Sources of diffuse zinc and lead contamination in an abandoned mine watershed

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Abstract

Synoptic monitoring of a mined watershed in north-west England aimed to quantify point and diffuse sources of zinc and lead. The main point source of pollution has Zn and Pb fluxes of 3.0 kg/d and 16 g/d, respectively, but stream Zn and Pb flux measured below the mine site were up to 6.1 kg/d and 300 g/d. Groundwater in riparian zones has very high metal concentrations, and appears to be a key source of diffuse metal flux to the receiving watercourse. The results have implications for point source remediation benefits, and for overall management of metal burden in mining-impacted watersheds.

Keywords: Synoptic monitoring, diffuse, abandoned mine, zinc, lead

Introduction

Synoptic mass balance monitoring is a critical technique to quantify diffuse inputs and their spatial distribution. It has previously been applied to many mining-impacted river catchments to quantify the spatial variation in metal loads (e.g. Jarvis et al. 2019; Onnis et al. 2023; Runkel et al., 2023). The approach entails synchronous water quality and flow monitoring of all point sources in a catchment, together with instream locations upstream and downstream of point sources. Pollutant loads in mining-impacted catchments have been shown to fluctuate considerably with varying hydrological conditions. Whilst the contribution of point sources to the overall instream metal load typically remains relatively constant across all hydrological conditions, the importance of diffuse sources has been shown to increase considerably at higher flows. It is therefore imperative that synoptic mass balance monitoring is undertaken across the full range of hydrological conditions so that the overall importance of diffuse sources of pollution can be determined and the variability of diffuse sources across hydrological conditions quantified.

Such data are crucial to inform remedial interventions at mine sites, but also to evaluate benefits of any such remedial efforts (Jarvis et al., 2019). However, to plan remedial interventions in more detail it is necessary to know the exact provenance of diffuse sources, and the pathway by which they reach sensitive receptors. At the abandoned Force Crag mine, north-west England, monitoring infrastructure has been installed to facilitate this more detailed evaluation of diffuse sources. The infrastructure available includes hydrometric monitoring installations (sharp-crested and flat-V weirs), a suite of piezometers on riparian ground that lies between the main mine site and the receiving watercourse (the Coledale Beck), and a surface water collection system to intercept runoff from waste rock.

Here we report on the findings of an investigation of diffuse pollution issues at the Force Crag mine site, and specifically the relationship between the results of synoptic monitoring in the watershed and water quality in shallow subsurface groundwaters of riparian areas between the mine site and the receiving watercourse. Whilst a previous investigation examined diffuse pollution across the whole of the Coledale Beck catchment (Jarvis et al., 2019), here we present results of more intensive, reach-scale monitoring of diffuse pollution, to enable a more refined understanding of the nature and location of diffuse sources of metals.

Methods

Study site

Force Crag mine lies towards the head of a steep valley (Figure 1) in the Lake District National Park of north-west England (54.5835°N 3.2397°W). The mine worked a mineralised vein in a steeply dipping fault, hosted in slates of the Ordovician Skiddaw Group (Young and Cooper, 1988). Glacial deposits of yellow boulder clay, overlain by peat, predominate in the valley floor, but there are also areas of waste rock, and an area adjacent to the mine that was the site of a tailings pond (now occupied by a passive mine water treatment system; see below).

The vein was accessed via eight levels (adits) at different elevations, the lowest of which was Level 0 (at an elevation of 267 m a.s.l.). Galena, and subsequently barite and sphalerite, were the primary minerals of interest through the 19th and early 20th Centuries, but mining was abandoned entirely in 1991 (Oswald and Pearson, 1999). The abandoned mine site is now owned by the National Trust, given the site's archaeological and geological value as the last working metal mine in this part of England.

The main point source of contaminated mine drainage at the site arises from Level 1, at an elevation some 20 m above Level 0 (which is largely blocked due to a collapse within the workings). The primary metal contaminants of concern are Zn, Cd and Pb. A detailed examination of the water quality and hydrology of the Level 1 discharge, and its variability, is provided by Jarvis et al. (2023). To alleviate pollution in the Coledale Beck, in 2014 a passive mine water treatment system was installed at the site by the UK Coal Authority (as part of the Water & Abandoned Metal Mines Programme, a partnership with the Environment Agency and the UK Department for Environment, Food and Rural Affairs). It treats a portion (up to 6 L/s) of the drainage from Level 1. Other point sources of mine drainage also exist at the site. Apart from Level 0 they emerge not from mine portals but as groundwater upwellings in areas immediately below the main mine site (and their exact provenance remains unclear). In addition, a previous investigation (Jarvis et al, 2019) concluded that diffuse

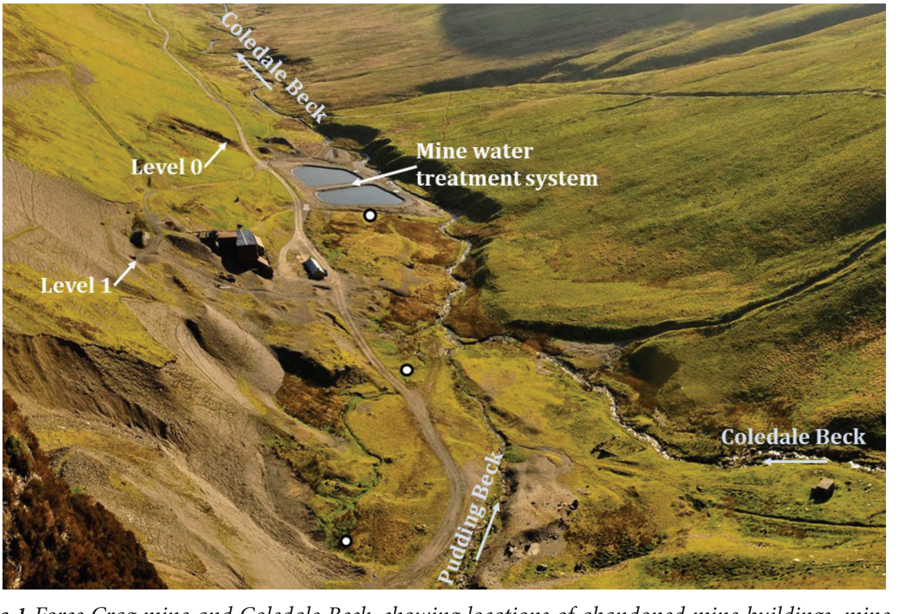

Figure 1 *Force Crag mine and Coledale Beck, showing locations of abandoned mine buildings, mine adits (levels), groundwater upwellings of metal-contaminated water (white circles), and mine water treatment system (Photo reproduced with permission of John Malley)*

pollution contributed to the metal flux of the Coledale Beck, and in fact that diffuse sources of pollution are the majority contributor to metal flux in the stream at high flows.

In late 2020 a suite of piezometers were installed at the Force Crag site, in areas of mine waste and riparian zones adjacent to the mine site (with one, BH16, located the opposite side of the Coledale Beck, as a control; Figure 2). During 2021 and 2022 this enabled synchronous synoptic monitoring of the Coledale Beck and point sources, alongside water level and water quality monitoring of groundwaters across the site.

Sampling and analysis

At each sampling location, field measurements of temperature, pH, oxidation-reduction potential (ORP) and electrical conductivity were taken using a pre-calibrated Myron L 6P Ultrameter. Total alkalinity was determined using a Hach test kit with 0.16 N sulfuric acid and bromcresol green-methyl red indicator powder to a pH 4.5 end-point. Three water samples were collected, for total and filtered (<0.45 μm) cations and filtered anions (<0.45 μm). Samples for cation analysis were acidified with 2% v/v concentrated nitric acid and 1% v/v concentrated hydrochloric acid. All samples were then stored at 4 °C prior to analysis using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES; Agilent Technologies 5800 Series) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Agilent Technologies 7700 Series). Anion concentrations were determined using a Thermo Scientific Dionex Integrion HPIC Ion Chromatograph (IC). QA/QC protocols were followed, including periodic collection and analysis of triplicate samples, use of blanks and standards throughout analysis, and calculation of charge balances to ensure they were within ±10%.

Flow-rate of point sources of mine water drainage were determined using sharp-crested V-notch weirs in all cases. For the Coledale Beck and tributaries, a flat-V weir enabled direct flow measurement at one key location (FC3) on the Coledale Beck. At all other locations salt gulp dilution gauging was used for flow measurement, since in this turbulent upland stream velocity-area measurement is inappropriate. Full details of the salt gauging method used are provided in Jarvis et al. (2019).

Results and Discussion

Figure 2 illustrates the results of intensive synoptic monitoring along a 500 m reach of the Coledale Beck, with the most upstream location above the mine site (FC16 on Figure 2), and the most downstream locations (FC3 and CB0; Figure 2) below the mine site. In addition to in-stream measurement of flow and water quality, all point sources were monitored. On each monitoring campaign all locations were measured on the same day, and during stable hydrological conditions, but campaigns on different days were intentionally under different hydrological conditions. Monitoring took place between April 2021 and February 2022, on eight occasions for surface waters and point sources (and six occasions for groundwaters; see below).

Diffuse metal input within an individual stream reach, between two instream monitoring locations, is defined as the difference between (1) the sum of the upstream metal load plus any point source metal loads within the stream reach and (2) the instream metal load at the downstream monitoring location. The cumulative diffuse metal input to a catchment is the sum of the individual reach-scale diffuse inputs.

Figure 2 illustrates that diffuse inputs of Zn to the Coledale Beck increase with absolute flow-rate over the 500 m study reach. At the lowest flows there is evidence of attenuation of zinc due to in-channel processes (e.g. adsorption; Jarvis et al., 2019), but at higher flows diffuse inputs contribute up to 41% of the Zn load in the Coledale Beck below the mine site. To put this in context, the total diffuse input along the 500 m study reach is up to 2.50 kg/d at the highest Coledale Beck flow reported here (250 L/s), which is approximately the same as the mean Zn load contributed to the Beck by the main point source of pollution in the catchment (2.59 kg/d), the Level 1 discharge (Figure 1). The flow of the Coledale Beck at FC3 can be substantially higher than conditions monitored during this work. Jarvis et al. (2019), for example, monitored at flows of up to 670 L/s at FC3. Under such flow conditions, the diffuse Zn load was concomitantly higher – in excess of 5 kg/d – and therefore under such hydrological conditions diffuse inputs of Zn are higher than point source inputs. Although not discussed in detail here, Pb dynamics in the Coledale Beck watershed were somewhat different. The data collected during this study indicated no diffuse contribution to filtered Pb load at the downstream Coledale Beck location (FC3), other than at the highest flow recorded (250 L/s at FC3). This is in contrast to the conclusions of Jarvis et al. (2019), who did observe an increasing trend of diffuse Pb input to the Beck, and therefore further work is required to clarify Pb dynamics.

Nevertheless, the reach-scale monitoring reported here enables more accurate identification of sources of diffuse metals inputs to the Coledale Beck. Figure 2 illustrates that the upper segment of the reach monitored, from FC16 (above the mine site) to approximately 100 m downstream, receives up to 0.84 kg/d of diffuse Zn. At higher flows there are also substantial diffuse inputs of Zn between 159 m and 257 m downstream of FC16 (Figure 2). Higher resolution identification of zones of diffuse pollution are an important first step in consideration of possible interventions to remediate diffuse pollution in abandoned mine watersheds.

To begin to ascertain the possible role of groundwater inputs as sources of diffuse pollution, samples collected from 15 piezometers across the mine site (Figure 2) were also analysed for Zn and Pb concentration. Filtered Zn and Pb concentrations in these groundwaters are shown in Figure 3(A) and (B), alongside equivalent data for the point sources of mine drainage across the site (Figure 3(C) and (D)). It is apparent that Zn and Pb concentrations are highly variable (over more than two

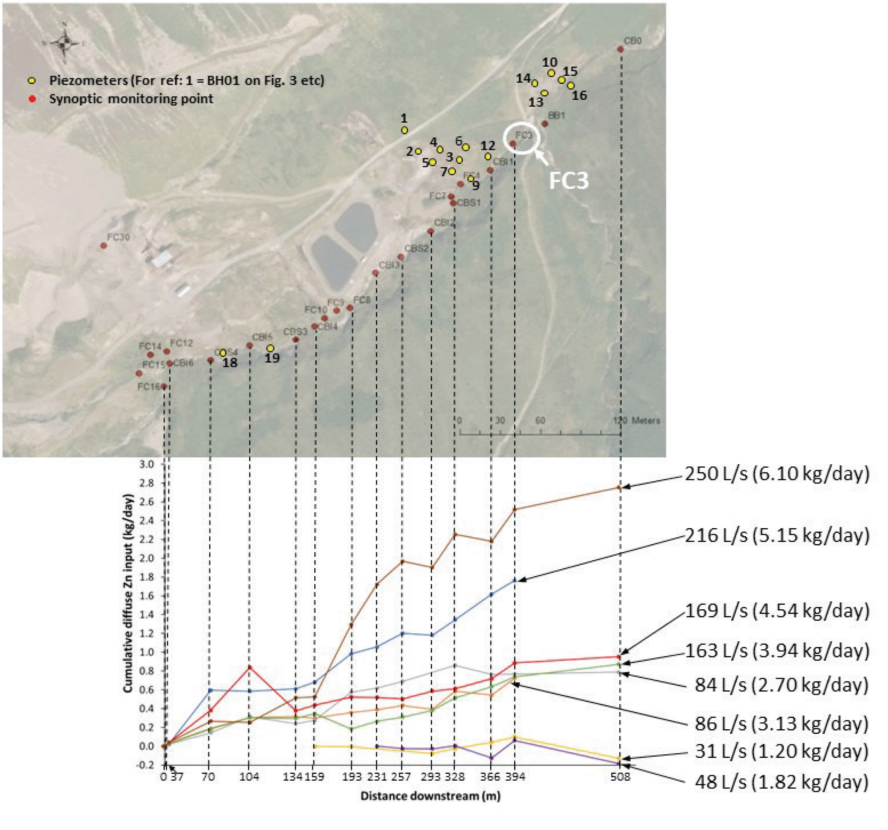

Figure 2 Cumulative diffuse filtered zinc input to the Coledale Beck during reach-scale synoptic mass balance monitoring. Flows are shown for monitoring point FC3 with zinc load at FC3 in brackets (High resolution (25cm) vertical aerial imagery, EDINA Aerial Digimap Service, https://digimap.edina.ac.uk)

orders of magnitude) in the groundwaters, even between piezometers located close to one another. It is also clear that Zn and Pb are substantially higher in many of the groundwaters than in the point source mine water discharges; up to 67 800 µg/L Zn and 3 020 µg/L Pb in groundwaters compared to concentrations of up to 3 700 µg/L Zn and 93 µg/L Pb in point source discharges.

The much higher concentrations of Zn and Pb in the groundwaters may reflect long residence times of water in close interaction with fine grained mine wastes in the subsurface, in contrast to the comparatively short residence time of water draining through the underground mine workings and emerging from mine adits. The variability of Zn and Pb concentrations in the groundwaters, even between piezometers in close proximity to each other (those to the north-east of the treatment system; Figure 2), suggests the presence of discrete bodies of groundwater and / or marked heterogeneity in subsurface lithology and mineralogy. A key issue is the extent to which these contaminated groundwaters are in hydraulic connection with the Coledale Beck, and therefore whether they are responsible for the diffuse source contribution to Zn and Pb loads in the Beck. Water levels in the piezometers respond to rainfall, and there is a correlation between piezometer water level and Coledale Beck flow (unpublished data). In some riparian areas of the Coledale Beck the ground is perennially waterlogged, indicating groundwater levels at surface, and visual observations confirm that water from these areas flows into the Beck in a dispersed manner (i.e. as seepages and trickles). Finally, Jarvis et al. (2019) showed that there was additional flow in the Coledale Beck that could not be accounted for by the sum of all upstream flows i.e. there are additional inflows to the Beck via diffuse pathways. These lines of evidence all suggest that groundwater inputs to the Coledale Beck are contributing to the diffuse metal load in the stream. However, the quantitative role of such groundwater inputs to metal load in the Coledale Beck has yet to be determined.

Conclusions

Synoptic monitoring of a stream impacted by an abandoned Ba-Pb-Zn mine, in an upland location in north-west England, illustrates the importance of diffuse sources of pollution

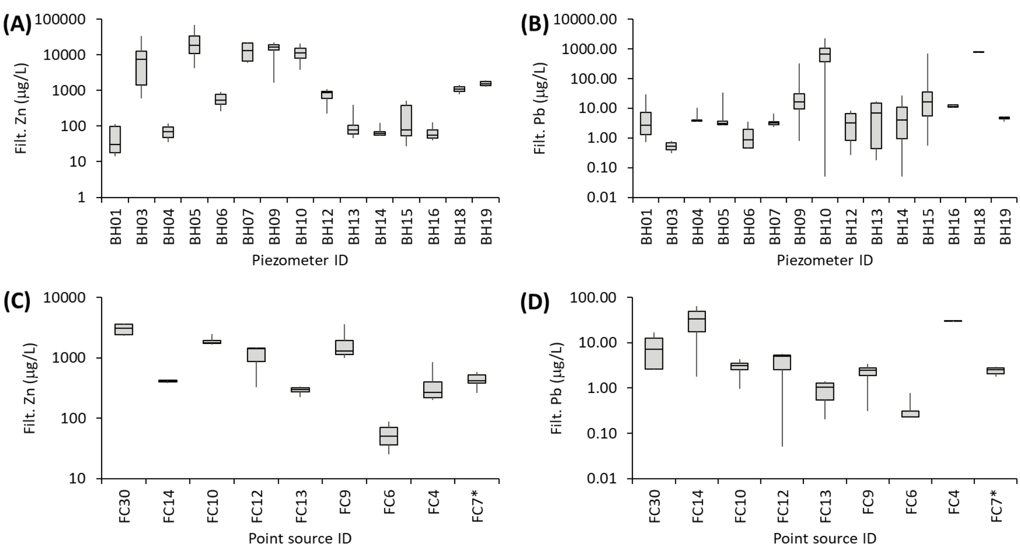

***Figure 3** Box plots of filtered (Filt.) Zn and Pb concentrations at various locations in the Force Crag mine catchment, showing (A) Zn concentrations in groundwaters, (B) Pb concentrations in groundwaters, (C) Zn concentrations of point sources and (D) Pb concentrations of point sources (See Figure 2 for locations; note: BH02 dry on all occasions).*

to absolute metal load in the receiving watercourse, which in turn influences aqueous metal concentrations. Intensive synchronous monitoring of stream flow-rate and metals concentrations (16 stream water locations and nine point sources over a 500 m stream length), across hydrological conditions, reveals specific reaches along which diffuse inputs occur. Groundwaters in riparian areas between the main mine site and the receiving watercourse, the Coledale Beck, collected in parallel to synoptic monitoring of the Beck, have very high concentrations of Zn and Pb (up to 67 800 µg/L Zn and 3 020 µg/L Pb) compared to concentrations up to 3 700 µg/L Zn and 93 µg/L Pb in point source discharges to surface. Although yet to be quantified, these contaminated groundwaters appear to contribute to the diffuse metal burden of the Coledale Beck.

A passive treatment system at the Force Crag mine site successfully removes metals from a portion of the main point source of mine water (the Level 1 discharge). Further improvements in downstream water quality could be achieved by treatment of other point sources of pollution at the site (land availability permitting), but diffuse source mining pollution would remain, and become the limiting factor to any subsequent improvements. Diffuse source pollution is evident at many other abandoned mine catchments across the UK (Jarvis et al., 2019; Onnis et al., 2023).

Design of engineering interventions to remediate such diffuse sources of mining pollution requires detailed information on the location and nature of such sources, in addition to a clear understanding of the likely benefits accruing from treatment (to ensure cost-effectiveness). At Force Crag, the locations of diffuse inputs are more clearly understood, but the quantitative impact of groundwaters to metal loading in the Coledale Beck still needs confirming, as does the exact role of other possible diffuse sources and pathways (e.g. surface runoff from mine waste). The Force Crag site is well equipped with infrastructure (piezometers and hydrometric facilities, in particular) to quantify diffuse sources, and to test new approaches (e.g. geophysics, remote sensing) to identifying and quantifying diffuse mining pollution.

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