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MINING AND THE ENVIRONMENT - UNDERSTANDING PROCESSES, ASSESSING IMPACTS AND DEVELOPING REMEDIATION

Mine water geochemistry and metal flux in a major historic Pb-Zn-F orefield, the Yorkshire Pennines, UK

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Abstract Recent studies have shown up to 6 % of rivers in England and Wales to be impacted by discharges from abandoned metal mines. Despite the large extent of impacts, there are still many areas where mine water impact assessments are limited by data availability. This study provides an overview of water quality, trace element composition and flux arising from one such area; the Yorkshire Pennine Orefield in the UK. Mine drainage waters across the orefield are characterised by Ca–HCO_3–SO_4-type waters, with moderate mineralization (specific electrical conductance: 160–525 $\mu S\ cm^{-1}$) and enrichment of dissolved Zn ($\leq 2003\ \mu g L^{-1}$), Ba ($\leq 971\ \mu g L^{-1}$), Pb ($\leq 183\ \mu g L^{-1}$) and Cd ($\leq 12\ \mu g L^{-1}$). The major ion composition of the waters reflects the Carboniferous gritstone and limestone-dominated country rock, the latter of which is heavily karstified in parts of the orefield, while sulphate and trace element enrichment is a product of the oxidation of galena, sphalerite and barite mineralization. Contaminant flux measurements at discharge sites highlight the disproportionate importance of large drainage levels across the region, which generally discharge into first-order headwater streams. Synoptic metal loading surveys undertaken in the Hebden Beck sub-catchment of the river Wharfe highlight the importance of major drainage levels to instream baseflow contamination, with diffuse sources from identifiable expanses of waste rock becoming increasingly prominent as river flows increase.

Keywords Mine water · Pollution · Zinc · Cadmium · Barium · Strontium · Mass balance · Remediation

Introduction

Mining processes expose sulphide minerals (e.g. pyrite (FeS_2), galena (PbS) and sphalerite (ZnS)), which are weathered in the presence of oxygen and water, to release sulphate and the associated metal ion in solution. The oxidation of pyrite (Eq. 1) creates an acidic environment in the mine (Wolkersdorfer 2008), which can both increase further dissolution of metal-bearing ores and the mobility of trace metals in the water column (Younger et al. 2002). While the terms *acid rock drainage* and *acid mine drainage* prevail in the literature (e.g. Younger et al. 2002; Sarmiento et al. 2009), this is not a true reflection of drainage chemistry in areas with carbonate-rich bedrock. Here, the acidic metal-rich water can be buffered during transit to the surface from dissolution of carbonates (notably limestone and dolomite) (Eq. 2), resulting in metal-rich, circumneutral pH discharge (Nuttall and Younger 2002; Rudall and Jarvis 2012).

$$FeS_{2(s)} + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4{}^{2-} + 2H^+ \qquad (1)$$

$$CaCO_3(s) + H^+ \rightarrow Ca^{2+} + HCO_3{}^- \qquad (2)$$

The impacts of mining and allied metal refining can be traced back millennia in the stratigraphic record (e.g.

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LeBlanc et al. 2000) and have been documented for decades (Rivers Pollution Commission 1874; van Geen et al. 1997; Palumbo-Roe et al. 2009). However, recent legislative drivers in Europe have given fresh impetus to programmes identifying sources of pollution and prioritising them for remediation (Environment Agency 2008). These include the EU Water Framework (2000/06/EC) and Mining Waste (2006/21/EC) Directives, which recognise the negative impacts of historic mining on the water environment and demand efforts to limit such pollution.

The UK has a long history of metal mining dating back to the Bronze Age, with the bulk of industrial-scale operations during the eighteenth, nineteenth and early twentieth century (Dunham and Wilson 1985; Younger et al. 2002). The vast majority of metal mine operations in the UK were abandoned prior to 1999 when a legislative loophole was closed to subsequently make mine operators responsible for any enduring pollution that may arise (Environment Agency 2008). As such, remedial efforts fall on the public purse, demanding well-considered and cost-effective prioritisation and remediation of sources (Defra 2011). Recent reviews have shown that up to 6 % of river catchments in England and Wales are impacted by abandoned mine discharges (Mayes et al. 2009), with many catchments in Cornwall and Devon (Bowen et al. 1998), Wales (Fuge et al. 1991) and the North Pennine Orefield (Younger 1999) shown to have elevated instream metal concentrations (notably Zn and Cd). While such national or regional exercises have provided useful data for identifying the most polluted catchments, there are numerous research challenges that remain to ensure that limited public funds can be effectively directed to maximise the length of streams remediated and deliver a healthier water environment. These include overcoming data disparities between regions, which currently limit the effectiveness of prioritisation methods. Some UK regions have far more detailed site inventories and data availability (in terms of contaminant loadings) than others, reflecting efforts of local agencies or research institutions (e.g. Environment Agency 2002). Prioritisation tools typically rank catchments based on known mine sites and chemical and ecological impacts (e.g. Jarvis and Mayes 2012). Where scale-appropriate data are not available from ambient monitoring records, catchments that are in fact heavily impacted such impact assessment methods will fail to register as high priorities. Similarly, lack of information about the character of pollution sources in terms of geochemical composition, contaminant loading can disguise the real state of impact of specific sites on instream contaminant fluxes. It is clear that accurate characterisation of sources is essential to underpin design of effective remedial tools (e.g. Jarvis and Mayes 2012) and to discern the relative significance of point discharges to diffuse sources (e.g. Mighanetara et al. 2009; Banks and Palumbo-Roe 2010; Gozzard et al. 2011).

This paper provides a multi-scale assessment of mine water and instream geochemistry across a globally important, yet understudied lead–zinc–fluorite orefield which produced in the region of 1 million tonnes of lead concentrates, 140,000 tonnes of fluorite as well as smaller tonnages of sphalerite, barite and witherite (Palumbo-Roe and Colman 2010). A range of approaches from regional mine water quality surveys through to catchment-scale mass balance estimates and analysis of mine waters at source are used to: (1) assess the geochemical nature and extent of pollution from metal mines across the Yorkshire Pennine orefield, (2) highlight key sources of metal flux arising from mine sites and (3) undertake targeted catchment monitoring to identify where remedial planning should be directed. As such, the paper provides a model for regional scale mine water pollutant impact assessments.

Methods

Study site

The Yorkshire Pennine Orefield covers an upland area of central, northern England (Fig. 1). The country rock of the area is of Namurian age (Westphalian to Asbian Stages of the Carboniferous) and encompasses a Caledonian granite intruded into lower Palaeozoic basement rocks, with a cover of Carboniferous rock around 1.5 km deep (Smart and Clayton 1985), dominated by limestones with subordinate sandstone and argillaceous rock; the former of which is heavily karstified in places. The area exhibits extensive fault-controlled mineralisation (Dunham and Wilson 1985), and mineral transport is aided by the chemical reactivity of carbonate rocks in the presence of mineral bearing solutions (Nuttall and Younger 2002). The most important economic mineral of the area is galena (PbS), although large quantities of other primary minerals sphalerite (ZnS), fluorite (CaF_2), barite ($BaSO_4$) and a relatively large amount of witherite ($BaCO_3$—quite rare at international scale) are found across the region. A small area of copper ore (chalcopyrite) is apparent in the north east of the region (Dunham and Wilson 1985). Over a million tonnes of metal ores, predominantly lead with smaller amounts of zinc and copper, have been mined in the area since Roman times (Dunham and Wilson 1985). The areas of mineralization are found in the upper reaches of four main river systems: the Swale, Ure, Nidd and Wharfe. Outliers of galena and barite mineralization are apparent to the south west of the region in the upper Aire (Cononley Pb mine and Raygill barite mine, respectively). All the rivers drain into the Humber Estuary in eastern England (Fig. 1). Land use in the catchments is dominated by upland grazing, with some areas of afforestation (notably in Wharfedale; Hey and Winterbottom 2006) and open moorland with extensive peat deposits.

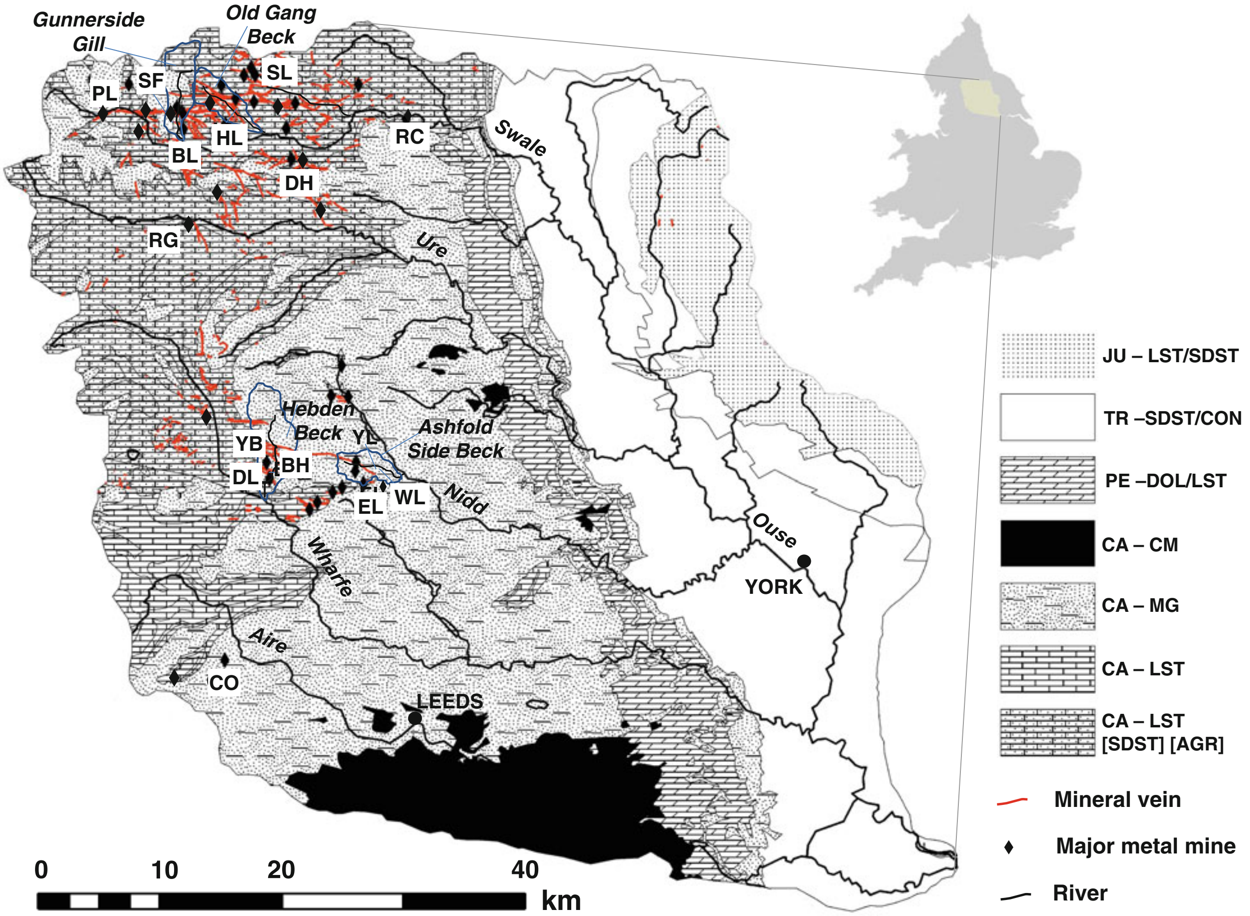


Fig. 1 Geological setting of the Yorkshire Pennine Orefield. Abbreviations for principal bedrock strata: *JU – SDST/LST* Jurassic sandstones, siltstones, mudstones and limestones; *TR – SDST/CON* Triassic sandstones and conglomerates (interbedded); *PE – DOL/LST* Permian dolomite and limestones; *CA – CM* Carboniferous Middle Coal Measures; *CA – MG* Carboniferous Millstone Grit Series (mudstone, siltstone and sandstone); *CA – LST* Carboniferous limestones; *CA – LST* [*SDST*] [*AGR*] Carboniferous limestone with subordinate sandstone and argillaceous rocks. Abbreviations for selected annotated mines referred to in text or figures: *BH* Bolton Haw Level, *BL* Bunton Level, *CO* Cononley Pb Mine, *DH* Devis Hole Level, *DL* Duke's Level, *EL* Eagle Level, *HL* Hard Level, PL Parkes Level, *RC* Richmond Copper Mines (Billybank Level), *RG* Raygill Level, *SF* Sir Francis Level, *SH* Shaw Level, *WL* Wonderful Level, *YB* Yarnbury surface runoff, *YP* Yarnbury Pond, *YL* Yorke Level

Sampling regime

Mine site identification was undertaken through a desk study utilising mineralogical and geological accounts (e.g. Dunham and Wilson 1985), a range of industrial archaeology resources (mine plans and online gazetteers: e.g. Northern Mines Research Group 2012) and Ordnance Survey topographic and British Geological Survey geological maps to identify mines which were potentially discharging metal-rich water into streams in the area.

Synoptic sampling (as per Mayes et al. 2008) was undertaken through synchronous flow and water quality measurements in the Hebden Beck sub-catchment of the Wharfe to identify the contribution of point discharges to instream contaminant flux (see Supporting Information). Flow was also recorded at each site, so flux of trace metals (i.e. the product of concentration and flow) entering the stream could be calculated; for this, a mean section velocity–area method was employed (Shaw et al. 2011). A Valeport 801 electromagnetic flow meter with flat sensor was used and is particularly suited to the nature of the discharges which predominantly arose from engineered mine drainage structures with smooth, shallow flow.

At each sample station, environmental parameters, pH, oxygen reduction potential, dissolved oxygen, conductivity, temperature and alkalinity, were measured in situ. All the variables excluding alkalinity where recorded on a Hanna HI 9828 multiparameter meter, calibrated before each sampling visit. The in-field total alkalinity measurement is by titration following the fixed endpoint method (Hach reference 8203) using 1.6 N H_2SO_4 with bromocresol green–methyl red indicators (to pH4.6). Three water samples were collected in low density polyethylene leak-proof bottles; one unfiltered sample for total cations and two filtered (0.45 μm) samples for dissolved cation and anions. The two cation samples where immediately acidified to preserve metal concentrations. Cation samples were analysed using a Perkin Elmer OES optima 5300DV Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). The ICP-OES was calibrated using standards made on the same day, with concentrations ranging from 0–10 ppm. A blank (2 % UHQ HNO_3 (Romil Spa)) and standard suite were analysed every 10 samples to check whether the calibration was maintained throughout, while Certified Reference Material was used to check instrument accuracy. Detection limits for each wavelength (selected according to USEPA Method 200.7) of every individual element where calculated from the blanks using the relative standard deviation. Anion (F^- and Cl^-) concentrations were determined using a Palintest 8000 photometer. In order to maintain the accuracy of analysis of the concentrations of anions and cations, charge balance testing was employed (Eq. 3).

$$\text{charge balance}(\%) = \left(\frac{\Sigma\text{cation} - \Sigma\text{anion}}{\Sigma\text{cation} + \Sigma\text{anion}}\right) \times 100 \qquad (3)$$

All charge balances fell within the ±10 % limit considered to be acceptable (Appelo and Postma 2005).

Data analysis

Solute data were analysed using the geochemical code PHREEQC v.1.5.10 (Parkhurst and Appelo 1999) with the WATEQ4F database (Ball and Nordstrom 1991) to calculate saturation indices of relevant mineral phases. All statistical analyses were undertaken in Minitab v15. Data were not normally distributed even after log-transformation (Kolmogorov–Smirnov: $p<0.05$) so non-parametric tests were used. Arc GIS® v9.3 was used for spatial analyses which included terrain analysis (as per Mayes et al. 2008) for calculations of drainage area, ore shoot density (total number of mineral veins/catchment area) and stream order (Strahler 1957).

Results and discussion

Major ion chemistry

Discharge waters throughout the area are fairly consistent in terms of major ion geochemistry, and reflect conditions that are indicative of groundwater from a carbonate host rock. Temperatures recorded ranged from 6 to 12 °C, and all had circumneutral pH (6.18–7.96). The pH distribution is typical of many metal mining regions in the UK and particularly those in carbonate-rich country rock (Fig. 2), which include all the Pennine orefield, Halkyn-Minera in North Wales, West Shropshire and Mendip (Mayes et al. 2009). Throughout the Orefield, there is a predominance of $Ca–HCO_3–SO_4$-type waters, although slight differences are apparent between the two main areas of mineralization (Fig. 1). Swaledale discharges typically have a lower total alkalinity and Ca^{2+}, with higher sulphate concentrations than Wharfedale and Nidderdale discharges. Ore-bearing strata differ between these areas, with mineral veins penetrating more recent strata (Grassington Grit of Late Pendleian (Silesian) Age) in the Ashfold Side/Hebden area. This is due to the absence of a thick shale band at the intra-Pendleian unconformity that prevails across the northern part of the region and is thought to have prevented rising mineral fluids penetrating into younger strata in the Swale and Ure catchments (Dunham and Wilson 1985). However, the Namurian country strata do not differ significantly in mineral facies, and the differences are likely to be controlled by the greater ore shoot density in the Swale (3.6 mineral veins/km^2) and Ure (1.7/km^2) compared to the Wharfe and Nidd (1.1 and 0.4/km^2, respectively; Fig. 1) and the subsequent products of sulphide mineral weathering. Other major ions are present in consistently low concentrations (Na^+, 5–25 mg/L; K^+, 0.5–5 mg/L; Cl^-, 7–40 mg/L) with peak concentrations occurring at the Raygill barites mine and Cononley Pb mine, where urban sources (e.g. highways runoff) are likely to be of greater prominence.

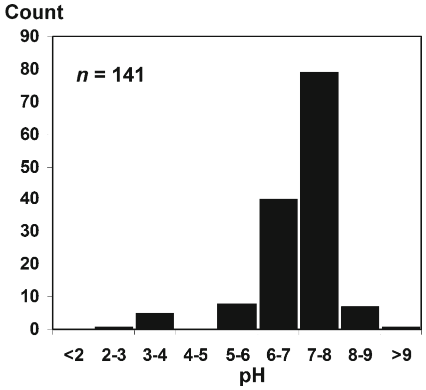


Fig. 2 Frequency distribution of metal mine water pH for discharges across England and Wales (data adapted from Mayes et al. 2010, incorporating data from this study)

Minor elemental composition

The key metal contaminants consistently present in the mine water discharges by dissolved concentration are Zn>Pb>Cd. Only occasionally (Yorke Level, Gillfield and Jackass Level are notable exceptions) is Fe present in elevated concentrations above 500 μg/L at values at which benthic smothering by ferric oxyhydroxides may be anticipated (Younger et al. 2002). While pyrite, marcasite (FeS_2) and to a lesser extent bravoite ($(Fe, Ni, Co)S_2$) are abundantly distributed through the orefield, they are usually in minor amounts in veins and flots (Dunham and Wilson 1985) and in far lesser quantities than adjacent orefields (Dunham 1990) where Fe-rich mine discharges are more common (e.g. Nuttall and Younger 1999). Mn and Fe correlate well (r_s 0.85; $p<0.001$) with peak concentrations occurring in the discharges of Ashfold Side Beck (up to 224 μg/L Mn at Yorke Level). Zn is ubiquitous at modest to high concentrations (up to 2,900 μg/L) at all mine discharges (Table 1). Zn exceeds current Environmental Quality Standards (EQS, 50–75 μg/L) at the hardness encountered in many of the receiving streams (unpublished Environment Agency data 2012). Significant positive correlations are apparent between Zn and Cd, and Pb and SO_4, which are consistent with the weathering products of galena and sphalerite; the latter of which is a common uneconomic mineral in galena deposits. Cd is consistently found as an impurity in sphalerite (up to 1.4 % Cd; Dunham and Wilson 1985), while the very strong correlation between Zn and Cd is also indicative of their similar geochemical mobility in oxidised waters (Langmuir 1997). Cd levels exceed 10 μg/L at discharges in Gunnerside Gill (Sir Francis Level and Bunton Level) and Hebden Beck (Bolton Haw Level; Fig. 3), and is an issue of particular regulatory focus given its status in Europe as a priority hazardous substance (European Commission 2008) which must therefore be phased out to background levels. The annual average EQS for Cd in these rivers is 0.08–0.09 μg/L (hardness-related).

Pb is found in dissolved concentrations up to 70 μg/L, with peak concentrations again occurring at Sir Francis Level in the upper Swale catchment. While galena is the most widely abundant mineral in the orefield, Pb mobility is limited in oxidised mine workings by the formation of surficial secondary minerals such as cerussite ($PbCO_3$) and anglesite ($PbSO_4$) which limits further weathering (Dunham 1990). Furthermore, the low solubility of Pb minerals (Langmuir 1997) means that even when it is released in modest to high concentrations at point of discharge, these do not necessarily translate to high instream concentrations. Environment Agency data show that Pb exceeds the EQS (7.2 μg/L) in several local mining-impacted rivers (unpublished Environment Agency data). Furthermore, concerns have been raised about the extensive legacy of Pb-contaminated floodplain sediments across the study region (e.g. Dennis et al. 2009; Coulthard and Macklin 2003; Hudson-Edwards et al. 1999; Macklin et al. 1997). Recent estimates suggest that 155,000 tonnes of Pb are stored in alluvial sediments in the Swale catchment (Dennis et al. 2009).

Cu is present either in modest or below detectable concentrations (10 μg/L) at the majority of sites (Table 1). While chalcopyrite ($CuFeS_2$) is widely distributed within other sulphides, it is usually present in volumes less than 0.1 % (Dunham and Wilson 1985). At the Billy Bank (near Richmond) discharge which drains the most notable Cu deposit in the region, Cu concentrations are 25 μg/L. Cu is a regulatory concern primarily due to the sensitivity of salmonids to Cu, which can affect olfactory cues at concentrations close to or below Environmental Quality Standards (e.g. Sandahl et al. 2007). However, water quality issues in this area as a result of Cu mine discharges are likely to be minimal given the low point source flux (6.5 g Cu/day), the hardness of the water (which limits bioavailability) and the high dilution capacity of the Swale at the Billy Bank discharge (mean flow of 10.4 m^3/s; CEH, 2012), giving instream concentrations of Cu that well are below EQS and detection limits (<1 μg/L).

The concentrations of Ba in mine discharges are in the range of 140–1,290 μg/L (Table 1). Although direct comparisons are limited by data availability (Ba is not ordinarily measured during ambient monitoring by many environmental regulators), the concentrations of Ba are raised relative to other sites in the UK and further afield (Table 2). $BaSO_4$ appears to control Ba solubility, as evidenced by the supersaturation with respect to $BaSO_4$ at most mine discharges (Table 1) and the significant albeit rather noisy negative correlation between Ba and SO_4^{2-} (Banks et al. 1997). As such, there are unlikely to be any immediate quality issues associated with elevated Ba at the ambient pH and redox conditions of the streams. Similar to Pb, there may be potential for downstream issues of remobilisation from sediments under suitable redox conditions (e.g. Merefield 1976). However, such conditions are likely to be limited to estuarine sediments where the highly reducing conditions required for elevated barite solubility are likely to be encountered, as has been seen in areas contaminated by $BaSO_4$ when deployed for fluid density control in drilling operations (e.g. Carbonell et al. 1999).

Figure 3 shows a strong and significant positive correlation between Sr and Ca which reflects a consistent ratio between the elements in the Carboniferous limestones and Millstone Grit country rock and is likely to be an indicator of the groundwater residence time for the discharges (i.e. subterranean "prior precipitation" of calcite and aragonite; Fairchild et al. 2000). At a small number of sites, particularly in the Hebden Beck and Ashfold Side Beck subcatchments of the upper Nidd, outliers associated with exceptionally high Sr concentrations above 4,000 μg/L are apparent (Fig. 3). This probably reflects areas of barite mineralization into which Sr is found to be substituted into across the region (Dunham and Wilson 1985) and to a lesser extent localised strontianite mineralization in Wharfedale (Dunham and Wilson 1985). Such high strontium contamination are not typically encountered in metal mine discharges (e.g. Davidson et al. 2005) and reflects the unusual geochemical characteristic of the mine waters in the region. There is no correlation between Ca and F although there are notable outliers of F enrichment occurring

Table 1 Major physico-chemical characteristics, major and minor elemental composition and selected saturation indices for spot samples of mine discharges under baseflow condition. Flow in L/s; E.C: electrical conductivity (in microsiemens per square centimetre); Major ions (Ca, Mg, SO_4, HCO_3, F) in milligram per litre; minor elements in microgram per litre

Site	Flow	pH	E.C.	Ca^{2+}	Mg^{2+}	SO_4^{2-}	HCO_3^-	F^-	Fe	Mn	Zn	Cd	Pb	Sr	Ba	Cu	Calcite	Barite	Hematite	$Fe(OH)_{3(a)}$	$Fe_3(OH)_8$
Billybank	0.16	7.9	564	85.8	16.9	55.1	218	0.1	<1	<1	74	3	<1	381	70	25	0.5	0.2	n/a	n/a	n/a
Blackhill Level	5.2	6.18	337	51.7	9.1	12.2	149	0.8	216	18	102	2	<1	84	78	3	0.2	−0.2	18.8	3.1	1.2
Bolton Haw	0.18	8.48	210	51.0	6.4	15.4	161	–	22	53	2,900	16	30	832	203	3	0.76	0.55	16.7	2.1	3.3
Bunton Level	2.0	7.22	243	39.0	3.1	95.1	109	0.6	<1	1	1,285	10	54	718	145	<1	−0.8	0.9	n/a	n/a	n/a
Cock Hill Level	5.2	7.3	514	75.2	6.2	18.4	175	0.9	37	55	135	<1	26	107	350	<1	−0.1	0.5	16.9	2.2	0.0
Cononley Pb mine	4.8	8.02	447	55.8	6.2	35.2	145	0.1	64	35	686	10	18	273	239	3	0.32	0.62	15.8	1.51	2.27
Crackpot	0.01	6.83	200	27.6	2.2	56.8	28	0.1	<1	2	2,914	32	91	242	213	3	−1.9	1.	n/a	n/a	n/a
Devis Hole Level	31.2	7.1	159	24.5	2.5	70.8	90	0.2	240	2	112	<1	28	82	115	1	−1.2	0.7	18.4	3.0	2.9
Duke’s Level	14	6.38	324	53.8	5.4	45.2	200	0.2	3	4	959	6	15	352	220	2	−1.4	0.3	10.4	−1.1	−7.8
Eagle Level	54	7.61	406	51.7	16.4	12.7	191	1.2	89	9	94	2	<1	253	212	<1	0.0	0.1	17.9	2.6	0.5
Gillfield Level	3.4	7.82	439	63.2	5.9	21.0	153	0.5	227	147	63	<1	17	152	239	<1	0.3	0.4	18.8	3.1	1.5
Gunnerside Gill discharge	0.1	6.99	228	35.1	3.6	79.3	95	0.9	18	2	679	6	183	446	971	21	−1.1	1.5	15.9	1.5	−1.6
Hard Level	12.2	7.76	280	43.5	5.2	212.2	147	0.6	12	6	541	3	33	720	372	2	−0.2	1.5	16.4	2.0	−1.6
How Lead Level	2.0	7.3	216	33.0	3.6	51.8	121	0.5	20	3	246	<1	1	105	145	<1	−0.8	0.7	16.5	2.1	−0.4
Jackass Level	0.8	7.2	195	35.5	9.2	20.3	184	0.2	900	175	50	5	73	465	92	2	0.0	0.0	19.4	3.0	2.4
Lanshaw Level	1.5	6.2	358	53.0	9.3	12.2	264	0.1	<1	1	59	2	<1	388	194	<1	−0.5	0.1	13.4	n/a	n/a
Lothersdale	12.2	8.18	525	75.2	5.0	36.1	198	0.4	54	50	75	2	20	445	129	3	0.74	0.27	16.8	1.87	3.14
Parkes Level	5.7	6.5	312	47.4	7.0	65.2	106	0.2	30	19	951	4	29	282	70	3	−1.2	0.4	15.5	1.6	−0.59
Perseverance Level	1.2	7.3	325	48.2	11.5	26.7	147	0.3	470	224	78	3	<1	425	428	<1	−0.4	0.8	19.1	3.2	2.9
Ray Gill Level	37.9	7.8	201	31.8	1.8	31.5	109	0.1	262	7	7	<1	47	148	44	3	−0.2	0.0	18.9	3.0	1.2
Sir Francis Level	12.4	6.75	362	52.4	8.1	104.7	211	0.8	14	3	2,003	12	72	1,807	544	<1	−0.9	1.4	15.1	1.3	−1.6
Spence Level	1.09	7.8	207	33.5	2.7	56.8	106	0.2	28	8	74	<1	4	172	395	2	−0.3	1.1	17.1	2.3	−0.9
Sunken Level	0.08	7.51	147	28.4	1.2	6.9	43	–	15	1	26	<1	<1	89	181	1	−0.87	−0.03	16.3	1.79	−1.86
Victoria Level	0.1	7.96	403	62.2	10.3	185.6	221	0.3	5	4	9	<1	<1	520	125	1	0.3	1.00	15.7	1.6	−3.2
Wonderful Level	0.9	6.64	273	32.0	7.8	28.3	118	0.6	7	56	811	7	<1	1,274	205	<1	−1.5	0.6	1.6	1.3	0.1
Yorke Level	3.2	6.78	439	53.2	11.5	46.5	277	0.8	903	334	281	<1	<1	4,033	619	<1	−0.7	1.1	18.9	3.1	3.7

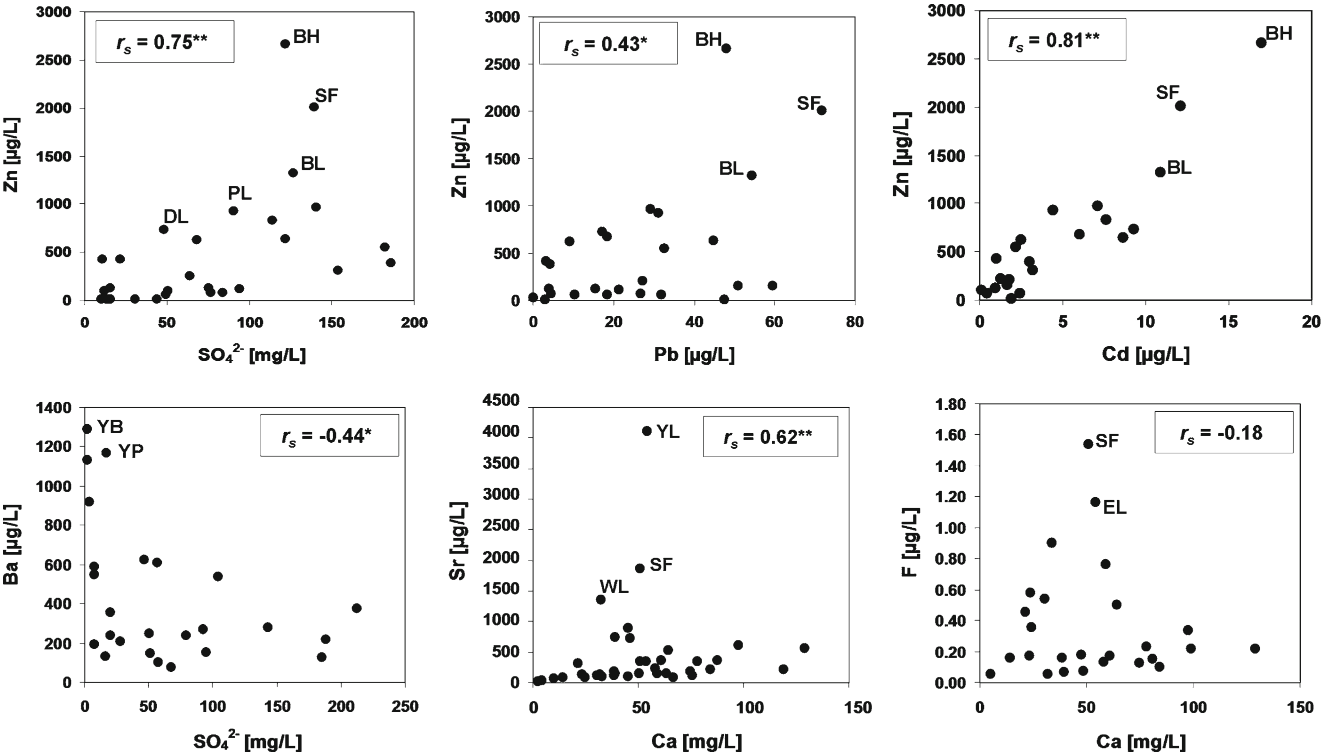


Fig. 3 Relationships between selected common contaminants and major ions in monitored mine water discharges. * denotes correlation significant at $p < 0.05$; ** denotes correlation significant at $p < 0.001$; $n = 28$ for all. (values reported below LOD are included at detection limits in correlations)

in the sub-catchments of Hebden Beck, Ashfold Side Beck and Old Gang Beck. These are areas of notable fluorite deposits and locations where some reworking of legacy lead mining spoil for CaF_2 and $BaSO_4$ took place during the mid to late twentieth century (Dunham and Wilson 1985).

A useful tool for assessing the nature of the weathering products of metal-rich minerals is the molar deficit approach proposed by Younger (1999) and Nuttall and Younger (2002). Dissolution of sulphide minerals should yield molar concentrations of sulphate and associated metals stoichiometrically consistent with weathered minerals (e.g. pyrite, as a bisulphide mineral, would yield 2 mol of sulphate for 1 mol of iron). As such, assessment of molar ratios in discharged mine waters can shed light on mobility of key contaminants within the oxidation zone. By aggregating the molar quantities for all metals predominantly occurring from sulphide ores (in this case Fe, Zn, Pb and Ba, Dunham 1990) and comparing those with the sulphate released (SO_4:Me_{total}), it is apparent that not one of the primary discharges in the region have ratios close to unity (Table 3). Although there are discharges with reasonably low ratios (SO_4:Me_{total} <15 was apparent at Duke's Level, Yorke Level and Sir Francis Level), they still suggest large excess sulphate fluxes leaving the mines. These observations are consistent

Table 2 Barium concentrations in various mining (and related) discharges

Ba (mg/L)	Discharge	Reference
0.04–0.970	Range from Pb-Zn-Ba mines in Yorkshire Dales, UK	This study
0.002–0.039	Bituminous coal mine discharges, Pennsylvania, USA	Cravotta (2008)
0.002–0.035	Zn-Pb mine, Santa Lucia, Cuba	Romero et al. (2010)
0.083–0.316	Pb-Zn-Ba mine discharges in Sunart, Scotland, UK.	Davidson et al. (2005)
0.279 (range, <0.01–23.0)	Close House $BaSO_4$ mine, Upper Teesdale, UK	Environment Agency ambient monitoring data (median of 143 samples 1982–2000)
<200	Coal mine discharges, Silesia, Poland	Pluta (2001)
0.001–0.1	Various coal and Pb mine discharges, Derbyshire, UK	Banks et al. (1997)
0.1–3.5	Natural mineral waters, Central Romania	Tudorache et al. (2010)
0.4–7.8	$BaSO_4$ precipitating spring, Stinking Springs, Utah, USA	Bonny and Jones (2007)

Table 3 Metal deficits in selected metal mine water discharges in the Yorkshire Pennines

Mine	Moles of SO_4^{2-}/ day	Moles of Zn /day	Molar ratio SO_4^{2-}:Me^{2+}	Kg Zn leaving mine per day	% Zn lost from mine per day
Wonderful Level	22.6	1.0	20.8	0.06	4.8
Yorke Level	131.9	1.2	11.8	0.08	8.5
Duke's Level	346.1	30.4	10.1	2.0	9.9
Cockhill Level	85.4	0.9	31.6	0.06	3.2
Eagle Level	616.8	6.7	21.3	0.44	4.7
Devis Hole	663.2	4.6	21.7	0.30	4.6
Sir Francis	389.4	32.8	10.2	2.15	9.8
Bunton Level	57.1	3.4	15.7	0.22	6.4
Hard Level	773.2	8.7	63.5	0.57	1.6
Parkes Level	264.0	5.7	41.6	0.37	2.4

with those of other workers (Younger 1999; Nuttall and Younger 2002) and are usually ascribed to attenuation of metals on/within secondary minerals (Zn-bearing phases in particular) within mine sites, given the more conservative geochemical behaviour of sulphate compared to most divalent metals at ambient pH (Younger 1999). Barite would represent the major feasible sink for sulphate within the mines (Table 1; gypsum and goslarite were well below saturation in all samples with highest values of −1.4 and −6.1, respectively) but this would have a corresponding effect on the SO_4:Me_{total} ratio. The sinks for metals are likely to be more widespread. While geochemical modelling suggests mine discharges are saturated on occasion with only calcite, barite and iron oxide minerals (Table 1), this does not preclude saturation of phases such as hydrozincite and smithsonite (which are mildly undersaturated upon emergence: values −4 to −1.5) within the mine workings. This is consistent with mineralogical accounts of the area which document extensive secondary Zn mineral deposits (notably smithsonite), which were themselves worked in areas to the west of the study region (Dunham and Wilson 1985). Furthermore, secondary Fe minerals (such as hydrous ferric oxides and goethite), present in some of the discharges, are noted in mineralogical surveys of the mines (Dunham and Wilson 1985) and are also known to be an efficacious sink for divalent metals (Dzombak and Morel 1990). Such secondary minerals are clearly important at limiting concentrations at point of discharge with the deficit data suggesting a median of 95.3 % (range, 90.1–98.4 %) of metals being attenuated within the mine workings.

Metal flux

In many mine pollution surveys, the principal focus has traditionally been solely on water quality, and synchronous flow measurements are rarely obtained (e.g. Piramid Consortium 2003; Younger et al. 2002). This limits our ability to compare the significance of mine pollution sources on instream metal fluxes. Consequently, many workers have recommended approaches to mine risk assessment and remediation planning that include routine flux measurements (e.g. Kimball et al. 1999) particularly as part of catchment-scale studies. Flow rates at the discharges had a median of 2.7 L/s (range, 0.1–22 L/s) under baseflow conditions which is within the typical range for many upland metal mine discharges (Mayes et al. 2010). To highlight the significance of individual sources, the cumulative frequency of Zn flux (given the ubiquity of Zn in the discharges) is shown in Fig. 4. The frequency distribution is heavily skewed by a small number of sites that discharge the bulk of the metals to these headwater rivers. Such patterns are typical of other orefields, where large gravity-driven drainage levels are used to dewater overlying mine sites (e.g. Younger et al. 2004; Cidu and Fanfani 2002; Shepley 2007; Gozzard et al. 2011) and are preferential contributors to instream metal flux. In this case, the Sir Francis Level and Duke's Level in particular are prominent. The latter is a major drainage system about 5 km in length that was driven in the eighteenth century to underdrain numerous lead mines in

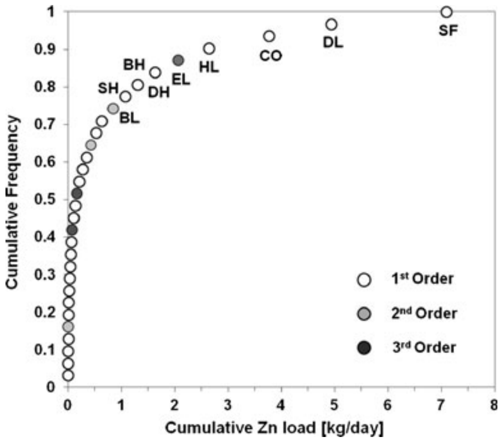


Fig. 4 Cumulative frequency of Zn flux arising from monitored point mine water discharges. Strahler (1957) stream order derived from terrain analysis shown in colour ramp

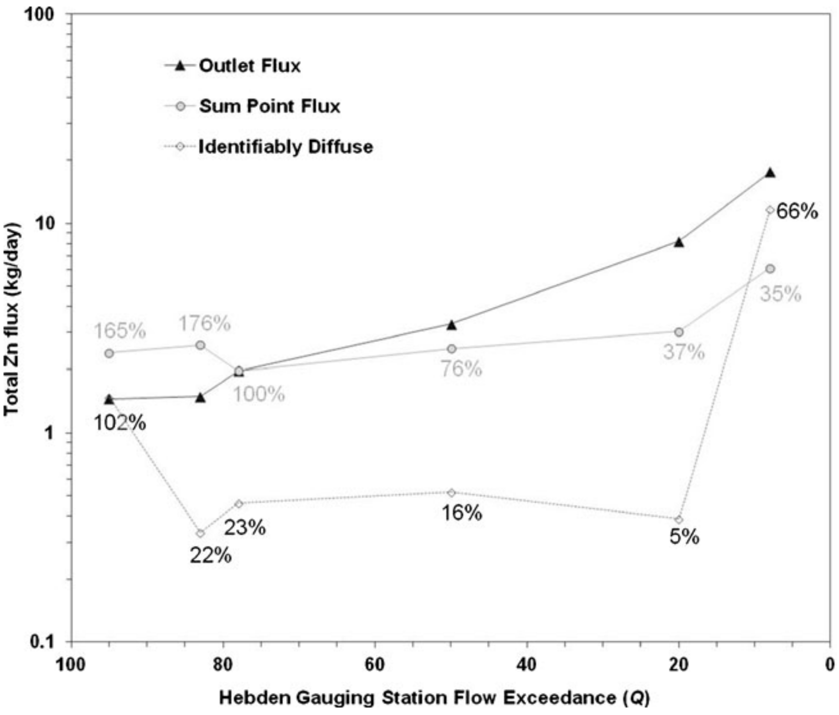
Hebden Beck and on Grassington Moor (Dunham and Wilson 1985).

Although the total flux of metals arising in the Yorkshire Pennine Orefield constitutes less than 4 % of the national metal mine point source pollution burden for Zn (Mayes et al. 2010), the location of the mining area in the headwaters of five major upland streams makes them particularly important. Stream order is presented on Fig. 4 to illustrate the relative size of the receiving streams. The vast majority of mine sites discharge into small first-order headwater streams, where baseflow dilution capacity is minimal. Of the sites with highest flux, only the Eagle Level and the Shaw Water Level discharge into larger second- or third-order streams. Furthermore, all the receiving streams are of excellent hydromorphic quality, with gravel-bed substrates suitable for salmonids while the area drains a National Park and a large expanse of Special Area of Conservation (under the EU Habitats Directive) providing numerous potential stakeholder issues to consider in remedial planning (e.g. Environment Agency 2002). The karstic nature of bedrock geology, particularly in Wharfedale and the Upper Nidd, presents additional issues with many headwater areas being ephemeral during baseflow. This is the case in the upper reaches of Hebden Beck (which is entirely ephemeral) and Old Gang Beck where the river source rises from abandoned mine workings and thus has a greater bearing on instream water quality. The influence of mining on changing the distribution of surface water is an issue that is understudied considering the impact on water quality it can have. However, the significance of mine-induced changes on groundwater flow has been noted in other studies which have demonstrated changes in catchment drainage areas and flow regimes (e.g. Vaht et al. 2011) in addition to spring flow derogation (e.g. Younger et al. 2004).

Synoptic sampling—the Hebden Beck example

Synoptic sampling of metal loads can yield useful information about both the relative importance of mine discharges to instream contamination as well as contaminant mobility. The Hebden Beck sub-catchment was chosen for repeated metal load-based surveys due to its high ambient instream metal concentrations (unpublished Environment Agency data). Description of the physical nature of sample stations is provided in supplementary information along with a schematic of the catchment (Fig. S1 and Table S1). Data from six separate sample days that represent a good range of flow conditions in the catchment are summarised in terms of the point source contribution to instream Zn flux at the catchment outlet under different flow conditions (Fig. 5). Under baseflow conditions, the point source-dissolved Zn flux exceeds that at the catchment outlet (by up to 176 %), with Duke's Level contributing between 87–98 % of the point source contribution. This highlights both the importance of Duke's Level as a source for instream Zn, but also the importance of instream baseflow metal attenuation processes. This attenuation is likely to be exacerbated during summer months by extensive benthic biofilm communities dominated by filamentous algae. Spot samples of digested biofilm from Hebden Beck showed Zn concentrations with a

Fig. 5 Outlet Zn flux with flow condition in Hebden Beck. Data also highlight the flux from point mine water discharges as well as identifiably diffuse sources from sub-catchments with large waste-rock inventories. Annotations show % contribution of point source (*grey*) and identifiably diffuse sources (*black*) as a percentage of outlet flux. Flow exceedance data derived from long-term flow duration curve available at CEH (2012)



median of 1,800 ppm (range, 800–4,100 ppm; n=12) compared to a median of 0.47 ppm (range, 0.08–1.28 ppm; n=12) in the surrounding ambient water, suggesting considerable bioconcentration of dissolved Zn from the water column.

As water flow increases, the absolute Zn flux from point sources rises, reflecting ingress of surface waters into the workings and flushing of metals from the oxidation zone as noted by other workers (Nordstrom 2009). However, the relative contribution of the point sources to the catchment outlet flux diminishes as the importance of diffuse sources increases, but only under flow conditions greater than about Q_{50} (i.e. flow at the outlet that is exceeded 50 % of the time). At the highest flow sampled (Q_8), the contribution of the point discharges to catchment outlet flux is less than 35 % (of which Duke's Level contribution is 96 %), and the contribution from key tributaries draining large expanses of unvegetated waste rock and tailings (termed 'identifiably diffuse') becomes more pronounced. The Coalgrove Beck and Yarnbury sub-catchments were the main sources of Zn under high flow; both of which drain large expanses of fine spoil material which contain up to 1.2 % Zn in Coalgrove (Dunham and Wilson 1985). Such assessments are useful in targeting key sources of instream metal flux. As with all catchments where such exercises have been undertaken, the significance of diffuse sources under high flow is appreciable (e.g. Mighanetara et al. 2009; Banks and Palumbo-Roe 2010; Gozzard et al. 2011).

Conclusions and management considerations

Discharges from abandoned mines across the Yorkshire Pennine region show geochemical features similar to other Pb mining districts with carbonate-rich country rock. Key contaminants in the circumneutral waters are Zn, Cd and Pb. An unusual geochemical characteristic of the waters are consistently high Ba and occasionally high Sr concentrations. The overall metal flux from the mine discharges is reasonably modest compared to other orefields nationally (total of 2.6 tonnes Zn/year). However, since these abandoned mines discharge into small upland headwater streams, their relative influence on instream geochemistry can be more pronounced with many receiving streams in breach of aquatic life standards. The regional scale assessment provided here is useful in highlighting the small number of mine drainage systems that contribute most flux to rivers. Various remedial technologies have been trialled by workers for Fe-poor, circumneutral pH metal mine drainage (e.g. Nuttall and Younger 2000; Piramid Consortium 2003; Mayes et al. 2009), which may be suitable here, although the abandoned nature of the mine workings would necessitate passive approaches being adopted. Catchment-scale assessment in the Hebden Beck highlights that point source discharges are the significant contributors to instream contamination under baseflow condition. The extensive spoil cover in Hebden Beck, however, means that diffuse metal pollution is a major issue, particularly under higher flow, and remains a more challenging management problem than point-source remediation alone.

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