lower flow conditions. Although environmental regulations typically focus on reducing metal concentration, the overall load of metals transported downstream is also an important

consideration, especially where there are potentially sensitive downstream receptors. To reduce the absolute load of metals downstream, and ultimately limit the export of metals to marine environments[4], remedial efforts must also be directed towards diffuse sources.

Previous studies evaluating the benefits of remedial options in mining-impacted watersheds have focused on low flow conditions.[22,24] The data presented here highlight the critical importance of quantifying metal loads over varying hydrological conditions since diffuse inputs become increasingly influential as flows increase. It has previously been shown that total remediation costs to achieve a given improvement in water quality are very sensitive to the magnitude of diffuse sources within a watershed.[42] That is quantitatively borne out here: considering only low flow conditions results in overestimation of the potential benefits of remediation of point sources of pollution to the Coledale Beck. Synoptic watershed-scale monitoring to identify diffuse sources across the full range of likely hydrological conditions is therefore critical to reducing uncertainty and achieving cost-effective remediation measures.

The relative importance of individual diffuse sources is difficult to quantify and requires greater spatial resolution in stream reaches where significant unmeasured inputs have been identified[18]. In particular, a quantitative distinction needs to be made between diffuse inputs that enter the stream directly, either via contaminated groundwater or in runoff from mine waste heaps or stream banks, and increases in metal load associated with instream processes (e.g. desorption from the streambed as pH decreases). If direct inputs represent the primary diffuse source, the benefits of point source treatment at high flows will be limited, as shown in Figure 3(C). Conversely, if metals associated with streambed sediment are a major cause of instream metal load increases, either physically remobilised or released due to decreases in

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pH, the mass balance approach may underestimate the long-term efficacy of point source remediation since a reduction in the point source load would lead to less metal becoming entrained in streambed sediments. The degree of underestimation, however, is dependent upon the quantity of metals present within the streambed sediment and rate of metal release during periods of high flow. The exceptional longevity of contaminated sediment in metal mining-impacted catchments has been well documented[43] and in the short term, at least, the increase in diffuse sources of pollution at higher flows will limit the benefits of point source remediation.

The particular phenomenon of decreasing pH with increasing flow, which drives increases in metal load due to instream processes, is common to many abandoned mine watersheds of northern England. These watersheds are predominantly located in areas of peatland[44], which are a well-known source of acidic waters[45]. It is common in such watersheds to observe decreases in stream pH as flow-rate increases[46], especially where increase in stream flow is primarily due to rainfall[45]. Figure 4 illustrates a strong inverse relationship between flow and pH in the majority of watersheds investigated (r = -0.666; p< 0.001) (see Figure S8 for relationships in individual watersheds). In all of these watersheds a relationship also exists between the metal flux of the major point sources of pollution and that in the receiving watercourse downstream. Specifically, as in the Coledale Beck, there is a sharp increase in downstream metal flux as flow increases, but this is not attributable to the point sources, the metal flux from which remains relatively constant (Figure S9). Thus, the implications for mine water management in these watersheds are much the same as for the Coledale Beck.
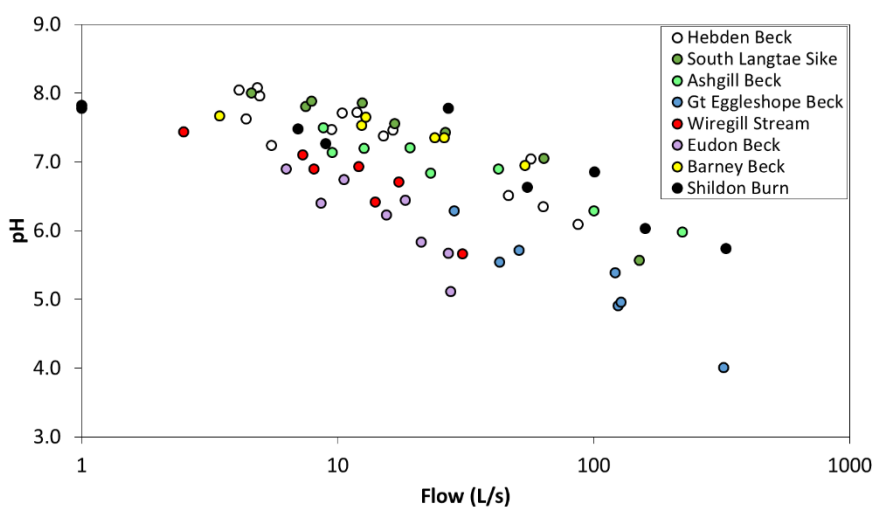
Figure 4. The relationship between stream flow-rate and pH in a selection of metal mining impacted upland streams in northern England, UK. Locations are shown in Figure S1

The benefits of point source treatment can be predicted using the synoptic mass balance approach, but this must capture data across the full range of hydrological conditions in a watershed to provide an accurate picture. Nevertheless, more accurately quantifying the importance of individual diffuse sources of pollution, as distinct from increases in metal load associated with instream geochemical processes such as those resulting from decreases in pH, is also necessary if remedial measures are to be designed that will address diffuse source pollution in abandoned mine watersheds. High resolution, reach-scale monitoring, and direct measurement of shallow groundwaters in riparian areas using piezometers, should be undertaken to improve understanding in this area. Such activities will of course have cost implications. However, the costs of construction of a treatment system for a point source are substantial, even for passive treatment systems. Although clearly site-specific, current experiences in the UK suggest that construction costs for a full-scale system would be at least US $ 1.0 million. Detailed, targeted, reach-scale monitoring costs would typically only be a

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fraction of this. Given that such monitoring would improve understanding of the true benefits of such a treatment system, these monitoring activities would be a worthwhile investment.

Supporting Information

Details of methods for interrogation of data from metal mining-impacted watersheds, QA/QC, flow measurement by salt gulp dilution gauging, quantification of metal loads and laboratory batch experiments; annotated photo of study area; diel cycling of zinc; sediment zinc concentrations; lead and cadmium concentrations in laboratory batch experiments; lead and cadmium loads in the Coledale Beck; flow discrepancies; relationship between (1) stream-flow and pH and (2) stream-flow and metal loads in metal mining impacted watersheds; hydrochemistry data for point sources and instream locations; BCR sequential extraction data.

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