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Effect of an extreme flood event on solute transport and resilience of a mine water treatment system in a mineralised catchment

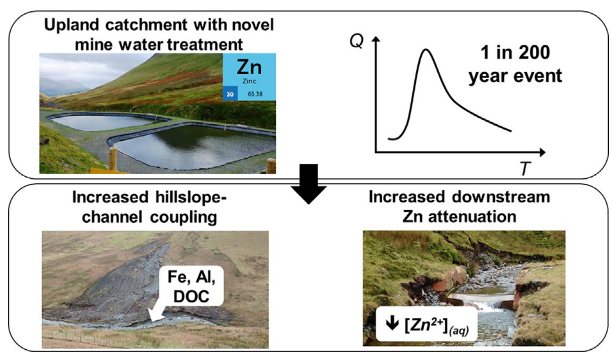
W.M. Mayes [a,*], M.T. Perks [b], A.R.G. Large [b], J.E. Davis [c], C.J. Gandy [c], P.A.H. Orme [c], A.P. Jarvis [c]

[a] Department of Geography, Geology and Environment, University of Hull, Cottingham Road, Hull HU6 7RX, UK
[b] School of Geography, Politics and Sociology, Newcastle University, Newcastle upon Tyne NE1 7RU, UK
[c] School of Engineering, Newcastle University, Newcastle upon Tyne NE1 7RU, UK

HIGHLIGHTS

- Extreme flood event in catchment containing novel mine water treatment system
- Mine water treatment system showed no change in performance related to flood.
- Longer term catchment water quality shows subtle response to extreme event.
- Input of hillslope material appears to attenuate dissolved zinc transport.

GRAPHICAL ABSTRACT



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ABSTRACT

Extreme rainfall events are predicted to become more frequent with climate change and can have a major bearing on instream solute and pollutant transport in mineralised catchments. The Coledale Beck catchment in north-west England was subject to an extreme rainfall event in December 2015 that equated to a 1 in 200-year event. The catchment contains the UK's first passive metal mine water treatment system, and as such had been subject to intense monitoring of solute dynamics before and after commissioning. Due to this monitoring record, the site provides a unique opportunity to assess the effects of a major storm event on (1) catchment-scale solute transport, and (2) the resilience of the new and novel passive treatment system to extreme events. Monitoring suggests a modest decline in treatment efficiency over time that is not synchronous with the storm event and explained instead by changes in system hydraulic efficiency. There was no apparent flushing of the mine system during the event that could potentially have compromised treatment system performance. Analysis of metal transport in the catchment downstream of the mine suggests relatively subtle changes in instream chemistry with modest but statistically-significant reductions in zinc in the lower catchment irrespective of flow condition after the extreme event, but most parameters of interest show no significant change. Increased export of colloidal iron and aluminium is associated with major landslips in the mid-catchment after the storm and provide fresh sorption sites to attenuate dissolved zinc more rapidly in these locations, corroborated by laboratory experiments utilising site materials to investigate the attenuation/release of metals from stream and terrestrial sediments. The data are important as they show both the resilience of passive mine water treatment systems to extreme events and the importance of catchment-scale monitoring to ensure continued effectiveness of treatment initiatives after major perturbation.

* Corresponding author.
E-mail address: w.mayes@hull.ac.uk (W.M. Mayes).

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1. Introduction

Flash Flooding from Intense Rainfall (FFIR) events are predicted to become more commonplace in mid-latitudes with global climate change (Hannaford, 2015). The impacts of extreme hydrological events on solute chemistry and potential pollution stressors are increasingly studied (e.g. Michalak, 2016). However, the often tightly-coupled influences of changes in the frequency and magnitude of extreme flow events on instream hydrochemistry and contaminant mobility are not well-understood due to logistical challenges for monitoring and a typical absence of long term pre- and post-change datasets (Michalak, 2016; Jarvis et al., 2019).

Globally, pollution arising from abandoned metal mines is a particularly pervasive form of aquatic pollution, with at least 6% of rivers affected in the UK (Mayes et al., 2009), while global assessments suggest mining waste to cover a land area in excess of 1 million km^2 (Lottermoser, 2007; Hudson-Edwards, 2016). Numerous studies have demonstrated the importance of hydrological boundary conditions in controlling contaminant delivery from point and diffuse sources to surface waters, as well as influencing instream solute dynamics (Mighanetara et al., 2009; Banks et al., 2010, Johnston et al., 2017). In catchments with a legacy of metal mining, extreme rainfall events may have major impacts on instream metal transport and bioavailability (Byrne et al., 2012). Researchers have long-cautioned of the potential 'chemical timebomb' posed by contaminated fluvial sediments of mining age that could be reworked and remobilised with increased frequency of high flow events (De Lacerda and Salomons, 2012; Dennis et al., 2009; Foulds et al., 2014).

In upland catchments, where the bulk of historical Pb and Zn mining took place in the UK, as well as in other parts of the world (Mayes et al., 2009), there are associated risks of increased metal mobility in high flow events which tend to be slightly acidic in their underlying nature, especially where draining upland peatlands (Gozzard et al., 2011). Any fall in pH could remobilise weakly-associated sediment metal phases as well as lead to dissolution of pH-sensitive transient and amorphous instream mineral phases, themselves well-documented sinks for divalent metals (e.g. Fe/Mn oxides, Al oxides and carbonates: Hudson-Edwards and Edwards, 2005). Metal flushing during storm events has been widely documented in mine-impacted catchments (e.g. Cánovas et al., 2008; Lin et al., 2007), with multi-season studies showing how flood chemographs can be influenced by antecedent conditions, with metal flushing more pronounced after extended dry periods (e.g. Byrne et al., 2012). Despite these potential risks for increased metal mobility under high flow conditions, increased erosion associated with extreme flow events may lead to greater input of uncontaminated surficial deposits, which in turn may offer relative dilution of instream metal-rich sediments and provide fresh sorption sites to attenuate aqueous contaminants.

The relative importance of these potential mechanisms in controlling metal dynamics is not well understood however, and remains difficult to quantify given the relative dearth of high quality hydrochemical monitoring datasets that both precede and follow major flood events. As such, our understanding of potential medium term changes to water quality baseline conditions as a result of major catchment perturbation is currently limited. In a recent study of metal availability in urban settings after major flood events, changes in metal(loid) mobility were found to be small and the extreme flood event did not significantly increase the availability of weakly-associated sediment-bound metals (Hurley et al., 2019). In catchments subject to remediation of legacy mine pollution sources, the impacts of such major flood events has implications not just for treatment infrastructure (Jarvis et al., 2019), but also to what extent baseline shifts in instream metal loads ensue. For example, extensive delivery of metal-rich waste rock from diffuse sources (e.g. Gozzard et al., 2011; Byrne et al., 2012; Foulds et al., 2014; Kincey et al., 2018) may undermine the effectiveness of ongoing point source remediation.

In December 2015 a major mid-latitude depression ('Storm Desmond') led to record rainfall and widespread flooding in north west England, UK. The event broke many UK hydrological records such as peak rainfall in a 24 h period (Honister Pass, Cumbria) and was extrapolated to be between a 1 in 100 to 1 in >200 year event in the most-affected catchments (Marsh et al., 2016). One of the areas severely affected by the event was the Cumbrian Lake District in NW England (Joyce et al., 2018) which contains a number of nationally-significant abandoned metal mine discharges (Jarvis and Mayes, 2012). Notable among these is the Force Crag mine in Coledale Beck (54°35′01.8″N 3°14′15.2″W) which has been subject to intensive catchment-scale monitoring since 2012 as part of remediation planning and implementation of a novel passive metal mine water treatment system (Jarvis et al., 2019). This offers a unique baseline from which to assess the effects of a major flood event on instream water quality. Here, we assess the impact of the Storm Desmond FFIR event on instream metal dynamics and the continued effectiveness of mine water treatment through comparison of pre- and post-storm datasets. By integrating geomorphological surveys with hydrological and water quality monitoring data, dominant metal sources, pathways and potential attenuation mechanisms are compared before and after this major perturbation to the catchment.

2. Materials and methods

2.1. Study site

The Coledale Beck is a rapidly responding upland catchment draining an area of 10 km^2 in the Lake District National Park, UK (Fig. 1). Elevation within the catchment ranges from 840 m AOD (Above Ordnance Datum) at the head of the watershed to 80 m AOD at the confluence of the Coledale Beck with the Newlands Beck. Through the active reach (Fig. 1b), Coledale Beck has an average gradient of 0.027 m m^{-1} and a meandering planform with pool-riffle sequences. The stream bed sediment calibre is comprised of cobble and boulder size material. Siltstones and mudstones of the Ordovician-age Skiddaw Group dominate the bedrock geology of the catchment, while superficial deposits comprise mainly glacial boulder clay, with small lenses of river terrace alluvial deposits along the river channel and in the riparian zone (Postlethwaite, 1913).

A single mine, Force Crag (54°35′01.8″N 3°14′15.2″W), is situated at the head of the watershed. Mined for barite ($BaSO_4$), galena (PbS) and sphalerite (ZnS) from 1835 until cessation of mining operations in 1991, the abandoned workings comprise nine interconnected levels (adits) (Tyler, 1990). These levels are numbered in sequence by elevation, with Level 0 being at the lowest elevation. Because of a historic collapse within Level 0, most of the water from the mine currently discharges from Level 1. In addition to the minerals of economic value, manganese and iron oxides accompany the barite in the upper parts of the mine workings. Pyrite and chalcopyrite are present in the lower parts of the workings that were rich in sphalerite, and to a lesser extent galena (Young and Cooper, 1988). As described by Green et al. (1997), a host of other, less abundant, Ag, Co, Cu, Pb and Zn minerals have also been identified in the workings.. As with many other abandoned mine sites, activities at Force Crag have also left a legacy of mine waste in the vicinity of the workings. A passive mine water treatment system based on two parallel vertical flow ponds containing a mixture of reactive organic (compost, woodchip) and inorganic (limestone) media was commissioned by the UK Coal Authority in March 2014 to treat the main discharge from Level 1 of the mine (Jarvis et al., 2019). Each pond covers an area of 760 m^2 and both are uncovered, so subject to variation in volume with rainfall and potential surface runoff from the land within the retaining bunds that surround them. This was the first full-scale passive treatment system for a metal mine discharge commissioned in England and Wales under the national strategy for management of pollution from non-coal mines (Jarvis and Mayes, 2012).

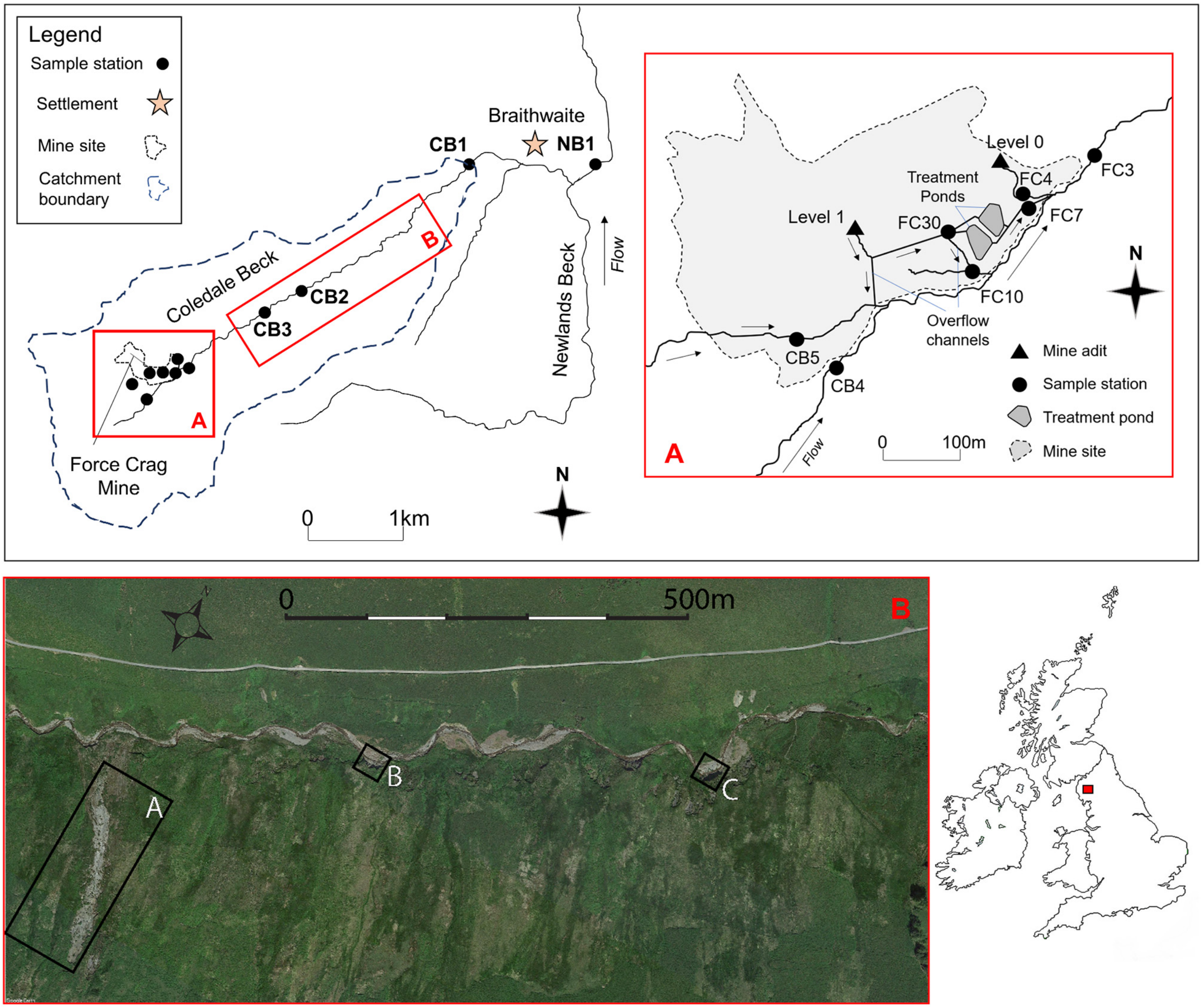

Fig. 1. Location map of the Coledale Beck catchment, Force Crag mine and water quality sample stations. Inset shows satellite image of the middle reaches of Coledale Beck, where significant hillslope failures were observed immediately following Storm Desmond in December 2015. Hillslope-channel coupling was observed to take place throughout 2016. Labelled rectangles indicate areas of interest, specifically: (A) shallow landslide; (B) and (C) riverbank erosion. Image credit: Google Earth 2018.

2.2. Geomorphological studies

Geomorphic change following Storm Desmond was determined for the reach of Coledale Beck between instream sample locations FC3 and 1 km upstream of CB1 (Fig. 1). In the absence of a high-resolution ($<5 \times 5$ m^2) pre-event terrain model, the pre-event surface of the area labelled A in Fig. 1 was estimated by extracting the post-event surface elevations just beyond the active landslide process domain and fitting a 2D natural neighbour interpolated surface to these observations. The post-event surface was surveyed using a terrestrial laser scanner in March 2016. For this, a Leica MS50 multi-station was used in conjunction with a GS14 Global Navigation Satellite System (GNSS) for georeferencing of the point cloud. The generated point cloud was gridded at a resolution of 0.1×0.1m^2. Change detection was conducted by performing 2.5D differencing in Z between the pre-event and post-event surfaces. Erosion volume was determined for each grid cell within the process domain and these were summed to provide total landslide erosion volume. Topographic surveys using the MS50 were repeated in December 2016 to assess longer-term evolution of erosional features and slope failures. Geomorphic change between March and December was determined using Multiscale Model to Model Cloud Comparison (M3C2) (Lague et al., 2013).

2.3. Water sampling and analysis

The instream sampling network (Fig. 1) was designed to incorporate instream locations upstream and downstream of point sources of contamination from the Force Crag mine and wastes associated with it. These point sources are (1) the major Level 1 discharge, which flows to the treatment system (FC30), (2) a second, smaller discharge from Level 0 of the mine, which is mixed with water captured in a groundwater drain around the treatment system (FC4), and (3) a metal-rich groundwater discharge that mixes with untreated water from FC30 (FC10: Fig. 1). The discharge from the treatment system (FC7) enters the Coledale Beck at the same location as FC4. The first instream monitoring location below these point sources of contamination is FC3, 70 m downstream from FC7 (Fig. 1). A tributary, Pudding Beck (CB5; Fig. 1), was also monitored, upstream of its confluence with the Coledale Beck, to assess its contribution to instream contaminant load, and the Coledale Beck itself was monitored upstream of the mine as a reference site (CB4). Additional monitoring locations on the Coledale Beck were included to provide data on the fate and transport of metals beyond the mine site; CB1 is the most downstream location on the Coledale Beck, and NB1 was monitored as it is the larger watercourse – the Newlands Beck – into which the Coledale Beck flows. Monitoring sites were also intentionally included around areas of major landslips after the flood event; sites CB2 and CB3, which were monitored only after the flood event. Flow was measured at all sampling locations to permit loading (product of metal concentration and flow) to be quantified throughout the catchment. Six sites are equipped with hydraulic structures (V-notch or equivalent weirs) while slug injection dilution gauging (using NaCl) was used at all other sites (see Jarvis et al., 2019 for detail). Monitoring of the three point source discharges, treatment system effluent, and four instream locations shown in Fig. 1 was undertaken on nine occasions between March 2014 and December 2014 (pre-storm, but after treatment system commissioning) and on twelve occasions from January 2015 until January 2017 (post-storm dataset). Sampling campaigns were targeted to capture a wide range of flow conditions (see Fig. S1 in Supporting Information for hydrological context). At each site, field measurements of water temperature, pH, redox state (Eh) and electrical conductivity were performed using a pre-calibrated Myron L 6P Ultrameter. Total alkalinity was determined using a Hach digital titrator. Samples were titrated against 0.16 N sulphuric acid with a bromcresol-green methyl-red indicator and results expressed as mg/L as $CaCO_3$. At each site, two 30 mL water samples were collected in polypropylene bottles and acidified with 1% v/v concentrated nitric acid. One sample was passed through a 0.45 μm cellulose nitrate filter for filtered metals analysis while the other was unfiltered for total metals analysis. A third, un-acidified, 30 mL sample was collected for anion analysis. All samples were stored at 4 °C prior to analysis. Metals analysis was undertaken using a Varian Vista-MPX Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) or an Agilent Technologies 7700 Series ICP-MS, while anion concentrations were determined using a Dionex DX320 Ion Chromatograph (IC). Certified 1000 ppm standards (accuracy of ≤ ± 1.0%; VWR Chemicals) were diluted using deionised water (Elga Purelab Ultra 18.2 MΩ at 25.8 °C) for calibration standards. Blanks (deionised water) and standards were run every 10 samples to check analytical accuracy and precision. For Quality Assurance/Quality Control purposes, replicate samples were taken on four occasions on the same dates as samples collected by these authors. Samples were collected from two contrasting locations (FC3 and FC7) by an independent contractor and analysed at a different laboratory. In the majority of cases analytical results closely match those collected for this research, as shown in Table S1. Reliability of sample analysis was also tested using charge balance calculations. In the majority of cases (56% of all samples) electro-neutrality was within ±5%, and in more than 85% of cases within ±10%. Because of the very low ion content of most of these waters (conductivity of the Coledale Beck is often around just 40 μS/cm) the charge balance is very sensitive to even very minor differences in sum of cations and anions. In cases where charge balance was greater than 10%, this appears typically to be due to minor errors with bicarbonate concentration determination, which is generally very low and measured in the field by colorimetric titration. In the August 2016 sampling round (Q_{50} condition), sequential filtration of water samples was undertaken (0.45 μm; 0.1 μm; 10 kDa filters) to partition the different metal load fractions downstream of the site.

2.4. Laboratory studies

Laboratory experiments supplemented and aided field data interpretation. In particular, these experiments simulated the likely role of sorption of contaminant metals to iron and aluminium hydroxides released to the Coledale Beck during Storm Desmond; having first ruled out precipitation reactions as a possible cause of attenuation via modelling using PhreeqC (see Section 3.6). Sediments were collected from four locations that represented as wide a range as possible of sediment character and metal concentration: (1) the Coledale Beck at FC3, immediately downstream of the mine site, where stream bed metal concentrations were expected to be at their highest; (2) the Coledale Beck at CB2, downstream of the main zone of landslips, and therefore the reach most likely to have been influenced by inputs of fresh sediments from landslips; (3) from a mine waste pile near Force Crag mine, representing the highest sediment metal concentrations in the catchment; and (4) from freshly exposed material from the major landslip in the catchment (Fig. S2). Semi-circular sections of plastic 'channel' (0.5 m length), with a cross-sectional area of 16.1 cm^2, were fabricated. Plastic end plates, fitted with inlet and outlet pipes, were attached to each end of the channel section (Fig. S3), and these reactors were then positioned on the lab bench, with the inlet end elevated by 3 mm relative to the outlet end (approximating a shallower gradient reach of the Coledale Beck). An exact volume of sediment was placed in each reactor (810 mL CB2 sediment, 790 mL FC3 sediment, 820 mL mine waste, 810 mL landslip sediment; the granular nature of the sediments meant it was not possible to use exactly 800 mL sediment in all cases). CB1 water, the most downstream monitoring location on the Coledale Beck, was then mixed with the sediments. CB1 water was selected because the objective of the experiments was to understand the influence of different sediments on Zn concentrations in the stream water. The only requirement, besides the water emanating from the Coledale Beck, was that the water used should have an elevated Zn concentration, such that any attenuation of Zn would be measurable. At CB1, Zn concentrations were in the range 87–135 μg/L post-storm ($n = 9$), and therefore this location was selected for the simple logistical reason that it was the only location accessible by vehicle, which was necessary given that large volumes of water were required (100 s of litres).

A measured volume of CB1 water was then carefully added to completely saturate the sediment, in order to determine the porosity of the sediment in each section of 'channel'. By adjusting flow rate through each reactor a nominal hydraulic residence time (HRT) of 4 min was achieved. This HRT is indicative of the comparatively fast hyporheic exchange processes expected in an upland stream with a gravel-cobble streambed (Harvey and Wagner, 2000). Reactors ran for 6 min before the first sample, in order to flush out water initially used to determine the sediment porosity. At 6 min, and at 15-minute intervals thereafter, 50 mL samples were collected. 10 mL of this was immediately filtered (0.45 μm filter) and acidified with concentrated nitric acid for subsequent analysis for metals concentrations using ICP-OES, as above. The remaining sample was used to determine pH, alkalinity and anion concentrations via ion chromatography (see above).

2.5. Statistical analysis

Principal Component Analysis (PCA) of major and minor aqueous parameters was undertaken to assess the different geochemical signatures of sample stations across the catchment under baseflow conditions (August 2016). Data were normalised using center log ratio (CLR) with values below detection limit recorded at half the detection limit given these accounted for less than 4% of data points (Farnham et al., 2002; Reimann et al., 2011). Time series analysis of mine water treatment data was undertaken using a Mann Kendall test to evaluate monotonic trends in system treatment efficiency (% influent load removed) using R (R Development Core Team, 2012) and MULTMK/PARTMK (Libiseller and Grimvall, 2002) for trend analyses. Data from pre- and post-storm monitoring over a range of flow conditions are used to test the hypothesis that there is no significant change in instream metal transport at the two key sample locations: FC3 immediately downstream of the mine site and CB1 on the Coledale Beck at the village of Braithwaite in the lower catchment. The CB1 sample station lies downstream of the major areas of mass movement induced by the extreme flood event. These two sample sites have the most extensive pre- and post-storm datasets so comprised the key focus of analysis. Analysis of co-variance (ANCOVA, using General Linear Model) tests were used to test for significant difference between pre- and post-storm key water quality parameters with flow included as a co-variate in the models (e.g. Rutherford, 2011). This permits hydrological condition to be included in the models of any change in water quality parameter before and after the flood event. Data were log-transformed where required to ensure equal variance and normality. Unless otherwise stated, all analyses were performed using Minitab v15.

3. Results and discussion

3.1. Geomorphological impacts

The 2015 Storm Desmond event caused extensive flooding in the Coledale valley and throughout the Newlands Beck catchment. This was accompanied by extensive shallow landslips across the region (Joyce et al., 2018) and evidence of hillslope-channel coupling at several other points along Coledale Beck (Fig. 1). Fig. 2 shows the evolution of the largest scar in the mid-catchment, which is a 220 m long translational evacuation, with an estimated erosional volume of 1565 m^3. The average scour depth was 0.46 m with scour depths of approximately 0.5 m measured at the head of the scar and maximum depths of 1.6 m occurring along scoured channels in the mid- and lower-sections of the failure (Fig. 2a). There is evidence of continued low magnitude surface lowering (up to a depth of 0.3 m) in the area within and beyond the initial erosional surface in subsequent months (Fig. 2b). Fig. S4 shows other areas of active erosion occurring after Storm Desmond, including significant outer bank retreat and point bar erosion in reaches between CB2 and CB1. These are key demonstrations of continuing sediment delivery from hillslopes to the stream following the flood event.

3.2. Spatial patterns in water quality

Under baseflow conditions the Force Crag mine site has a major bearing on instream water quality. Fig. 3 shows PCA of major water quality parameters across the catchment with the first component (*x* axis) highlighting the signal of mineral and metal-rich (notably Zn and Cd) waters at the mine site (plotting to the right of Fig. 3) and the sample stations with lower levels of mineral enrichment, and low Zn, Cd and SO_4 concentrations in particular, upstream of the mine site (CB4 and CB5) and in the lower catchment (CB1–3, NB1). Sample stations immediately downstream of the mine site (FC3) plot centrally on Fig. 3a and reflect the relative mixing of mine discharges and surface runoff. The key source of both metals and other products of groundwater and mineral weathering (e.g. Ca, Mg, SO_4) are associated with the level discharges (notably station FC30 [Level 1]) and shallow groundwater discharges in the vicinity of the mine site (see Tables 1 and S2, and Jarvis et al., 2019). Site FC7 (lower right of Fig. 3a) represents the outlet of the treatment system which is characterised by lower Zn and Cd (compared to the influent FC30; Tables 1 and S3). The vertical flow treatment ponds utilise sulphate-reducing bacteria in anoxic conditions (indicated by negative oxidation-reduction potential (ORP) in FC7 water; Table S1) in a mixed reactive media of compost and woodchip overlying a layer of limestone (Gandy et al., 2016). Zn and Cd are removed as their sulphides. One product of bacterially-mediated sulphate reduction is bicarbonate alkalinity (Neculita et al., 2007). In addition, limestone dissolution releases both calcium and bicarbonate alkalinity. Concentrations of calcium and alkalinity are consequently elevated in the effluent water (FC7; Table S1) compared to the mine discharge water (FC30; Table S1), which also results in the FC7 water having an elevated conductivity. Across the catchment, Zn exhibits a significant positive correlation with Cd (note the similar strength and direction of eigenvectors in Fig. 3b) suggesting a common source from sphalerite (ZnS – into which Cd is commonly substituted: Schwartz, 2000)

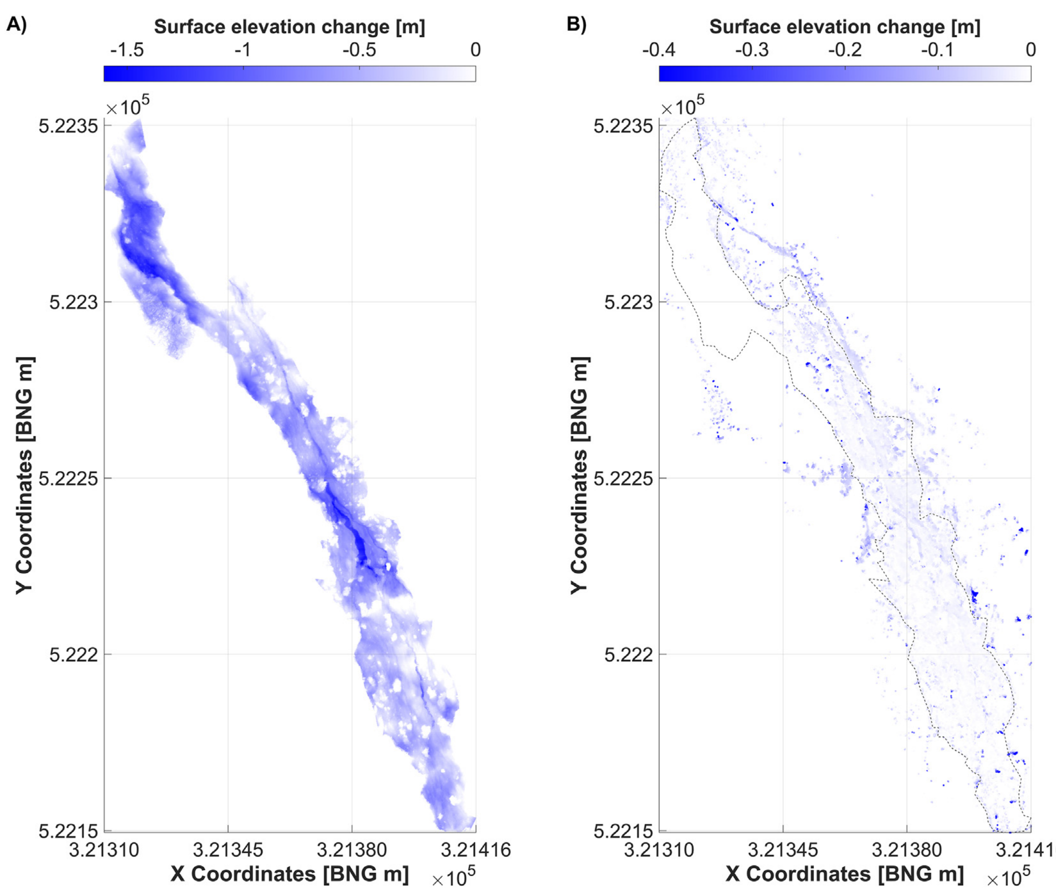

Fig. 2. A) Estimated surface change within the region labelled (A) in Fig. 1 as a result of Storm Desmond (March 2016 survey). B) Estimated surface change of the main hillslope failure in the Coledale valley during the recovery period (March–December 2016) following Storm Desmond. Coordinates are in British National Grid (BNG).

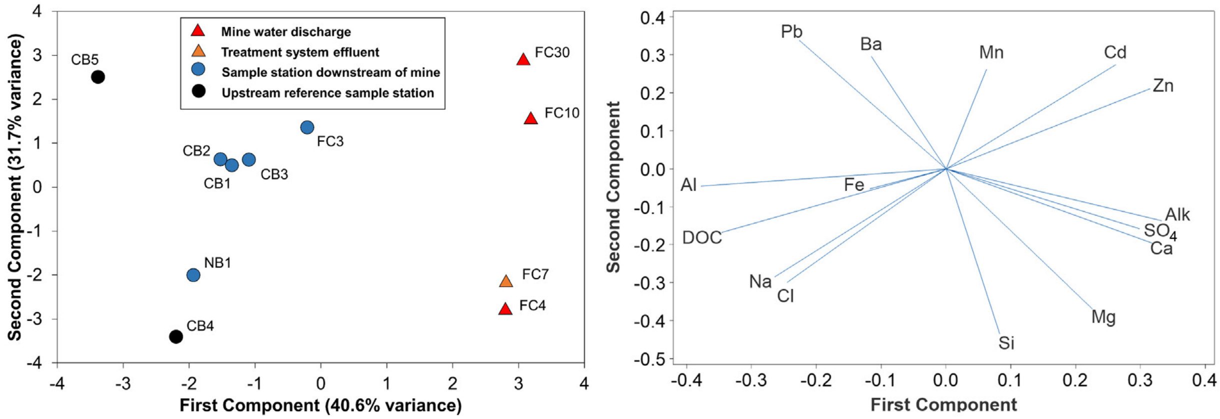

Fig. 3. Principal Component Analysis for major aqueous parameters in Coledale Beck sample stations under baseflow conditions (August 2016, equivalent of Q_{95} event based on flow at CB1). See Fig. 1 for sample locations (CB prefix: Coledale Beck; NB: Newlands Beck; FC: Force Crag mine samples). Left hand plot shows PCA by sample site, with eigenvectors in right hand plot showing key characteristics of sample stations and inter-relationships between variables (DOC: Dissolved Organic Carbon; Alk: Total Alkalinity). Based on scree analysis, there are four significant components accounting for a cumulative variance of 92.2% in the data. The first component maps well with mineral-enrichment in the sites with mine discharges to the right of the plot and surface runoff to the left. The second component relates to level of metal enrichment (high values on *y* axis) and silicon concentrations (low values on *y* axis). Table S4 (Supporting Information) shows loading scores for each variable.

weathering in the mine galleries and spoil. Mn also plots towards Zn and Cd (Fig. 3), which may relate to dissolution of sparingly soluble Mn oxides reportedly present in the upper parts of the mine workings (Young and Cooper, 1988). This would explain the elevated concentrations of Mn in the Level 1 mine water (FC30) compared to upstream reference sites (Table 1). Pb and Ba concentrations are typically low; they show no significant relationship with other mine-related contaminants (Table 2, Fig. 3) and plot towards upstream reference sites (CB5). The latter is consistent with the low solubility of lead minerals at the circum-neutral pH of the mine waters and receiving stream waters (Appelo and Postma, 2004). Interestingly, DOC, Al and Fe appear to be more generally associated with surface runoff (see eigenvectors plotting to the lower left of Fig. 3b and Table S4) than mine discharges, and are a likely indicator of drainage from clay and organic-rich upland soils in the area (Krachler et al., 2010).

The majority of Zn at sample stations throughout the catchment (typically 70–90%) passes through a 0.45 μm filter (Table 1) and would be operationally defined as dissolved (e.g. according to regulatory monitoring criteria: Comber et al., 2008), even though a significant portion of this could be colloidal. Prior to commissioning of the Force Crag treatment system, dissolved Zn was the regulatory priority in the catchment given downstream breaches of environmental quality standards and sensitive ecological receptors (Jarvis et al., 2019).

3.3. Pre- and post-Storm Desmond patterns - mine water treatment

Since commissioning, the overall treatment efficiency of the mine water treatment system has varied between 70 and 99% influent Zn load being removed (Fig. 4). There has been a modest, but significant, decline in efficiency over time since commissioning (Fig. 4; Mann

Table 1
Descriptive statistics showing median and range for trace metals before (in bold; $n = 9$, except $^{a}n = 5$, $^{b}n = 3$, $^{c}n = 7$, $^{d}n = 2$, $^{e}n = 6$) and after (in italics; $n = 12$) Storm Desmond at key sample stations (see Fig. 1 for locations). Median and range used given the skewed nature of the data (see Fig. 4).

Parameter	Fraction	CB4	FC30	FC7	FC3	CB1	NB1
Al (μg/l)	Total	**150 (70–180)**	**66 (50–90)[c]**	**20 (17–80)[a]**	**103 (50–150)[e]**	**70 (50–160)[e]**	**54 (28–140)[e]**
		94 (72–146)	*58 (46–122)*	*19 (12–24)*	*63 (34–132)*	*66 (0.3–610)*	*65 (23–981)*
	Dissolved (<0.45 μm)	**140 (70–173)**	**28 (8–34)**	**16 (12–16)**	**79 (50–130)**	**54 (38–80)**	**28 (21–31)**
		93 (70–138)	*20 (8–46)*	*14 (9–19)*	*55 (27–114)*	*49 (19–99)*	*35 (19–68)*
	Particulate	**3 (0–10)**	**32 (29–41)**	**4 (4–5)**	**19 (10–44)**	**18 (10–80)**	**11 (7–19)**
		4 (0–13)	*41 (25–77)*	*6 (1–9)*	*8 (2–18)*	*51 (8–511)*	*30 (11–913)*
Fe (μg/l)	Total	**10 (7–20)[a]**	**560 (324–650)**	**550 (277–2620)**	**80 (27–320)**	**110 (40–190)**	**60 (33–120)**
		13 (4–22)	*451 (306–615)*	*172 (137–210)*	*39 (27–52)*	*171 (67–495)*	*107 (34–862)*
	Dissolved (<0.45 μm)	**6 (4–20)**	**124 (110–160)**	**480 (244–2460)**	**60 (16–290)**	**70 (29–160)**	**40 (15–60)**
		11 (3–15)	*174 (142–184)*	*120 (76–173)*	*22 (18–31)*	*90 (46–150)*	*51 (21–106)*
	Particulate	**4 (0–14)**	**438 (187–540)**	**70 (33–160)**	**20 (10–30)**	**30 (14–80)**	**18 (5–70)**
		1.3 (0.3–7.3)	*278 (139–450)*	*47 (20–80)*	*17 (8–30)*	*51 (13–382)*	*51 (11–756)*
Mn (μg/l)	Total	**20 (20–30)**	**620 (386–760)**	**350 (239–730)**	**90 (48–160)**	**50 (27–50)**	**15 (10–30)[c]**
		15.9 (14.8–20.4)	*497 (363–690)*	*212 (93–259)*	*48 (34–73)*	*42 (37–57)*	*19 (9–63)*
	Dissolved (<0.45 μm)	**20 (20–30)**	**620 (386–760)**	**350 (228–720)**	**90 (48–160)**	**40 (26–50)**	**14 (10–20)**
		16.0 (14.6–19.5)	*499 (362–694)*	*211 (93–254)*	*48 (33–71)*	*40 (30–57)*	*17 (9–19)*
	Particulate	**<1**	**<1 (<1–6)**	**2 (<1–11)**	**<1 (<1–2)**	**<1 (<1–10)**	**1 (<1–10)**
		0.2 (<0.1–0.9)	*0.5 (<0.1–11.5)*	*1.6 (0.1–5.3)*	*0.4 (<0.1–3.5)*	*2.6 (<0.1–9.8)*	*2.4 (0.2–50)*
Zn (μg/l)	Total	**22 (18–30)**	**3660 (2200–4370)**	**80 (31–140)**	**350 (289–430)**	**132 (100–160)**	**43 (29–50)**
		19 (14–23)	*2882 (2194–3875)*	*174 (137–680)*	*348 (199–456)*	*105 (86–135)*	*37 (26–44)*
	Dissolved (<0.45 μm)	**20 (17–30)**	**3570 (2200–4250)**	**60 (23–100)**	**350 (287–420)**	**132 (100–160)**	**42 (27–50)**
		18 (14–24)	*2874 (2174–3833)*	*144 (97–519)*	*344 (192–448)*	*104 (84–133)*	*36 (20–44)*
	Particulate	**<2**	**60 (0–140)**	**10 (8–40)**	**3 (0–20)**	**<2**	**<2**
		<2	*52 (0–110)*	*51 (17–161)*	*6.2 (0–14)*	*2.3 (1.2–6.0)*	*<2*

Table 2
Output of ANCOVA GLM testing whether there are significant changes in a range of parameters at two sites in the Coledale Beck catchment. FC3 is immediately downstream of the mine in the upper catchment; CB1 is at Braithwaite in the lower catchment downstream of areas of mass movement. Testing before and after Storm Desmond with flow as a co-variate. Bold terms show significant ($P < 0.05$) predictors of water quality parameters, underlined terms are significantly greater than non-underlined for pre- and post-storm monitoring. Degrees of freedom were 19 for all tests.

Parameter	FC3 (downstream mine)	CB1 (Braithwaite)
pH	**Flow: F = 16.5, P = 0.001;** Pre/post: F = 1.6, P = 0.221	**Flow: F = 10.25, P = 0.005;** **Pre/post: F = 12.67, P = 0.002**
Total Zn	**Flow: F = 28.5, P < 0.001**; Pre/post: F 0.36, P = 0.55	Flow: F = 3.24, P = 0.09; **Pre/post: F = 6.63, P = 0.019**
Dissolved Zn	**Flow: F = 23.7, P < 0.001;** Pre/post: F = 0.6, P = 0.445	Flow: F = 3.23, P = 0.09; **Pre/post: F = 7.27, P = 0.014**
Particulate Zn	Flow: F = 3.73, P = 0.069; Pre/post: F = 0.5, P = 0.489	Flow, F = 0.16, P = 0.698; Pre/post: F = 0.14, P = 0.709
Total Fe	**Flow: F = 8.4, P = 0.009**; Pre/post: F = 4.2, P = 0.054	**Flow: F = 25.2, P < 0.001;** Pre/post: F = 3.76; P = 0.073
Dissolved Fe	Flow: F: 1.43, P = 0.247; Pre/post: F 3.63, P = 0.072	**Flow: F = 1.12, P = 0.304**; Pre/post: F 3.32, P = 0.084
Particulate Fe	Flow: F = 2.51, P = 0.130; Pre/post: F = 0.2, P = 0.659	**Flow, F = 27.85, P < 0.001;** Pre/post: F = 3.28, P = 0.092
Total Al	**Flow: F = 85.6, P < 0.001**; **Pre/post: F = 26.10, P < 0.001**	**Flow, F = 18.43, P < 0.001;** **Pre/post: F = 4.86, P = 0.043**
Dissolved Al	**Flow: F = 112.57, P < 0.001;** **Pre/post: F = 21.2, P < 0.001**	**Flow, F = 61.8, P = 0.002;** Pre/post: F = 0.40., P = 0.535
Particulate Al	Flow: F = 2.08, P = 0.115; **Pre/post: F = 6.75; P = 0.018**	**Flow: F = 11.46, P < 0.001;** **Pre/post: F = 5.40; P = 0.033**
Total Mn	**Flow: F = 11.7, P = 0.004** **Pre/post: F = 10.7; P = 0.005**	Flow: F = 0.97, P = 0.34 Pre/post: F = 0.24; P = 0.160
Dissolved Mn	**Flow: F = 11.5, P = 0.004** **Pre/post: F = 10.8; P = 0.005**	Flow: F = 3.8, P = 0.070 Pre/post: F = 0.07; P = 0.730
Particulate Mn	Flow: F = 0.8, P = 0.787 Pre/post: F = 2.9; P = 0.114	**Flow: F = 14.3, P = 0.002** Pre/post: F = 0.72; P = 0.409

Kendall S: −3503; d.f. 103; P < 0.001). Very effective performance during early operation is likely ascribable to a combination of (1) the 'honeymoon effect' of high metal removal in early weeks and months after commissioning (e.g. Younger et al., 2002), associated with good hydraulic performance (i.e. good contact between water and reactive media) and fresh sorption sites on reactive filter media (limestone, organic matter) and, (2) warmer summer weather during early operation favouring higher rates of bacterial sulphate reduction, and therefore metal attenuation.

While there is a significant decline in treatment efficiency over time, there is no sudden break in the curve at the time of the Storm Desmond

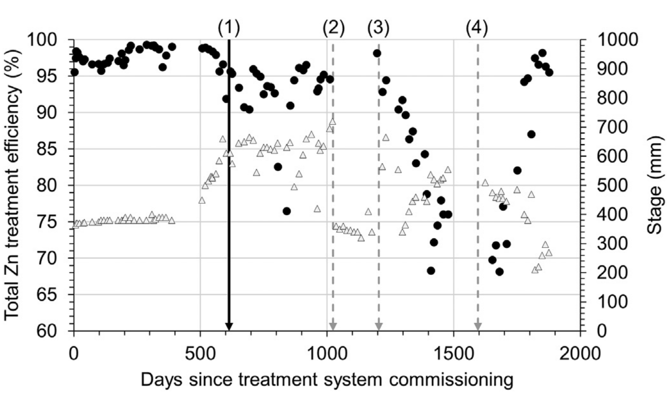

Fig. 4. Trends in mine water treatment efficiency (closed circles) and treatment system water level (open triangles) since commissioning. Vertical arrows indicate timing of: (1) Storm Desmond at Day 613 (5–6 December 2015); (2) treatment system switch off due to rising stage at Day 1024; (3) Clearance of algal mat and treatment system switch on at Day 1204; and (4) turnover of treatment system media, and mixing of woodchip, to increase permeability at Day 1596 (other minor interventions not shown).

flood event (Fig. 4). A slight decrease in performance, and synchronous rise in stage (i.e. water level in the ponds), commenced some three months prior to Storm Desmond, and ultimately resulted in temporary system shutdown after 1024 days of operation, when stage exceeded 700 mm (Fig. 4). During shutdown untreated water had to be discharged directly to the Coledale Beck. There is no evidence that this decrease in performance was due to either bacterially-mediated sulphate reduction ceasing, or to exhaustion of limestone; decreases in sulphate concentration (indicative of sulphate reduction) continued, albeit at lower rates over time (Table S5), and effluent calcium and alkalinity concentrations higher than influent concentrations, throughout the monitoring period, demonstrate ongoing limestone dissolution (Table S5). The simultaneous decline in treatment efficiency and increase in stage in the treatment ponds is, in fact, indicative of a reduction in media permeability and consequent preferential flow at the interface between the media and the plastic liners of the ponds (given influent flow rates have been constant or lowered: Fig. 4). Field observations showed the generation of dense algal mats on the surface of the ponds (notably the northern pond) which appear to have reduced permeability and resulted in hydraulic short-circuiting. After clearance during routine maintenance (Day 1204 following commissioning), field observations showed a near instantaneous drop in stage (Fig. 4). This drop in stage and improvement in performance was temporary though, and ultimately complete turnover of the compost substrate, together with mixing-in of woodchip (on Day 1596), was required to affect a longer-term improvement in hydraulic efficiency (i.e. no hydraulic short-circuiting), and also treatment system performance with respect to metals removal.

Immediately after the Storm Desmond FFIR event, treatment system stage (i.e. water level) did not show any abrupt change, and Zn treatment efficiency remained at 90–95% for over a year following the event. Rising stage and a gradual decline in treatment performance were therefore due to the operational problems described above rather than a result of Storm Desmond. Although no automatic flow monitoring equipment was in place at the time of Storm Desmond, hydraulic controls on influent flows in the treatment system suggest no major flushing of the system from increased mine water flow related to ingress of runoff into mine workings occurred. These hydraulic controls comprise a series of valves on pipes that carry water to the treatment system, which throttle absolute flows, and overflow weirs with a hydraulic capacity far greater than the influent pipes that discharge water to the treatment system. The two treatment units have a combined surface area of approximately 1500 m^2. Nevertheless, an approximation of the additional volume of water flowing through the treatment system due to incident rainfall during the FFIR event suggests that the increase in effluent flow would in fact amount to <0.01 L/s over the period of the event; negligible compared to the design flow-rate of 6 L/s.

Neither is there any evidence of change in influent water quality after the storm event (see Tables 1 and S2). Given extreme high flow events pose documented risks in mining settings for changing subterranean flow paths, generating high contaminant load flushing events and potentially even catastrophic release of ponded subterranean water (Nordstrom, 2009; Mayes and Jarvis, 2016), it is encouraging that the treatment system at Force Crag did not appear to be adversely affected by the extreme event in this case. It may be that the sampling resolution (i.e. fortnightly to monthly) did not capture any short term (hourly to daily timescale) flushing of efflorescent salts that have been observed in other mined catchments (e.g. Caraballo et al., 2016; Cánovas et al., 2018).

3.4. Pre- and post-storm Desmond patterns - catchment dynamics

As the chief contaminant of concern, zinc dynamics were assessed before and after the flood at two key sites in the catchment. The flow-concentration curves (Fig. 5) for total zinc at the sample stations immediately downstream of the mine (FC3) and in the lower catchment (CB1 at Braithwaite) show similar overall patterns of decline in zinc

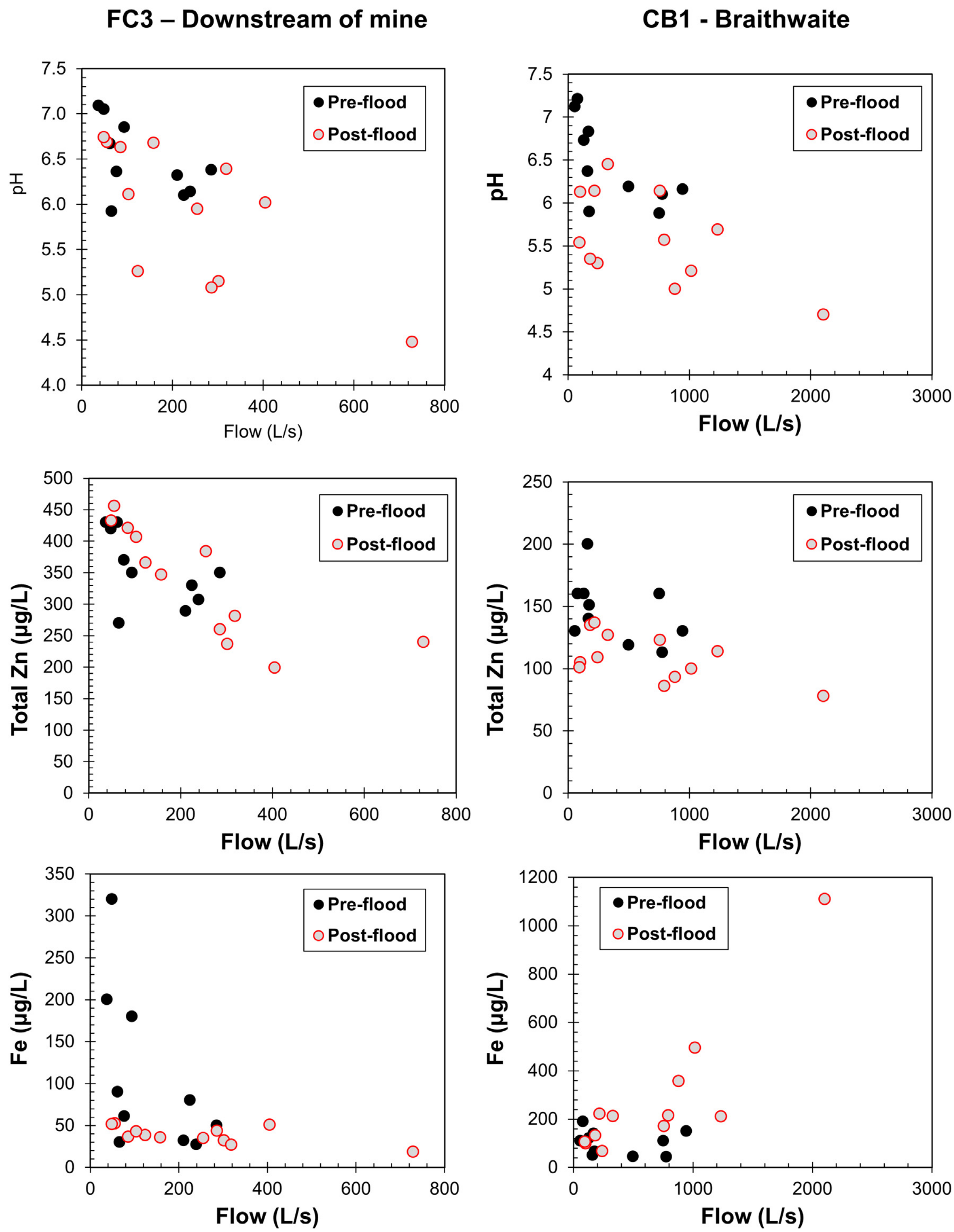

Fig. 5. Flow-concentration curves for selected parameters before and after Storm Desmond immediately below the mine site (FC3) and in the lower Coledale Beck catchment (CB1).

concentration with flow as perennial baseflow sources (circum-neutral pH diffuse and residual discharges from the mine site) are diluted with surface runoff (Jarvis et al., 2019; Table 1). There is no significant ($P > 0.05$) difference in the average zinc concentration at FC3 before and after the flood event (see statistical output in Table 2), although flow (as the co-variate in the model) is a highly significant ($P < 0.001$) predictor of both total and dissolved Zn concentration at the mine site (Table 2), with Zn concentration decreasing with increasing flow. This is a clear signal of perennial baseflow mine discharge sources being diluted by the mineral-poor surface runoff common in mine-impacted catchments (e.g. Gozzard et al., 2011; Byrne et al., 2012; Jones et al., 2013).

There is however a significant decline in average total zinc concentration after the flood event in the lower catchment (CB1) compared with pre-storm values (Table 2; Fig. 5). Samples taken during the year after the major flood event suggest the rate of instream total Zn attenuation between the mine site and lower catchment has increased. The lower Zn concentrations across a range of flow conditions are accompanied by a significant ($P < 0.001$) fall in pH in the lower catchment after the flood event irrespective of flow condition (Table S2; Fig. 5). While flow was a significant predictor of pH as a co-variate ($P < 0.001$) at both sites, there was no corresponding change in pH in the upper catchment (Table S2; Table 2). This shows the importance of surface runoff in lowering instream pH under high flow conditions consistent with mineral-poor, surface runoff from organic-rich, base-poor soils (Gozzard et al., 2011). Such a lowering of pH at the CB1 site in the lower catchment (from a median of 6.2 in pre-storm data to a median of 5.5 post-storm: Table S2) would be anticipated to increase Zn solubility (Appelo and Postma, 2004), so the decline in Zn concentration after the flood is not likely ascribable to pH changes. Total Al shows positive correlations with flow in both the upper and lower catchment (Table 2), while significant increases in total Al after the storm in the lower catchment appear to be driven by increased concentration of particulate Al (Table 2). In the upper catchment, significant declines in Al (total, particulate and dissolved) are apparent after the flood event (Tables 1 and 2). With the exception of Mn, which showed significant decreases in total and dissolved concentration after the event in the upper catchment only, no other variable of interest showed any significant change in pre- and post- average at either the FC3 (upper catchment) or CB1 (lower catchment) sample stations (Table 2; Supporting Information Table S2).

3.5. Metal loadings

Zinc concentrations typically follow a decline in concentration downstream of the mine site under baseflow to moderate flow (Q_{95}-Q_{50}) conditions (Fig. 5). This fall in concentration is accompanied by and modest decline in Zn loading immediately downstream of the mine site associated with instream attenuation mechanisms (e.g. sorption of dissolved zinc onto mineral surfaces / complexation with organic matter), before rising again after the confluence with the Newlands Beck (Fig. 6). Under higher flow conditions (~Q_{15}), total zinc loading increases downstream associated with resuspension of sediment-bound particulate Zn into the water column and/or pH-induced remobilisation of weakly-bound metals because of acid-flushing events (Fig. 7; Jarvis et al., 2019). A comparison of metal load change between the mine site and lower catchment highlights subtle changes in metal input and attenuation before and after the storm event (Fig. 7). The decline in Zn concentration with flow (Fig. 5) is coupled with a relative decline in Zn export from the upper catchment (Fig. 5) after the storm event across a range of flow conditions (Fig. 7). The trends in total Fe load export from the upper catchment suggest that there has been a relative increase in Fe load across a range of mid- to high-flow conditions since the storm event, which may be related to increased delivery of sediments from active landslips.

Using sequential filtration to partition the post-storm loading curves downstream of the mine shows a significant influx of particulate Fe and Al in the mid catchment around the zone of major landslips (Fig. 6). The bulk of the Fe and Al entering the stream in this area (downstream of FC3 and between CB3 and CB2) is in colloidal form (i.e. passes a 0.1 μm filter, but not a 10 kDa filter). The instream loads of Fe and Al remain relatively consistent along Coledale Beck downstream of this point to the confluence with the Newlands Beck. In the larger Newlands Beck catchment, significant increases in Fe and Al load are apparent (also affected by the flood and extensive landslips: Joyce et al., 2018), and significant increases in Al concentration are also evident (Table 2). The longitudinal Zn loading curves through the catchment after the storm event (Fig. 6) show a very different pattern, with clear decline in loading downstream of the mine site to the confluence with the Newlands Beck, where additional Zn input from the adjacent catchment elevates loading (Environment Agency, 2014). The majority of this Zn is in truly dissolved form (i.e. passes a 10 kDa filter; as distinct from operationally dissolved, which passes a 0.45 μm filter) and the decline in instream loading in the Coledale Beck is attributed to Zn being lost from solution.

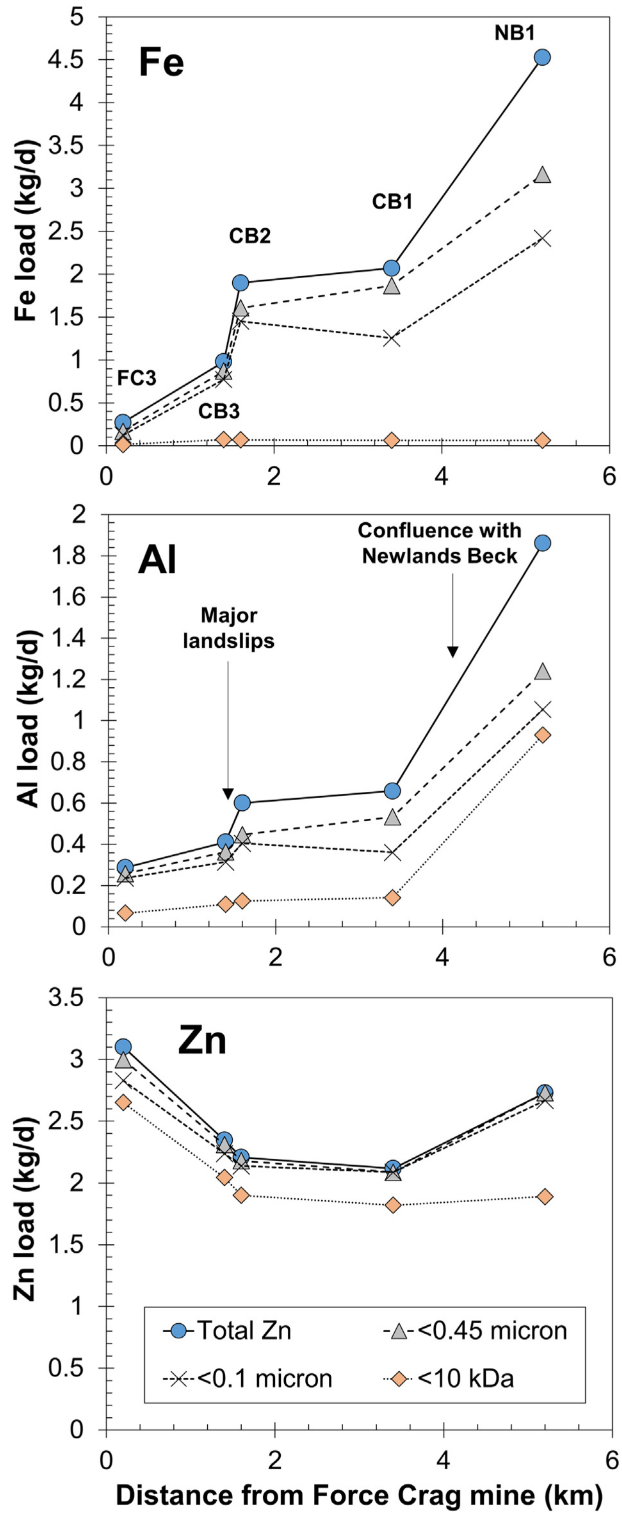

Fig. 6. Downstream loading curves for Fe, Al and Zn under moderate flow conditions after Storm Desmond (717 L/s at NB1 equates to an approximate Q_{50} event).

At the circum-neutral pH of the catchment under ambient conditions, Fe and Al colloids are predicted to be present as oxide/oxyhydroxide phases (Appelo and Postma, 2004); these phases are widely regarded as key sinks and vectors for divalent metals in many environments (Johnson, 1986; Axe and Trivedi, 2002). Fig. 8 clearly reveals the signature and provenance of the dominant particulate Fe sources in the catchment post the December 2015 extreme event, and

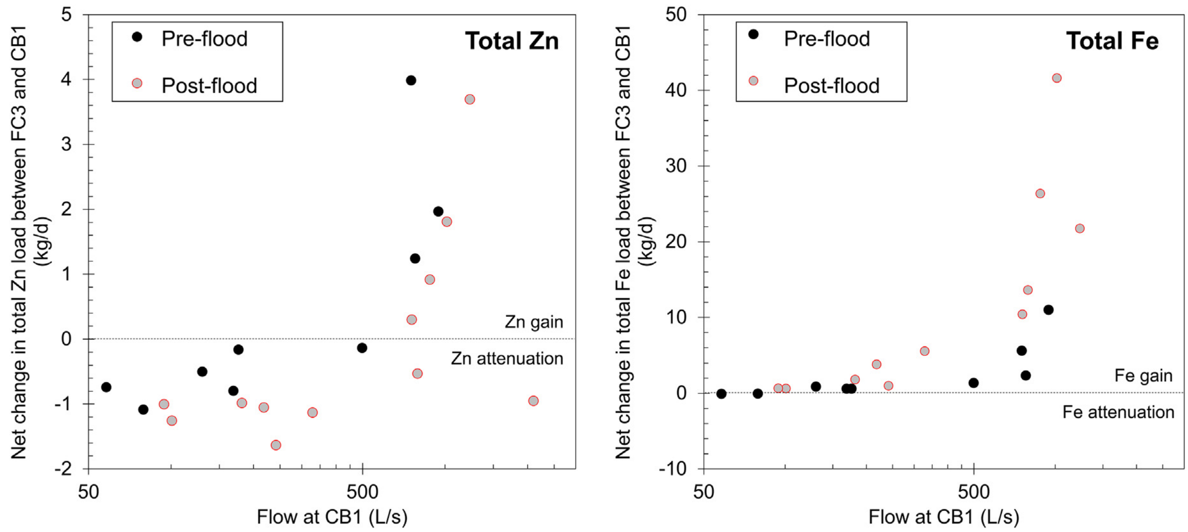

Fig. 7. Net change in total zinc and total iron load (kg/day) between FC3 (downstream of mine site) and CB1 (Coledale Beck at Braithwaite) under different flow conditions. Horizontal line marks zero net change in each plot to highlight periods of metal load gain and loss between the sites. Note: logarithmic *x* axis is solely to aid clarity of data presentation.

two distinct relationships are apparent between particulate Fe and particulate Al across all samples in the catchment since the flood. The low gradient cluster covers mine site discharges and suggests a consistent ratio of particulate Fe:Al of approximately 9:1 evidenced by the significant and strong regression line (ANOVA $F = 192$, d.f. $= 59$; $P < 0.001$). Instream samples cluster on a separate curve (ANOVA $F = 832$, d.f. $= 79$, $P < 0.001$) with a ratio of particulate Fe:Al in the region of 1:1.4, suggesting a different geochemical signature and therefore a different dominant source for instream particulates than those associated with pyrite dissolution around the mine site. Only sparse pre-storm DOC data are available which limits scope for statistical comparisons, however, there is a clear significant positive correlation across the catchment between DOC and Fe throughout post-storm monitoring in 2016 and 2017 (Spearman r_s 0.62, d.f. 64, $P < 0.001$), with correlation indicated by similar eigenvector directions in Fig. 3b. This suggests a common source of Fe, Al and DOC in the system, most likely related to shallow sub-surface

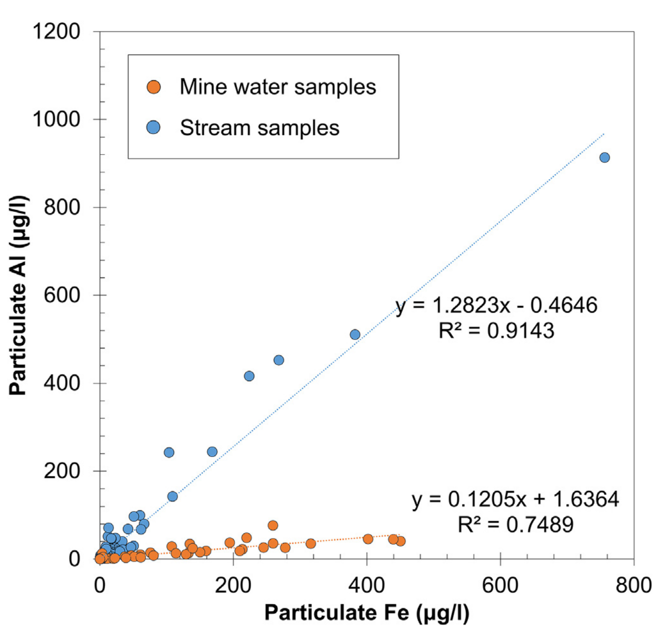

Fig. 8. The relationships between particulate (i.e. >0.45 μm fraction) aluminium and particulate iron in stream samples in Coledale Beck and mine water discharge samples.

flow from the organic-rich peatland soils that cover the catchment (Krachler et al., 2010; Knorr, 2013). The input of fine particulates with a high specific-surface area alongside DOC into the stream, as a result of the 2015 landslips, is therefore seen as a dominant driver behind the Zn attenuation apparent in the catchment.

3.6. Laboratory studies

Laboratory experiments simulated the extent to which contact of stream water (from CB1, the most downstream location monitored on the Coledale Beck) with different materials in the post-storm landscape resulted in release or attenuation of metals. The aim of these experiments was to explore the role of sorption as a mechanism of metal attenuation. As a prelude to this, geochemical modelling using PhreeqC indicated that Coledale Beck water at CB1 was undersaturated with respect to solid Zn phases (smithsonite and zinc hydroxide), and with respect to all other contaminant metal solid phases, under all conditions, both before and after Storm Desmond (saturation indices shown in Table S6). Thus, precipitation reactions were ruled out as a likely mechanism of metal attenuation.

In the laboratory experiments, mixing of sediment from CB2 (stream bed material from Coledale Beck below the main landslips) with stream water from CB1 resulted in negligible change in aqueous Zn concentration (Fig. 9a). In contrast, mixing of CB1 water with mine waste from the vicinity of the mine resulted in a sharp increase in aqueous Zn concentration (up to 1270 μg/L; Fig. 9a). The mine waste is known to have very high Zn concentrations (up to 20,000 mg/kg; Jarvis et al., 2019), and therefore an increase in CB1 Zn concentration when mixed with this waste was anticipated. Stream bed sediment at FC3 has Zn concentration in the order of 500 mg/kg (Jarvis et al., 2019); when mixed with CB1 water aqueous concentration increases, but much less so than for the mine waste. In contrast, mixing fresh sediments exposed by the landslips with CB1 water results in a substantial decrease in CB1 Zn concentration (54–78 μg/L, compared to starting concentration of 131 μg/L; Fig. 9a). Therefore the delivery of fresh highly-organic sediment to the Coledale Beck from the landslips during Storm Desmond is a likely cause of greater in-channel attenuation of Zn along the Beck between the mine site and the confluence with the Newlands Beck, and sorption processes appear to be the main cause of this. Reflecting this, the aqueous Zn concentration was consequently significantly lower (Table 2) at the downstream reaches of the Coledale Beck post the 2015 FFIR event as compared to before.

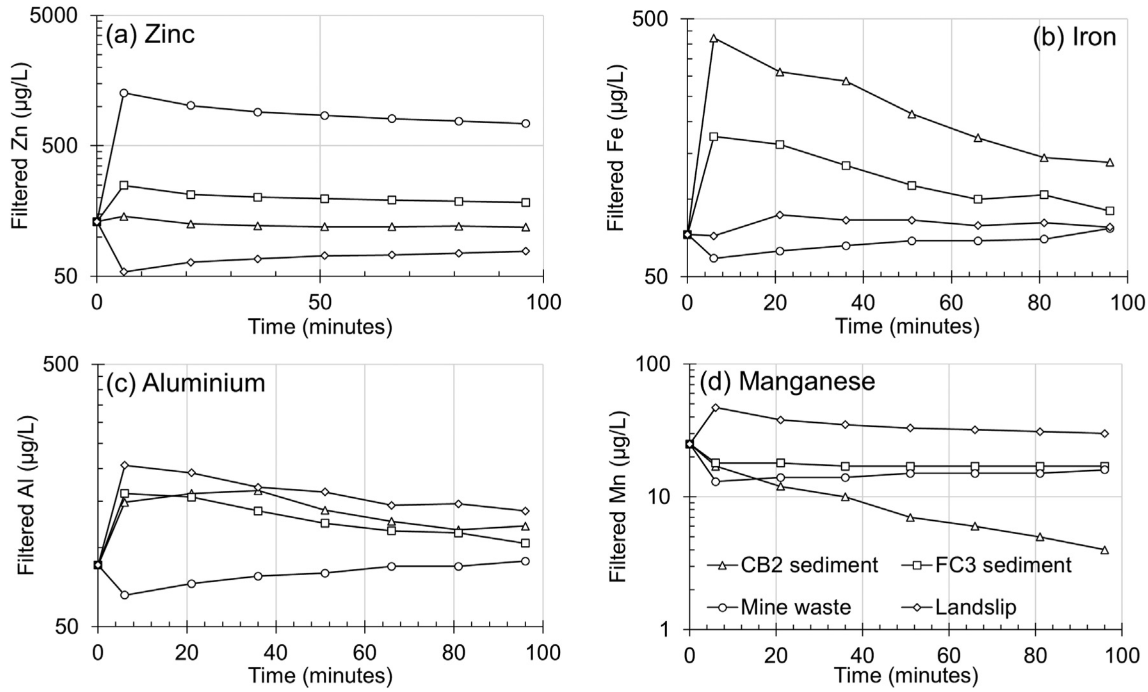

Fig. 9. Change in metal concentration over time of Coledale Beck water mixed with sediments of different provenance from the catchment (Time 0 is the initial metal concentration in the Coledale Beck water, immediately prior to mixing with the sediment).

Previous studies have shown that sorption to/coprecipitation with iron and aluminium oxides/oxhydroxides are key controls on Zn attenuation in mine-impacted catchments (e.g. Hudson-Edwards and Edwards, 2005; Gozzard et al., 2011). The data in Fig. 9 corroborate this; iron, and especially aluminium, are released from the landslip sediment when mixed with CB1 water (Fig. 8b and c), albeit this source of Fe and Al is additive in the sense that the stream sediments at CB2 and FC3 are also sources of these metals. Manganese is also released from the landslip sediment, whereas the stream sediments at CB2 and FC3 are a sink for Mn (Fig. 8d). The net effect of the changes in metal dynamics driven by Storm Desmond was that there was a statistically significant increase in particulate and total Al concentration post-storm event compared to pre-storm, but not in dissolved Al concentrations (Table 2). In addition, there was an increase in post-storm Fe concentration that was not statistically significant, and there was a statistically insignificant decrease in Mn concentration post-storm (Tables 1 and 2).

3.7. Management implications

In the UK and elsewhere, a significant number of upland rivers have been impacted over centennial timescales by mining-related pollution. These impacts are due to a combination of point source discharges and diffuse metal sources associated with waste rock heaps (e.g. Mayes et al., 2009). As such, catchment responses after major flood events and feedbacks due to instream pollutant mechanisms are of relevance to river managers. Overall changes in catchment metal dynamics apparent in the Coledale Beck after the significant perturbation in 2015 are relatively modest, which may in part reflect the effectiveness of management of the mine waters and potential diffuse sources associated with mine spoil (Jarvis et al., 2019). The relative balance of particulate input from contaminated and uncontaminated sources will drive the instream response after major flood events (Foulds et al., 2014). In this case, the visible erosion from waste rock heaps was modest (Fig. S5), while the former tailings area was stabilised as part of mine water remediation (Jarvis et al., 2019). As such, the extensive shallow landslips in the mid and lower catchment (Fig. S2; Fig. 2) constituted the major mode of delivery of fine organic and clay particulates to the system, and these were not accompanied by equivalent delivery of metal-rich sediment from the vicinity of the mine. The more rapid Zn attenuation after the flood created transient metal stores within the channel that are potentially subject to flushing events. Detailed monitoring of such events, particularly when accompanied by pH reductions associated with upland runoff (a common phenomenon in many upland catchments: Jarvis et al., 2019) should be a research priority given the documented ecological effects of analogous acid-flushing events in systems recovering after acid deposition (Ormerod and Durance, 2009). Catchment-scale response is likely to differ on a case-by-case basis; in catchments with less stringent, or absent management of mine discharges, as is often the case in mine-impacted catchments (e.g. Mayes et al., 2009), there may be greater potential for remobilisation of secondary sources of metal pollution.

The fact that the Coledale mine water treatment system itself appeared largely unaffected by such a major perturbation to the catchment is a positive aspect of the study. This highlights the importance not only of sound treatment system engineering, but also of considering point- and non-point sources in remedial planning to ensure that point source remediation is not likely to be compromised by remobilised diffuse metal pollution sources after major flood events (Gozzard et al., 2011; Banks and Palumbo-Roe, 2010; Jarvis et al., 2019).

4. Conclusions

- Despite the severe magnitude of the December 2015 Storm Desmond flood event on the Coledale Beck catchment (a 1 in 200-year event), the medium-term effects of the event on instream contaminant transport appear to be unexpectedly subtle.
- A slight, but significant, fall in Zn concentration in the lower portions of the catchment was apparent which was synchronous with increased export of Fe, and especially Al, in these reaches.
- The signal of Fe input correlates well with Al, DOC and other potential vectors for dissolved metal attenuation in the catchment.
- The fresh influx of uncontaminated hillslope material in the mid-catchment is the likely driver of increased instream zinc attenuation rates through provision of fresh sorption sites and complexation of dissolved Zn.

- While there has been a decrease in mine water treatment system efficiency, the fall is not synchronous with the flood event and suggests other mechanisms and/or feedbacks are driving the pattern observed. Given the strong relationship observed between reduced treatment efficiency and treatment system water level, these mechanisms appear to be influenced by reduced hydraulic efficiency.
- Finally, the study highlights the benefits of long-term monitoring programmes (particularly in post-remedial phases) to yield crucial information on the effects of extreme flood events and their role in metal transport in mine-impacted catchments.

CRediT authorship contribution statement

W.M. Mayes: Conceptualization, Investigation, Formal analysis, Writing - original draft. **M.T. Perks:** Conceptualization, Investigation, Formal analysis, Writing - review & editing. **A.R.G. Large:** Conceptualization, Investigation, Formal analysis, Writing - review & editing. **J.E. Davis:** Investigation. **C.J. Gandy:** Investigation, Formal analysis, Writing - review & editing. **P.A.H. Orme:** Investigation. **A.P. Jarvis:** Conceptualization, Investigation, Formal analysis, Writing - original draft, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data and scripts used for the determination of morphological change along the Coledale Beck can be found at https://zenodo.org/record/3979280#.XzKRvihKj-g and https://github.com/CatchmentSci/ColedaleChangeDetection respectively.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.141693.

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