**Article:**

Valencia-Avellan, M, Slack, R, Stockdale, A orcid.org/0000-0002-1603-0103 et al. (1 more author) (2017) Understanding the mobilisation of metal pollution associated with historical mining in a carboniferous upland catchment. Environmental Science: Processes and Impacts, 19 (8). pp. 1061-1074. ISSN 2050-7887

https://doi.org/10.1039/C7EM00171A

# Understanding the mobilisation of metal pollution associated with historical mining in a carboniferous upland catchment

*Published in Environmental Science: Processes & Impacts*
*DOI: 10.1039/c7em00171a*

Magaly Valencia-Avellan[1], Rebecca Slack[2], Anthony Stockdale[3], Robert John George Mortimer[4]

[1]water@leeds, School of Geography, University of Leeds, Leeds LS2 9JZ, UK.
[2] The Royal Horticultural Society, Harlow Carr, Crag Lane, Beckwithshaw, Harrogate, North Yorkshire, HG3 1QB.
[3]School of Earth and Environment, University of Leeds, Leeds LS2 9JZ, UK.
[4]School of Animal, Rural and Environmental Sciences, Nottingham Trent University, Brackenhurst Campus, Southwell, Nottinghamshire, NG25 0QF, UK.

## Abstract

Point and diffuse pollution from metal mining has led to severe environmental damage worldwide. Mine drainage is a significant problem for riverine ecosystems, it is commonly acidic (AMD), but neutral mine drainage (NMD) can also occur. A representative environment for studying metal pollution from NMD is provided by Carboniferous catchments characterised by a circumneutral pH and high concentrations of carbonates, supporting the formation of secondary metal-minerals as potential sinks of metals. The present study focuses on understanding the mobility of metal pollution associated with historical mining in a Carboniferous upland catchment. In the uplands of the UK, river water, sediments and spoil wastes were collected over a period of fourteen months, samples were chemically analysed to identify the main metal sources and their relationships with geological and hydrological factors. Correlation tests and principal component analysis suggest that the underlying limestone bedrock controls pH and weathering reactions. Significant metal concentrations from mining activities were measured for zinc (4.3 mg/l), and lead (0.3 mg/l), attributed to processes such as oxidation of mined ores (e.g. sphalerite, galena) or dissolution of precipitated secondary metal-minerals (e.g. cerussite, smithsonite). Zinc and lead mobility indicated strong dependence on biogeochemistry and hydrological conditions (e.g. pH and flow) at specific locations in the catchment. Annual loads of zinc and lead (2.9 and 0.2 tonnes/year) demonstrate a significant source of both metals to downstream river reaches. Metal pollution results in a large area of catchment having a depleted chemical status with likely effects on the aquatic ecology. This study provides an improved understanding of geological and hydrological processes controlling water chemistry, which is critical to assessing metal sources and mobilization, especially in neutral mine drainage areas.

.

# 1. Introduction

Anthropogenic activities have become an important driver of the global biogeochemical cycling of metals. Present day and historical mining have caused the release of heavy metals into fluvial environments. Globally, pollution from metal mining has led to severe damage to riverine ecosystems in many catchments [1-6]. In the United Kingdom, old mines from the 18th and 19th centuries represent the major diffuse source of metals having an adverse effect on aquatic ecosystems [7-10]. Rivers draining these mining areas are heavily affected by metal pollution as mineral veins present elevated concentrations of lead and zinc ores with variable concentrations of cadmium, barium and fluorine [11].

Water chemistry in surface waters are particularly vulnerable to biogeochemical and hydrological processes which are controlled by seasonality [12-14]. In this context, knowledge about metal mobility in natural water systems is extremely complex [15]. Biogeochemical partitioning of metals results in a diversity of forms. Within the dissolved phase metals are present as hydrated free ions, and associated with organic and inorganic complexes. Within the suspended particulate phase, metals may be complexed with inorganic or organic particles and biota or be present as discrete metal minerals. Adsorption and desorption of metals depend on a number of factors including pH, redox conditions, mineral ore sources and the composition of suspended particulate matter. For this reason, developing an improved understanding of the mechanisms determining the mobility and toxicity of metals within aquatic ecosystems is a key issue, which can in turn support efforts to manage or mitigate pollution [16].

Several countries have developed guidelines to obtain good ecological and chemical status of and ground waters [17]. In the European Union (EU), the implementation of the Water Framework Directive (WFD) obliges member states to assess surface waters through improved catchment scale management (River Basin Management Plans, RBMPs). However, surface water bodies such as headwater streams have been excluded from early RBMPs due to their small size. Studies from Freeman et al.,[18] Dodds and Oakes,[19] and Meyer et al.[20] have shown the importance of these waterbodies as biodiversity richness, migration corridors, origin of stream networks and diffuse source of chemicals. Consequently, sound management is crucial for maintaining ecosystem health in higher order streams that are targeted by the WFD aims.

A serious environmental hazard caused by mining is the generation of acid mine drainage (AMD). Mine drainages, spoil wastes run-off and spoil erosion constantly discharge large amounts of dissolved and particulate metals through AMD, representing a persistent and acute pollution source and reducing water and sediment quality [13, 14, 21]. Studies of mine wastes chemistry have identified two types of mine effluents, acid mine drainage (low pH and high concentration of dissolved sulphate) and circumneutral mine drainage (major ion concentrations reflect the mineralogy of the catchment bedrock) [22, 23]. Thus, mine drainage is dependent on the geologic setting, local water chemistry, kinetic rates, and permeability of ore and gangue minerals [24-28]. Mine drainage flowing through Carboniferous limestone host rock is consequently metal-rich but with a circumneutral pH [13, 14]. Research from Lindsay et al.[29] and Desbarats and Dirom[30] indicates that circumneutral mine drainage might support natural attenuation of some metal-sulphides (e.g. ZnS, PbS) through the precipitation of secondary minerals. Consequently, catchments under these conditions may be more vulnerable to environmental harm due to changes in geochemical or hydrological conditions, producing high pulses of dissolved metal concentrations or long leaching processes in response to decades of chemical weathering [31, 32].

Another long-standing metal pollution problem is physical and chemical mobilisation of metals through the passive dispersal and active transformation of abandoned tailings, spoil heaps, bed sediments and contaminated floodplains. Studies on metal transportation from mine wastes have reported the mobility of metals over long distances as free ions and complexed forms within rivers. In addition, solid phases can be stored within floodplain deposits for decades to millennia [8, 33-37]. In an area of the UK with Carboniferous bedrock, the north Pennines, historical metal mining has directly affected surface and subsurface floodplain soils with heavy metal concentrations above background levels [38]. Specifically, the Yorkshire Ouse basin which drains the Pennine Orefield is estimated to contain 620 million tonnes of lead and 640 million tonnes of zinc stored within its floodplains [3]. Given the large differences in chemistry between acid and circumneutral mine drainage, particularly in the concentrations of protons and of Fe and Al whose solubility is controlled by pH, there will be significant differences in the degree of availability of metal forms that can interact with aquatic organisms. This necessitates dedicated studies of such Carboniferous catchments.

This study aims to understand metal occurrence and mobilisation in a Carboniferous limestone upland catchment impacted by former lead and zinc mining. Comprehensive water monitoring and analysis of sediment and spoil samples are used to describe the effects of historical mining on a whole small river catchment in the northern Pennines region of North Yorkshire, UK. We sought to provide a better understanding of how geochemical processes control the concentration and mobility of dissolved metals in neutral metal-rich drainage. The results have wider implications for management strategies of potential environmental harm in such catchments.

## 2. Site characteristics of Hebden Beck

### *2.1. Lithology and geology*

Hebden Beck is a sub-catchment of the River Wharfe located in the northern Pennines region of the United Kingdom and within the Yorkshire Dales National Park. Hebden Beck rises from Grassington Moor and is joined by multiple tributaries including Coalgrove Beck, Bolton Gill and Loss Gill before the confluence with the Wharfe. It is approximately 12 km long, with the upper reach (6.4 km) of the main channel being the most heavily impacted by historic mine working. It drains an area of 26 km$^2$ and subsequently flows into the River Wharfe which drains the Wharfedale valley. The Wharfe flows into the River Ouse and ultimately reaches the sea at the Humber Estuary which is one of the largest in the UK (24,750 km$^2$). The geology of Hebden Beck is dominated by Millstone Grit sandstone (approx. 20 km$^2$) but crucially also contains bands of Carboniferous limestone (approx. 6 km$^2$) (Figure 1). The catchment cover comprises 46% peatlands, predominantly in the upstream areas, 35% Carboniferous limestone, mainly in the south and 19% glacial sediment, predominantly in the west [39].

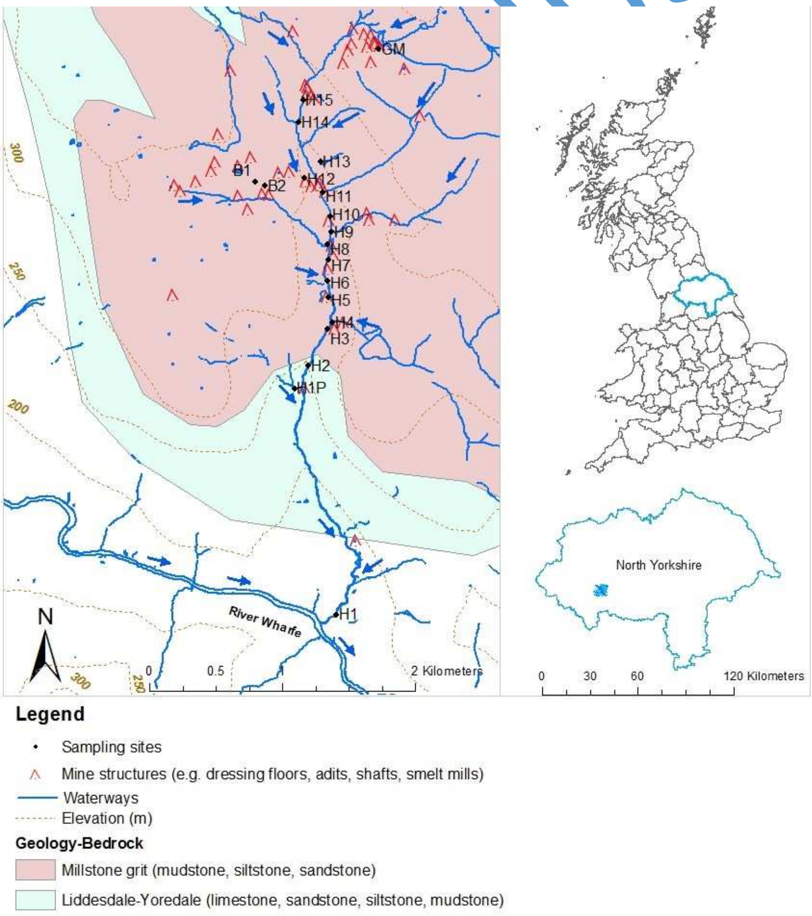

Figure 1. Hebden Beck with sampling sites and mine structures located in the Millstone grit and Liddesdale-Yoredale bedrock. Blue arrows indicate the direction of flow.

### *2.2. Ore processing and mine wastes*

Hebden's orefield comprised coal and lead-zinc mineral deposits, where galena ($PbS$) is the most common mineral, but with associated sphalerite ($ZnS$), chalcopyrite ($CuFeS_2$), barite ($BaSO_4$), fluorite ($CaF_2$) calcite ($CaCO_3$) and witherite ($BaCO_3$) [39]. These minerals occur mostly in vertical veins along fault planes. Early mine workings were open cuts and shafts to extract deeper layers of lead ore. In later years until around 1850, the hushing method was used to scour away the soil using the erosive power of water to expose mineral veins. This method required the construction of dams to control streams, and manmade channels to divert water. Horizontal drainage levels (adits) were driven from the valley bottoms to enable deeper working and easier removal of minerals. Lead ores were crushed, classified and bagged at the dressing floors located at the surface close to the mines, then transported to the smelting mills to be processed. Water power was also applied at the dressing floors and smelt mills, therefore spoil tips or mine wastes are located next to rivers. Approximately, 124 mining features exist in the Hebden Beck catchment area, however main features are 5 lead-zinc mines, 15 adits, 7 spoil tips and 4 smelters. From 1700-1900, 1686.5 tonnes of lead were extracted from these mines [40].

## 3. Methods

### *3.1. Sampling strategy*

Sites were selected from the most impacted area, covering an area of 5 km$^2$ including point and diffuse sources flowing downstream from mine sites. A total of sixteen sites were chosen for water sampling including the main channel, minor and major tributaries, together with a source pool feeding a tributary (Table 1). Eight of these sites (about 3.3 km) were part of a water quality monitoring programme performed by the Environment Agency [39]. The other eleven sites were selected based on their proximity to mine wastes (e.g. tailings, spoils). Monthly sampling campaigns were carried out from November 2013 to December 2014.

Table 1. Sampling sites along Hebden Beck. Table indicates type of sample, site elevation, coordinates, and distance from River Wharfe. Sites are listed from upstream to downstream. Locations adopted from the Environment Agency monitoring programme are indicated with (*).

| Site ID | Site Description | Type of sample | Elev. (m) | Coordinates | | From R. Wharfe (m) |
|---|---|---|---|---|---|---|
| | | | | East | North | |
| **H15** | Head water reservoir (Next-smelt mill) | Water | 368 | 402798 | 466766 | 4970 |
| **GM** | Grassington moor, spoil wastes | Spoil | 380 | 403014 | 466663 | |
| **H14** | Perennial tributary (Coalgrove Beck) | water, sediment | 294 | 402413 | 466106 | 4207 |
| **H13** | Ephemeral tributary | Water | 287 | 402443 | 465931 | 4030 |
| **B1** | Beaver, spoil wastes (from heap) | Spoil | 320 | 402087 | 465660 | |
| **B2** | Beaver, spoil wastes (silt runoff) | Spoil | 317 | 402163 | 465630 | |
| **H12** | Ephemeral tributary (downstream-Yarnbury mine-Beaver spoil) | water, sediment | 285 | 402451 | 465822 | 3921 |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| **H11** | Perennial tributary (Loss Gill Dike) | Water | 278 | 402597 | 465578 | 3637 |
| **H10*** | Main channel | water, sediment | 267 | 402656 | 465324 | 3377 |
| **H9*** | Perennial tributary (Bolton Gill) | Water | 266 | 402661 | 465285 | 3338 |
| **H8*** | Ephemeral tributary (from-Yarnbury mine) | Water | 268 | 402632 | 465176 | 3226 |
| **H7*** | Perennial tributary (Adit) – Bolton Haw | Water | 266 | 402648 | 465164 | 3206 |
| **H6*** | Main channel | Water | 257 | 402630 | 464916 | 2958 |
| **H5*** | Perennial tributary (Duke's adit) | Water | 256 | 402638 | 464793 | 2836 |
| **H4** | Ephemeral tributary (Waterfall) | Water | 254 | 402668 | 464604 | 2645 |
| **H3*** | Perennial tributary (Laneshaw adit) | Water | 246 | 402632 | 464550 | 2580 |
| **H2*** | Main channel at gauging station | Water | 235 | 402488 | 464275 | 2271 |
| **H1P** | Perennial tributary | water | 233 | 402382 | 464104 | 2071 |
| **H1** | Main channel - Confluence R. Wharfe | water, sediment | 152 | 402695 | 462400 | 140 |

## *3.2. Water sampling*

Samples were taken from downstream to upstream (H1 to H15) in order to minimise contamination of other sites by disturbance[41]. At each site, a sample was taken with a pre acid washed (10% $HNO_3$, Nitric acid-Sigma Aldrich 69% and Milli-Q water) 750 ml polypropylene bottle attached to a plastic pole. Four subsamples were then extracted from this bottle. For total metals, unfiltered samples were placed individually into a pre-weighted 50 ml tube (polypropylene) containing 1 ml of preservation solution (10% $HNO_3$) to reach 1% v/v of the final volume and pH ≤ 2 [41, 42]. For dissolved metals analysis, samples filtered through syringe filters (0.45 $\mu$m, polyethersulfone-hydrophillic, Sartorius) were placed individually into a pre-weighted 50 ml tube (polypropylene). Then preservation solution (10% $HNO_3$) was added as used for total metals. For quantifying major anions, the sample was filtered (Sartorius syringe filters 0.45 $\mu$m, polyethersulfone-hidrophillic) and placed into polypropylene tubes. For inorganic and organic carbon analysis the samples were passed through syringe filters (0.45 $\mu$m, nylon-polypropylene, Avonchem) and placed into polypropylene tubes. All samples were kept in a cool box during sampling and transported the same day to the laboratory for storage. Samples for major anions analysis were stored frozen at -20°C, while samples for all other analyses were refrigerated at 4°C.

A carbon Analyser (Analytik Jena Multi N/C2100) was used for measuring carbon compounds (dissolved inorganic carbon-DIC and dissolved organic carbon-DOC), Ion Chromatographer for major cations (Ca, Mg) and anions ($Cl^-$, $NO_3^-$, $SO_4^{2-}$) (Dionex ICS-3000), and SEAL Analytical AA3 was used for orthophosphate quantification. For metal analysis, nine elements were measured (Pb, Ba, Cd, Sr, Zn, Cu, Fe, Mn, Al), using inductively coupled plasma mass spectrometry (ICP-MS; Thermo Fisher iCAPQc) with specific limits of detection (Pb: 0.0001 $\mu$g/l, Ba: 0.06 $\mu$g/l, Cd: 0.0001 $\mu$g/l, Sr: 0.08 $\mu$g/l, Zn: 67 $\mu$g/l, Cu: 0.05 $\mu$g/l, Fe: 0.11 $\mu$g/l, Mn: 0.04 $\mu$g/l, Al: 0.16 $\mu$g/l). Field blanks (n= 3) and replicates (n= 3) were collected at each sampling campaign.

### 3.3. Sediment and spoil sampling

Most sites were dominated by large rocks and coarse sediment. Sediment samples were collected during a single campaign at specific sites (H14, H12, H10 and H1) to assess the evolution of mineral composition. Plastic scoops were used for their collection by wading along a cross-section of the stream. Sediments were sieved through a <250 um stainless steel mesh and transferred into 50ml polypropylene tubes. Spoil sampling was carried out at single spoil heaps at Grassington Moor (GM) and the Beaver spoil area (B1), in addition a further sample was collected at the Beaver spoil area that represented material that had been subjected to movement and size sorting by the actions of rainfall events (B2).

In the laboratory, sediment samples were centrifuged at 3200 rpm for 10 mins to allow removal of the supernatant. The supernatant was decanted and the resulting slurries were placed in a petri dish to air dry. After drying, sediments were placed into zip log bags for disaggregation. Spoil samples (B1, B2, and GM) were dried to calculate percentage water composition. The surface area was also measured to estimate the mineral area available for dissolution reactions. This was performed using the Brunauer, Emmett and Teller method (BET; Micromeritics Gemini VII 2390a) on 2 g of sample dried overnight under $N_2$ gas at 75 °C. In addition, both sediment and spoil samples were analysed by X-ray Diffraction (XRD, Bruker D8-Discover instrument) for determining mineralogy of the major constituents and X-ray Fluorescence (XRF, Innovex X-5000) for chemical composition. The minimum mineral fractions required for detection on this instrument is 2-3%. The standard reference material STSD-3 (stream sediment) was used as XRF quality control.

### 3.4. In situ measurements

Pre-calibrated multiple sensor probes (Model HQ30d flexi 1032) were used in the field to measure pH, dissolved oxygen (DO: mg/l) and conductivity (EC: $\mu$S/cm). Flow rate ($m^3$/s) was calculated from in situ flow velocity measurements (m/s) (flow meter: Global 800-876) together with data from river depth (m) and width (m). Flow data from the UK Environment Agency gauging station (H2) was also obtained from their continuous monitoring records. This flow data together with metal concentrations were used for the calculation of annual metal loading and comparison with Environmental quality standards (EQS) for freshwater in the UK [39].

### 3.5. Data analysis

Geochemical modelling

The PHREEQC code (version 3)[43, 44] was used for modelling main geochemical reactions occurring in aqueous solutions. This software allows the prediction of mineral precipitation that potentially controls the composition of the aqueous phase. Equilibrium reactions and thermodynamic constants were retrieved from the built-in WATEQ4F database [45-47]. Mineral saturation indices and metal free ion activities for hydroxide, carbonate and sulphate minerals were calculated for the pH range 3.5-9 and based on mean values across our field sites and all sampling dates: temperature 10 °C, $SO_4^{2-}$ (x̄: 13592 μg/l) and $Cl^-$ (x̄: 7730 μg/l). With calculations for carbonate minerals the $pCO_2$ was fixed at three times the atmospheric concentration (0.0012 atm), consistent with typical supersaturation of this gas in streams. These model predictions are compared with metal free ion activities calculated for each sampling site and date to investigate the controlling mineral phases.

### Principal Component Analysis

Principal component analysis (PCA) was conducted to identify the main factors influencing metal distribution. Linear correlation analysis was applied to evaluate the relationships among the studied metals, other compounds and in situ parameters. Results of Pearson and Spearman tests showed no significant difference between them. As such, we report the Pearson correlation, as this test is more sensitive for the identification of outliers. Both test were performed using Rstudio (version 3.1.0).

## 4. Results

### *4.1. Characterising metal pollution in the catchment*

In water samples, metal concentrations occurred in the following order for total: Zn>Fe>Sr>Ba>Pb>Al>Mn>Cd>Cu and dissolved forms: Zn>Fe>Sr>Ba>Al>Pb>Mn>Cd>Cu (Table 1-SI). Two metals, Zn and Pb were chosen as the focus for this study based on their significant concentrations derived from mining activities (Table 2). Annual pH averages reflected the considerable contribution of the underlying limestone bedrock showing a dominant circumneutral pH (mean= 6.8) in 80% of the studied sites. Some sites (e.g. H4 and H13) represent moorland runoff with little interaction with underlying rock, thus pH is lower (<6.3) due to high DOC and no carbonate buffering.

Table 2. Mean, maxima and minima from water chemical analysis. Metal forms are denoted as total (T) and dissolved (D). Description of sites are indicated as main channel (MC), ephemeral tributaries (ET) and perennial tributaries (PT). Units are in μg/l. Values below the detection limit are represented by (b/d).

| Site | Description | | $Pb_T$ | $Pb_D$ | $Zn_T$ | $Zn_D$ |
|---|---|---|---|---|---|---|
| H15 | Reservoir | Ave | 316.7 | 279.6 | 2058.8 | 2028.0 |
| | | Max | 411.9 | 423.6 | 2542.4 | 2759.5 |
| | | Min | 96.3 | 103.6 | 722.4 | 1080.7 |
| H14 | PT | Ave | 178.3 | 157.6 | 1318.6 | 1397.9 |
| | | Max | 292.3 | 375.5 | 1778.9 | 2193.1 |
| | | Min | 106.9 | 75.7 | 864.7 | 900.3 |
| H13 | ET | Ave | 227.1 | 205.9 | 260.4 | 207.4 |
| | | Max | 331.3 | 283.4 | 1619.8 | 1435.5 |
| | | Min | 141.2 | 138.0 | b/d | b/d |
| H12 | ET | Ave | 686.4 | 284.2 | 5168.8 | 4252.3 |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  |  | Max | 2701.2 | 439.9 | 12619.3 | 7438.4 |
|  |  | Min | 261.8 | 184.1 | 66.5 | 73.6 |
| H11 | PT | Ave | 64.0 | 31.6 | 295.7 | 410.5 |
|  |  | Max | 765.6 | 355.2 | 3493.9 | 5276.2 |
|  |  | Min | 3.7 | b/d | b/d | b/d |
| H10 | MC | Ave | 108.1 | 80.7 | 468.8 | 444.4 |
|  |  | Max | 268.1 | 145.2 | 787.4 | 777.0 |
|  |  | Min | 11.8 | 3.1 | b/d | b/d 33.5 |
| H9 | PT | Ave | 28.5 | 20.8 | 125.2 | 95.7 |
|  |  | Max | 171.9 | 94.3 | 572.2 | 518.6 |
|  |  | Min | 12.7 | 2.0 | b/d | b/d |
| H8 | ET | Ave | 38.1 | 19.0 | 318.5 | 269.0 |
|  |  | Max | 123.5 | 28.2 | 438.3 | 435.2 |
|  |  | Min | 12.2 | 5.3 | b/d | b/d |
| H7 | PT | Ave | 7.7 | 4.3 | 3440.2 | 3220.5 |
|  |  | Max | 21.1 | 47.7 | 5425.8 | 4312.3 |
|  |  | Min | 0.8 | b/d | 2062.0 | 1936.7 |
| H6 | MC | Ave | 60.4 | 49.4 | 537.6 | 510.2 |
|  |  | Max | 102.0 | 85.6 | 664.1 | 674.1 |
|  |  | Min | 20.5 | 13.8 | 468.3 | 390.2 |
| H5 | PT | Ave | 60.4 | 54.3 | 883.5 | 867.2 |
|  |  | Max | 132.3 | 157.8 | 1216.5 | 1206.0 |
|  |  | Min | 17.1 | 10.0 | 688.0 | 613.5 |
| H4 | ET | Ave | 8.3 | 4.4 | b/d | b/d |
|  |  | Max | 26.7 | 6.6 | 68.6 | 68.6 |
|  |  | Min | 3.2 | b/d | b/d | b/d |
| H3 | PT | Ave | 2.8 | 0.2 | b/d | b/d |
|  |  | Max | 10.6 | 0.7 | 98.6 | 84.7 |
|  |  | Min | 0.05 | b/d | b/d | b/d |
| H2 | MC | Ave | 46.7 | 39.4 | 515.0 | 485.9 |
|  |  | Max | 93.5 | 87.4 | 765.4 | 606.9 |
|  |  | Min | 17.0 | 4.2 | 194.5 | 360.5 |
| H1P | PT | Ave | 3.0 | 1.9 | b/d | b/d |
|  |  | Max | 5.2 | 8.3 | 68.6 | 68.5 |
|  |  | Min | 0.8 | b/d | b/d | b/d |
| H1 | MC | Ave | 31.1 | 16.6 | 217.5 | 158.9 |
|  |  | Max | 146.8 | 43.7 | 375.9 | 302.9 |
|  |  | Min | 5.1 | b/d | 77.9 | 67.8 |

Across the catchment, $Zn_D$ was the most abundant pollutant with concentrations ranging from 95.7 to 3220.5 μg/l in perennial tributaries. Ephemeral tributaries also showed high concentrations up to 4252.3 μg/l while sites along the main channel had $Zn_D$ concentrations from 158.9 to 510.2 μg/l. The second toxic pollutant of concern was $Pb_D$, where main contributions were observed in ephemeral tributaries with ranges from 4.4 to 284.2 μg/l, and perennial tributaries ranged from 1.9 to 157.6 μg/l. The main river channel showed concentrations of Pb from 16.6 to 80.7 μg/l. Major cations were dominated by calcium, with concentrations from 2.6-54.9 mg/l, and major anions comprised sulphate (3-24.9 mg/l), nitrate (1-17.8 mg/l), phosphate (0.002 to 0.1 mg/l) and chloride (7.2-10.5 mg/l). Dissolved inorganic carbon concentrations ranged from 0.9 to 42.7 mg/l and dissolved organic carbon from 1.2 to 16.8 mg/l (Table 2-SI). Field blanks measurements shown concentrations below limit for all the elements and replicates a standard deviation of ≤ ±0.5 μg/l (Cd and Cu), ≤ ±3.6 μg/l (Mn and Sr), ≤ ±12 μg/l (Pb, Al, Ba).

From mineralogical analysis of spoil and sediment samples, the most abundant minerals were quartz ($SiO_2$) and fluorite ($CaF_2$). Spoil samples (B1, B2 and GM) included barite ($BaSO_4$) as an additional dominant mineral. Other secondary minerals like muscovite ($KAl_2(Si_3AlO_{10})(OH)_2$) and kaolinite ($Al_2Si_2O_5(OH)_4$) were present at B1 and GM. Furthermore, the mineral cerussite ($PbCO_3$) was detected at B1. In sediments (H14, H12, H10, H1), the mineralogy of H14 was similar to B2 (principally the presence of quartz, fluorite and barite) whereas H12 and H10 contained calcite ($CaCO_3$), and H1 (140 m from the confluence with the River Wharfe) presented mainly quartz and calcite. Chemical composition analysis detected significant fractions of Pb in spoils B1 (35.1 g/kg) and Zn in GM (34.2 g/kg), while for sediments, major Pb concentrations were present in H12 (15.3 g/kg) and Zn in H14 (11.9 g/kg). Total Pb plus Zn in the sediment samples showed a decrease the further downstream the sample origin (Figure 2). Analysis of water composition and surface area in spoil samples showed higher percentages of water composition in GM (34.29%) followed by B2 (18.77%) and B1 (18.6%), while surface area values were: GM (20.6 $m^2/g$), B1 (5.82 $m^2/g$), B2 (1.34 $m^2/g$).

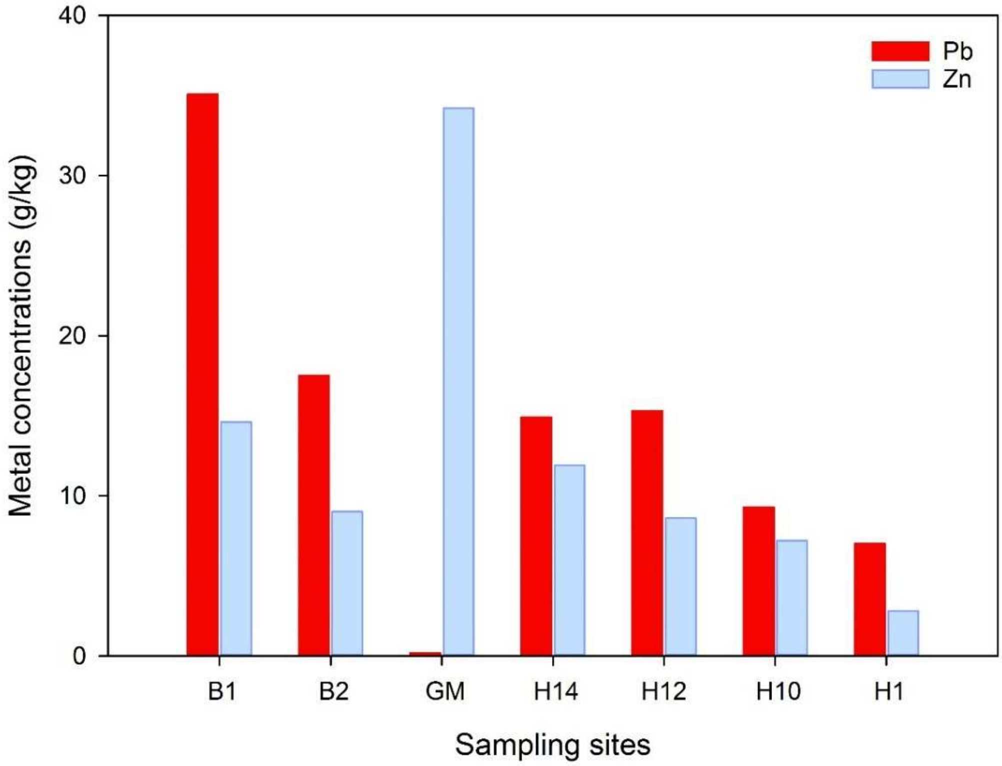

Figure 2. Lead and zinc composition in spoils and sediments.

### *4.2. Mineral phases controlling dissolved metal concentrations*

The metals Zn and Pb are the most significant toxic pollutants derived from mining activities. However, we modelled the geochemical behaviour of the additional metals Al, Fe, Ba and Sr as they are present in significant concentrations in the catchment. Geochemical modelling predicted that kaolinite ($Al_2Si_2O_5(OH)_4$) may account for the Al source with the solubility being controlled mainly by amorphous Al oxide phases ($Al(OH)_3$). Concentrations of Fe are more likely derived from secondary minerals. Iron solubility is controlled by amorphous phases such as ferrihydrite ($Fe(OH)_3$). The supersaturation of the Al and Fe phases may suggest the presence of some colloidal metal measured as part of the dissolved fraction. Barium concentrations are controlled by barite ($BaSO_4$), while Sr activity was too low to infer a controlling phase, perhaps being controlled by a mineral where it is present as a secondary metal. Lead and Zn concentrations are largely regulated by secondary minerals as metal-carbonates, cerussite ($PbCO_3$) and smithsonite ($ZnCO_3$), respectively (Figure 3).

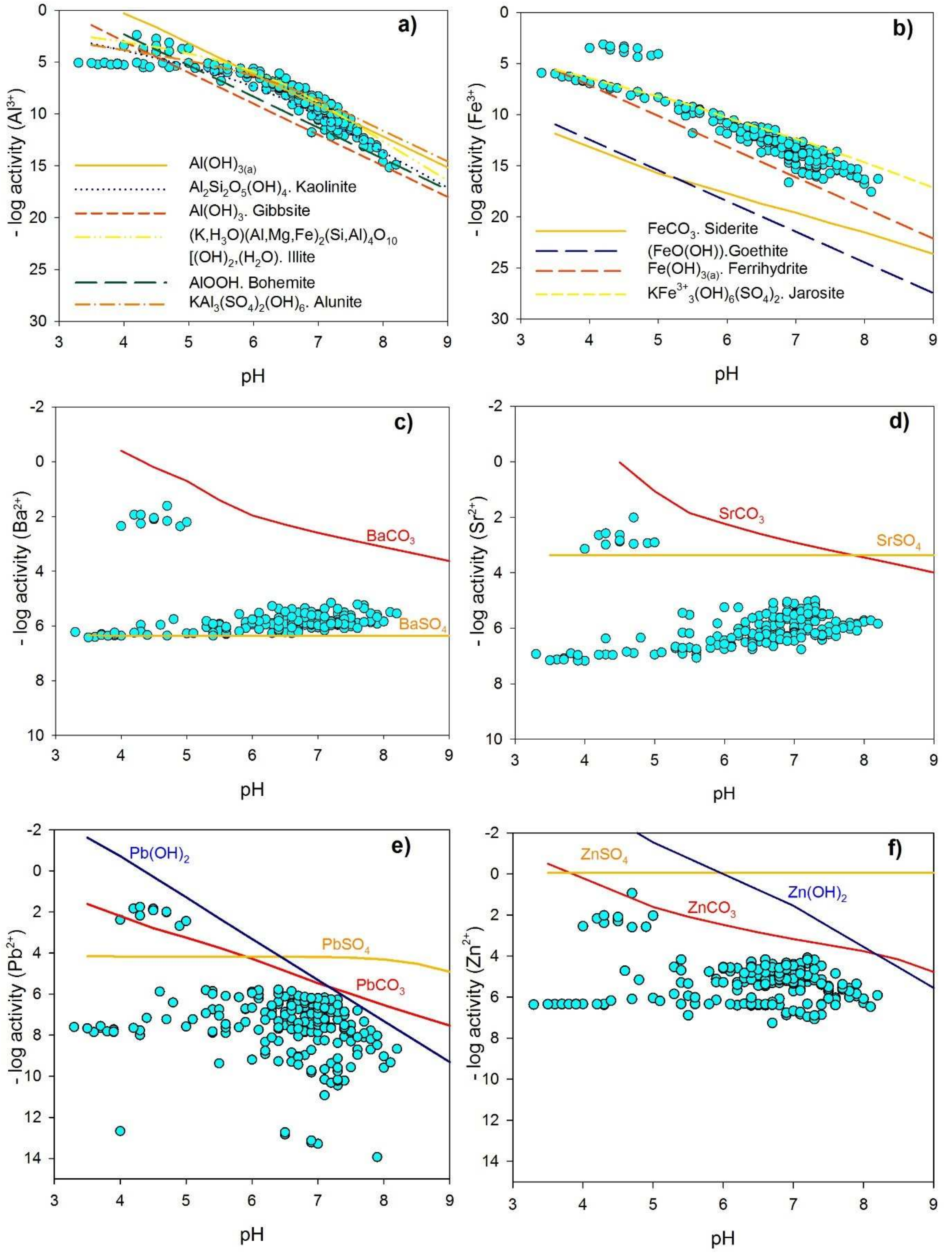

Figure 3. Aluminium, Fe, Ba, Sr, Pb and Zn activity as a function of pH, $SO_4^{2-}$ (13592 μg/l), Cl$^-$ (7730 μg/l) and $pCO_2$ = 0.0012 atm. Theoretical saturation of mineral forms are represented by solid lines and calculated metal free ion activity of experimental data by dots.

### *4.3. Key chemical relationships*

Table 3 summarises correlation analysis of metals derived from mining activities (Pb, Zn) and bedrock weathering (Ca) with major water chemistry parameters (pH, $SO_4^{2-}$, DIC and DOC). Zinc presented good correlation with $SO_4^{2-}$ (r= 0.6), Ca showed very strong association with DIC (r= 0.9), while Pb presented poor correlations (r≤ 0.3). Principal component analysis (PCA) shows key geochemical processes in influencing the water chemistry of Hebden Beck (Figure 4). The first component (PC1) with a 32% of variance indicates strong correlations between dissolved and particulate forms of calcium, magnesium, with DIC, EC and pH, reflecting weathering of the bedrock, while moderate correlation between iron and DOC refers to the transport of metals through colloidal matter in aquatic systems. Furthermore, the second component (PC2) with 21% of variance shows good correlations between strontium, zinc and cadmium with $SO_4^{2-}$, reflecting the oxidation of sulphide minerals. Other in situ parameters like temperature, DO, flow and anions ($NO_3^-$ and $Cl^-$) were not significantly associated with metals when considering all sites.

Table 3. Relationships between metals (Pb, Zn, and Ca) with pH, $SO4^{2-}$, DIC and DOC. Pearson correlation coefficient is denoted as r, p-value as p and confidence interval (95%) as CI.

| | **Stats** | **pH** | **$SO4^{2-}$** | **DIC** | **DOC** |
|---|---|---|---|---|---|
| **$Pb_D$** | r | -0.1 | -0.1 | -0.4 | 0.3 |
| | p | 0.084 | 0.194 | <0.001 | <0.001 |
| | CI | [-0.257 0.016] | [-0.228 0.047] | [-0.517 -0.284] | [0.135 0.393] |
| **$Zn_D$** | r | 0.2 | 0.6 | 0.04 | -0.2 |
| | p | 0.008 | <0.001 | 0.588 | 0.022 |
| | CI | [0.051 0.319] | [0.517 0.692] | [-0.101 0.176] | [-0.295 -0.024] |
| **$Ca_D$** | r | 0.6 | 0.7 | 0.9 | -0.6 |
| | p | <0.001 | <0.001 | <0.001 | <0.001 |
| | CI | [0.526 0.698] | [0.571 0.730] | [0.963 0.978] | [-0.701 -0.529] |

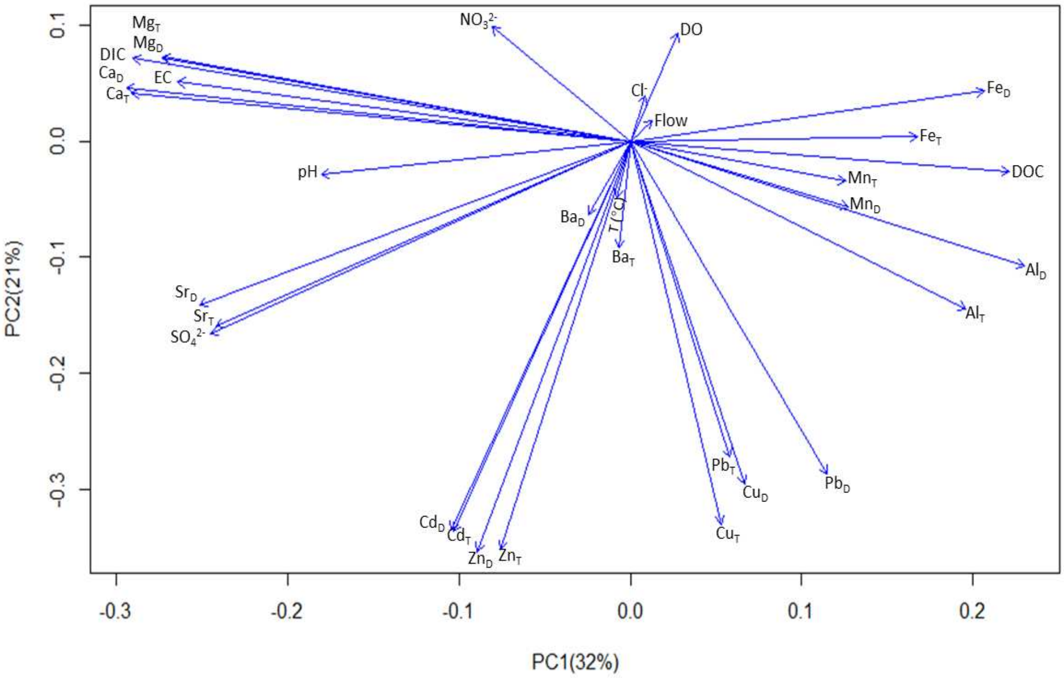

Figure 4. Scree plot from PCA analysis, horizontal axis shows projections of the first principal component PC1 which represents 32% of the total variance and the vertical axis the second component PC2 representing the 21% of variance.

Complementary linear regression analysis was carried out at sites with highest concentrations of $Zn_D$ and $Pb_D$ (H15, H14, H12 and H7) for evaluating their relationships with DIC and $SO_4^{2-}$. Since H15 is a reservoir with lower variance in chemical concentrations, it was not considered for this and subsequent analyses. Strong correlations between $Zn_D$ and DIC ($R^2$= 0.95) and $SO_4^{2-}$ ($R^2$= 0.93) were identified at H7. Moderate correlations between $Zn_D$ and $SO_4^{2-}$ ($R^2$= 0.4) and between Pb and DIC ($R^2$= 0.5) were present at site H12 (Figure 5 and 6). No significant correlation was evident at site H14, therefore results are not shown.

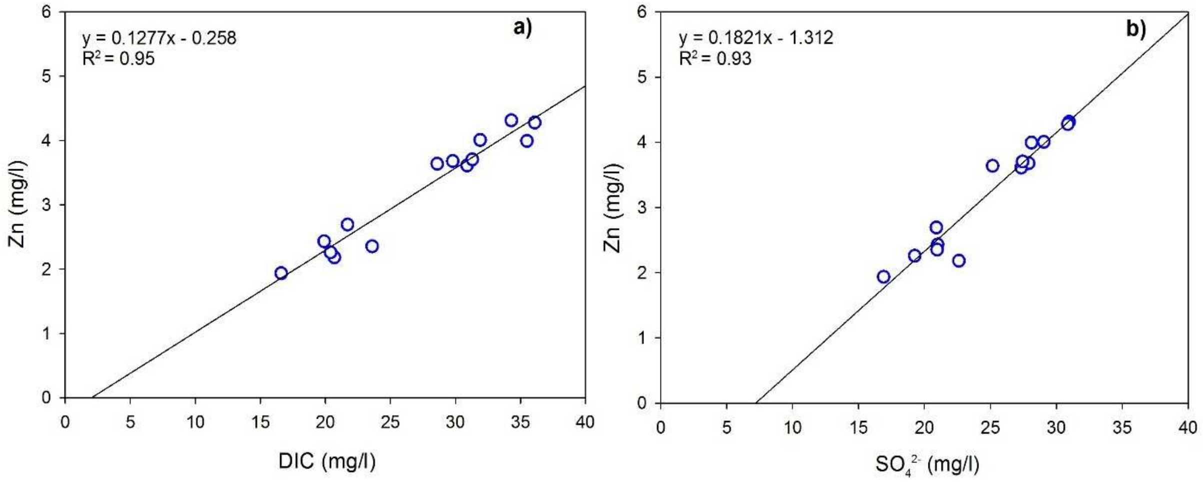

Figure 5. Relationships in tributary H7 between $Zn_D$ and DIC (left panel) and $SO_4^{2-}$ (right panel).

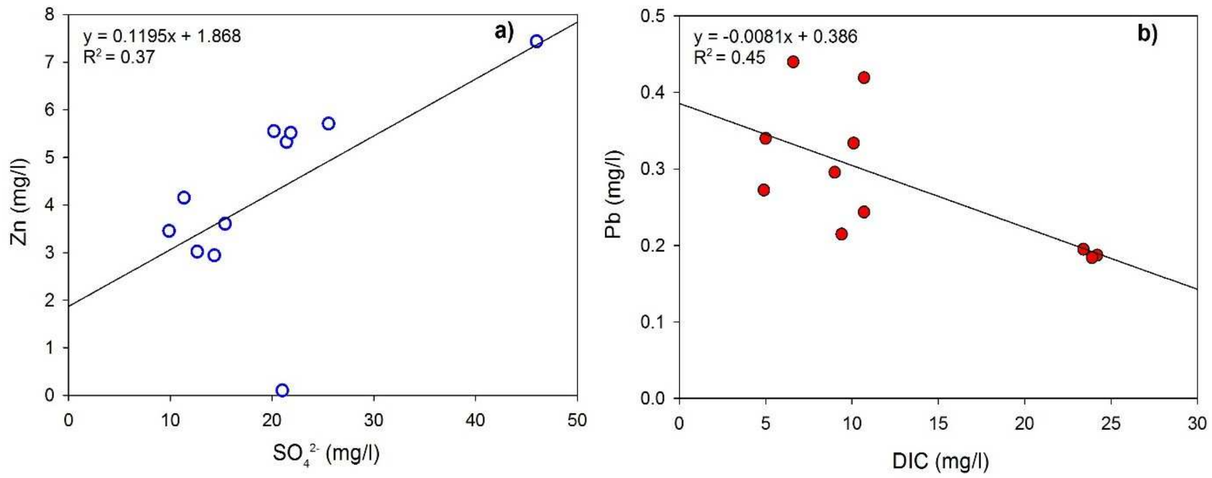

Figure 6. Relationships in tributary H12 between $Zn_D$ with $SO_4^{2-}$ and $Pb_D$ with DIC.

## *4.4. Seasonality and trends*

Across the sampling campaigns, water temperature ranged from 3.6 to 15.6 °C, with higher values in summer (July) and lowest in winter (February). Consistent with temperature, low monthly average of EC values were recorded in winter (78 μS/cm) and high average values during summer (209 μS/cm). Dissolved oxygen levels showed similar values, ranging from 10.2-14.0 mg/l, with lower concentrations recorded in winter (December) and highest levels in autumn (September). For flow, highest annual rates were recorded in November (2666.1 l/s) and lowest rates in July (54.0 l/s) (Table 3-SI).

Fluctuations were also dependent on the type of tributaries (e.g. perennial and ephemeral) (Table 4-SI). Flow values in perennial tributaries ranged from 3.0 to 192.7 l/s and in ephemeral from 9.0 to 57.0 l/s when flow was measurable, as some tributaries were dry for 5 or 6 months. Across all tributaries, two significant sites were identified as metal contributors of $Zn_D$ (H12: 4252.3 μg/l and H7: 3220.5 μg/l) and $Pb_D$ (H12: 284.2 μg/l) (Table 1). Across all sites, mean values of pH were highest in September (7.1) and lowest in November 2013 (5.6) (Table 3-SI). In individual sites, pH means ranged from 3.9 to 7.5, showing large monthly variations (SD≥ ±0.7) in sites H15, H11, H9, and H1P. Despite these variances a circumneutral pH (6.2-7.4) was predominant in the catchment.

Trends of flow and pH were considered to analyse their influence on metals concentration. Regression analysis was performed using all sampling sites. However, the results demonstrate the site specific nature of trends, with no catchment wide trends revealed (Figure 2-SI). We investigate further the trends for H2, as the chemistry is representative of a significant distance of the downstream reach and it has limited dilution before entering the

River Wharfe. Strong positive relationships were present for $Pb_D$-flow ($R^2$= 0.51) and $Zn_D$-pH ($R^2$= 0.58) and no clear relationships for $Pb_D$-pH ($R^2$= 0.06) and $Zn_D$-flow ($R^2$= 0.02) (Figure 7).

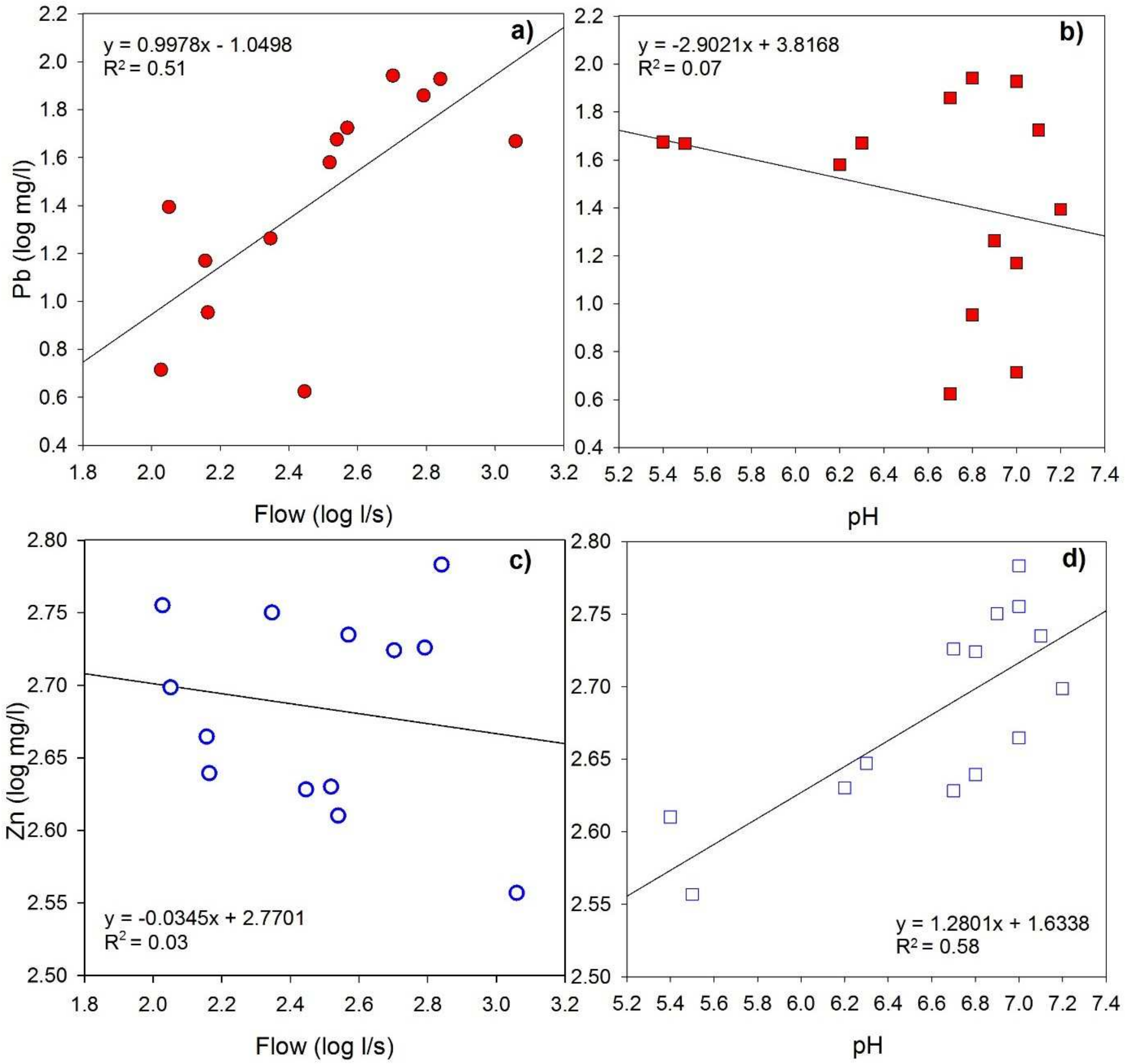

Figure 7. Trends of metals in function of flow and pH in H2. Panel a and b show trends of Pb and panel c and d indicate Zn trends. Solid lines represent regression lines.

### *4.5. Annual metal load*

The contribution of $Pb_D$ and $Zn_D$ in the catchment was estimated through the annual metal load (tonne/year). Only site H2 was considered for this calculation due to the availability of flow data and the lack of significant additional mine runoff downstream. Table 4 shows the average annual load of Pb is 0.2 tonne/year and for Zn 2.9 tonne/year. These values were compared with well-established EQS metals and showed maximum exceedances of 12-fold for Pb and Zn.

Table 4. Estimation of annual Pb and Zn load by using flow records from Environment Agency (EA) gauging station at H2 (main channel).

| **Stats** | **H2-Flow (l/s) from EA station** | **$Pb_D$ (µg/l)** | **$Pb_D$ (tonne/year)** | **$Zn_D$ (µg/l)** | **$Zn_D$ (tonne/year)** |
|---|---|---|---|---|---|
| **Average** | 189 | 39.4 | 0.2 | 485.9 | 2.9 |
| **Maximum$^{(a)}$** | 556 | 87.4 | 1.5 | 606.9 | 10.0 |
| **Minimum$^{(b)}$** | 36 | 4.2 | <0.1 | 360.5 | <0.9 |
| ***EQS-Hardness based*** | | ***7.2*** | | ***50.0*** | |

a) Maximum values recorded in February 2014.
b) Minimum values recorded in July 2014.

## 5. Discussion

In the catchment, biogeochemical actions such as weathering and erosion are significant processes in the generation of dissolved metals, which are likely derived from bedrock weathering and oxidation or dissolution of mineral ores. Carboniferous limestone bedrock, mainly composed of calcite ($CaCO_3$) is weathered, releasing significant amounts of calcium and carbonate, and creating a neutralizing capacity and circumneutral pH in environments surrounded by sulphide ore wastes. The influence of the geology in the catchment was shown by strong relationships between $Ca_D$ with DIC ($r= 0.9$, $p<0.001$) and pH ($r= 0.6$, $p<0.001$). For metals derived from mining activities, a potential primary source of $Zn_D$ is the oxidation of sphalerite (ZnS) as a good correlation was observed between $Zn_D$ and $SO_4^{2-}$ ($r= 0.6$, $p<0.001$) (Table 3). However, additional $Zn_D$ concentrations may be attributed to the presence of secondary zinc minerals (e.g. smithsonite) [48]. Contributions of $Pb_D$ are associated with dissolution of metal-carbonate compounds (cerussite) rather than oxidation of metal-sulphide as no correlation between $Pb_D$ with $SO_4^{2-}$ was identified ($r\leq -0.1$, $p<0.001$) (Table 3). The presence of secondary minerals such as metal-carbonate might affect the solubility and mobility of metals as they present slower dissolution kinetics than primary minerals [49-52].

Geochemical modelling has revealed the importance of secondary minerals such as carbonates, sulphates and hydroxides in the control of dissolved metals (Figure 3). For instance, Pb and Zn concentrations are greatly influenced by the dissolution of metal-carbonate forms (e.g. cerussite and smithsonite) [49, 53]. Carbonates released from the dissolution of metal-carbonate also contribute to the river alkalinity, enhancing the buffering capacity of the system. In addition, the source of Al can be associated with the presence of kaolinite, which was identified by the XRD analysis in most of the spoils/sediments. The presence of Fe concentrations can be associated with jarosite, and although this mineral was not detected by XRD analysis, it is a common secondary Fe mineral in mining areas [27, 28]. Figure 3 shows that Fe activity follows closely the prediction for jarosite, which at pH > 3 tends to dissolve and release sulphate ions and $Fe^{3+}$ [54]. In alkaline environments the activity of $Fe^{3+}$ is likely controlled by hydrous ferrous oxides, the presence of colloids in the dissolved fraction may explain the supersaturation. Aluminium and Fe solubility are controlled by amorphous phases, specifically $Al(OH)_3$ and $Fe(OH)_3$ (known as ferrihydrite). The presence of hydroxide compounds in the catchment could affect metal mobility, as they might sorb or co-precipitate with metals like Pb and Zn, acting as natural scavengers of these toxic elements [55]. Nordstrom [56] indicated that hydrology is another factor influencing metals mobility as concentrations of constituents in natural waters depend to a large extent on the rate of dissolution relative to flow rate. This condition was observed in the upper site of the catchment (a pond) as concentrations of metals were closer to saturation due to longer residence time of the water than under stream flow conditions (Figure 1-SI). Clustered sites with high metal free ion activities were identified and associated with sites with low pH values (<5), possible caused by high DOC concentrations (>8 mg/l), which are not considered in the modelling. The presence of metal-organic complexes will reduce the activities of metal free ions.

Analysis of sediments and spoils were consistent with water chemistry results showing Zn (11.9 and 34.2 g/kg) and Pb (15.3 and 35.1 g/kg) as major metals present in spoils due to lower extraction efficiency methods common in historical mining [40]. Preliminary sequential batch leaching experiments of spoil samples into deionised water showed consistent Zn and Pb concentrations of at least one order of magnitude above other metals across several leaching cycles (except Pb in GM where it is not present in significant concentrations). For leaching with acid (0.1 M HCl) most Zn was solubilised in the first two batches. Similar concentrations of Pb and Ca were leached but over five acid addition cycles, suggesting different dissociation kinetics of Pb and Zn minerals [57]. Future work will further explore the kinetics of leaching from the mineral forms in the spoils and sediments. Mineralogical results revealed the presence of secondary minerals such as cerussite ($PbCO_3$) as a source of Pb. Current chemical characterisation is in agreement with previous studies of water quality, metal composition and flux in the Yorkshire Pennine Orefield [14].

The impact of former metal mining on water quality has been evidenced by Pb, Zn and Cd pollution in the Yorkshire Pennine region, particularly in Hebden Beck [14, 39]. In expanding the range of Hebden Beck tributaries from earlier works, we have included sites close to mine wastes (e.g. tailings, spoils) for the identification of principal sources of metals. Major contributions of $Zn_D$ and $Pb_D$ were identified from mine water discharges (H7) and spoil wastes (H12) [14]. For these two sites there are statistically significant relationships between Zn and Pb with $SO_4^{2-}$ and DIC inferring the composition of their respective mineral sources. At site H12, an extended area covered by spoil wastes from Yarnbury mines, moderate correlations were identified between $Zn_D$ with $SO_4^{2-}$ ($R^2$= 0.37), and $Pb_D$ with DIC ($R^2$= 0.45) reflecting the $Zn_D$ contribution from the oxidation of sphalerite and $Pb_D$ contribution from the dissolution of cerussite (Figure 6). These correlations revealed the type and grade of ores mined during the eighteen and nineteenth centuries, producing spoils with different particle sizes and permeabilities, influencing their capacity to form secondary minerals [58]. At site H7, a mine channel from Bolton Haw, strong correlations were observed between Zn and $SO_4^{2-}$ ($R^2$= 0.93) and Zn and DIC ($R^2$= 0.95) (Figure 5). Both correlations suggest the oxidation of sphalerite as the main Zn source, however, if all sulphate was from ZnS the expected molar ratio between $Zn_D$ and $SO_4^{2-}$ should be 1:1 instead of the observed value of 5:1. Furthermore, the mineralogical and geochemical results did not show extensive evidence of pyrite mixed in mineral veins (correlation of Fe/$SO_4^{2-}$ r= -0.5; p= 0.076). Likewise, Dunham and Wilson[59] have reported that although pyrite, marcasite ($FeS_2$) and bravoite ($(Fe, Ni, Co)S_2$) are abundant in the orefield, they are found in minor amounts in veins, representing small quantities in relation with adjacent deposits rich in Fe discharges. Thus, secondary zinc minerals such as smithsonite ($ZnCO_3$), hydrozincite ($5ZnO.2CO_2.3H_2O$) and hermimorphite ($Zn_4[Si_2O_7](OH)_2.H_2O$), should be considered as possible sinks [49]. No correlation for Pb was observed in this site, probable due to the presence of low concentrations (4.3 μg/l) as consequence of aging [60] or the sorption effect of biofilms, becoming a significant sink for Pb [61].

In Hebden Beck, flow events can alter the river water chemistry and metal concentrations [14]. During base flow conditions, the circumneutal pH and buffering capacity are maintained by groundwater rather than surface water. This condition contributes to the presence of secondary zinc minerals and other carbonate minerals that sequester zinc, also influences the complexation of Pb with carbonate and organic matter, and affects its transformation to other forms like hydroxide, oxyhydroxide, hydroxysulfate minerals, limiting solubility and further weathering [49, 52, 56, 62]. Flow fluctuations caused by drought or heavy rainfall allowed the identification of major point and diffuse sources (H7 and H12) and their metal contributions under different flow events. At the point source H7 (mine adit-Bolton Haw), metal concentrations were generally constant at both flow conditions, therefore this site can be considered as a continuous source of metals (particularly for Zn: 3220.5 μg/l). At the diffuse source H12 (ephemeral tributary-draining spoil wastes from Yarnbury mine), metal concentrations become more significant during high flow, but greater contributions were also observed after dry periods (e.g. July [0 l/s, $Zn_D$ and $Pb_D$ below detection limits], August [8.4 l/s, 5709.0 μg $Zn_D$/l, 419.2 μg $Pb_D$/l]). This might be explained by the capacity of soluble sulphate minerals to store metals (e.g. Zn) during dry seasons and release them into the environment during wet seasons[63]. In addition, Byrne et al.[64] and Cánovas et al.[65] have indicated the influence of runoff produced by storms in increasing metals dissolved from weathered metal salts (smithsonite, cerussite) located in superficial mine spoils. Rothwell et al.[66] showed differences in metal concentrations not only between base and high flow conditions but also within and between storm events. Thus, further studies of metal concentrations and fluxes under a range of hydrological conditions are pertinent since the frequency and magnitude of floods are increasing the transport of dissolved and particulate metal forms from sources to river channels and floodplain soils, which are often used for agriculture [67].

Seasonal variations of pH and flow were considered to assess metal mobility. In the main channel (H2)strong correspondence occurred between pH-$Zn_D$ (r= 0.7) and flow- $Pb_D$ (r= 0.6) while relationships for $Pb_D$-pH and $Zn_D$-flow were unclear. The absence of a relationship of Zn with flow suggests that dissolution of zinc minerals is not kinetically limited (Figure 7), although solubility has been shown to depend on mineral composition in some cases [58]. The Pb relationship with flow may be related to greater flushing of areas where minerals have had longer to leach Pb into waters (e.g. H15 or the ephemeral pond feeding H12) (Figure 2-SI). Sims et al.[68] have also reported the role of flow in the generation of suspended matter, affecting the transport Pb forms. Once they enter into the aquatic system they tend to be adsorbed to suspended matter, while for the case of carbonate minerals they are likely to break down in acid waters, liberating significant quantities of Pb to sediments further down the river [69]. Thus, understanding the chemical tendencies of Zn and Pb under local pH and flow conditions is extremely important for estimating the potential fate and extent of polluters.

Metal contributions from point and diffuse sources decreased downstream (H2) ($Zn_D$: 479.4 μg/l, $Pb_D$: 35.1 μg/l), indicating a dilution effect from non-mine affected tributaries. Two dilution behaviours were observed in the main river, an abrupt reduction of $Zn_D$ after high concentrations were converged with relatively clean tributaries (from 3220.5μg/l (H7) and 4252.3μg/l (H12) to 444.4μg/l (H10)), and a gradual decrease of $Pb_D$ (284.2μg/l (H12) to 80.7μg/l (H10)) as dilution is likely to be related to the distribution of particulate matter from sediments [70]. Pb forms showed a higher fraction present as particulate (≥50%) in certain tributaries (e.g. H12, H11, H8, H3, H1) where dissolved organic carbon (H12 and H11>16 mg/l) and other complexing compounds like bicarbonates (DIC in H8, H3 and H1>22 mg/l) or hydroxides (e.g. $Fe(OH)_3$ and $Al(OH)_3$) may bind Pb. Thus, knowing solubility and speciation properties of Zn and Pb could help in the explanation of their mobility. Low solubility of Pb conceals high concentrations released at diffuse sources, due to binding to particulates [71]. In addition, sorption properties also affect metal dynamics, for instance, Pb has a greater affinity for binding to dissolved organic matter and surface reactive mineral complexes, as reflected in higher fractions present as particulate forms. These mechanisms are fundamentally associated with metal speciation, bioavailability and toxicity. The bioavailability of Zn and Pb in Hebden Beck has been assessed, revealing quality standard failures of Pb and Zn throughout the catchment at all monitoring sites [39].

Calculations of the dissolved Zn and Pb being transported downstream to the River Wharfe indicate annual loads of 0.2 tonnes/year of Pb and 2.9 tonnes/year of Zn. Although, these loads might increase depending on physical or chemical conditions caused by seasonal variations or particular flow conditions. Several studies in river systems have reported that metals associated with suspended sediments can make a major contribution to the total load of metals [72, 73]. Horowitz[74] compared and contrasted metal concentrations in suspended and bottom sediments versus dissolved levels, results indicated that bottom sediment concentrations were more than 100,000 (5 orders of magnitude) times higher than dissolved levels. Applying this approach in a downstream site (H1), higher results were observed for Pb (>430,000) and to a lesser extent for Zn (>17,000). Considering the importance of sediments in the transport and cycling of metals further work is needed in Hebden Beck. Comparisons between maximum measured concentrations of total dissolved metal concentrations in the main channel (site H2) with established regulatory limits for metals indicated that maximum annual concentrations of $Al_D$ (188 μg/l), $Fe_D$ (657 μg/l), $Ba_D$ (306 μg/l) and $Sr_D$ (356.4 μg/l) were within established regulatory limits (e.g. Al: 200 μg/l; Fe: 1000 μg/l; Ba: 1000 μg/l; Sr: 1500 μg/l). Conversely, maximum annual concentrations of $Pb_D$ (87 μg/l) and $Zn_D$ (607 μg/l), when compared with environmental quality standards (EQS) showed maximum exceedances of 1200% with likely ecological effects [75, 76] (Table 4).

Metal toxicity and bioavailability are mainly controlled by metal concentrations, pH conditions and concentration of organic matter. Although the last two factors might have a stronger effect on biotic communities. For example, Ramsey[77] reported that soil acidity and organic matter concentration exerted stronger effects on plant and microbial community than metals. Thus, discriminating the influence of these key factors in biological processes is important from the perspective of dealing ecotoxicological effects of metals and potential restoration efforts [5, 78]. In this context, environmentally friendly and cost-effective techniques such as bioremediation have been developed for heavy metal removal/recovery where microbial remediation is particularly used in mine drainages due to the ability of microorganisms to generate alkalinity and immobilise metals [79]. For instance, in the UK the sulphur-reducing bacteria (e.g. *Desulfovibrio vulgaris*) has been used in the treatment of mine drainage due to its diverse metabolic strategies to reduce sulphate ($SO_4^{2-}$) to hydrogen sulphide ($H_2S$), other elements like iron (Fe(III)), oxygen and compounds like nitrate and nitrite and fumarate [80]. Aquatic organisms such as diatoms and invertebrates have an important role as biomonitors and bioindicators for assessing the impact of metal pollution. These organisms together with established EU-WFD classification tools and diversity indices (e.g. ASPT, N-TAXA) were used in a preliminary assessment of this catchment, however the effects of elevated metal levels were unclear [81]. Studies in neutral mine drainage carried out by Byrne et al.[82] indicated that the use of standard macroinvertebrate biotic and diversity indices (EU-WFD tools) could lead to erroneous classifications of aquatic ecosystem health. These results revealed that failure in the interpretation of biogeochemical interactions could lead to inaccurate analysis of organisms at risk of exposure, hence ineffective management decisions. Thus, the assessment of metal effects on living organisms is complex since biota might have different responses according to physiological processes, and because metals are subject to a range of factors affecting their level of reactivity, toxicity and bioavailability [15]. Considering WFD goals, more nuanced approaches are needed for assessing metals and their ecological effects. In this context, current chemistry data and updated chemical speciation tools will be used in future work to assess metal availability and toxicity and advising improvements to river basin management plans.

## 6. Conclusions

- Underlying limestone bedrock controls pH and weathering reactions, and therefore metal mobility within such catchments.
- Mobilisation of Zn and Pb have a strong dependence on site specific biogeochemistry and hydrological conditions. No dependence of Zn with flow suggests that $Zn_D$ has no kinetic limitations on Zn mineral dissolution, whereas $Pb_D$ varied according with flow variations, reflecting its tendency to be complexed with colloidal or particulate forms.
- Point sources are regular contributors of $Zn_D$ despite flow fluctuations, while diffuse sources like spoil wastes produced higher contribution of $Zn_D$ and $Pb_D$ in overflow conditions after dry periods.
- Not all contributions of $Zn_D$ and $Pb_D$ are derived directly from oxidation of sphalerite and galena. Mineralogical and geochemical analysis revealed the contribution of secondary minerals such as smithsonite and cerussite, which are continuously leaching into the river and represent an added complexity for future remediation.
- Metal pollution results in a large area of catchment having a depleted chemical status with likely effects on the aquatic ecology.

## 7. Acknowledgements

This research was funded by the National Secretariat for Higher Education, Sciences, Technology and Innovation of Ecuador (SENESCYT in Spanish) through a PhD scholarship granted to M. Valencia-Avellan in June 2013 (Grant No. 82-ARG5-2013). The authors express their gratitude to the Yorkshire Dales National Park for granting the sampling permission in Hebden Beck and to the UK-Environmental Agency for sharing scientific reports and flow data (gauging station-F1960). We also thank the anonymous reviewers for their helpful comments.

## 8. References

1. A. J. Horowitz, K. A. Elrick and R. B. Cook, *Hydrol. Process.*, 1993, **7**, 403-423.
2. M. G. Macklin, in *Floodplain processes.*, ed. M. G. Anderson, Walling, D. E. and Bates, P. D., John Wiley & Sons, Inc., Chichester, England., 1996, pp. 441-460.
3. K. A. Hudson-Edwards, C. Schell and M. G. Macklin, *Applied Geochemistry*, 1999, **14**, 1015-1030.
4. S. A. Nagorski, J. N. Moore and D. B. Smith, *Mine Water and the Environment*, 2002, **21**, 121-136.
5. J. R. Miller, K. A. Hudson-Edwards, P. J. Lechler, D. Preston and M. G. Macklin, *Science of The Total Environment*, 2004, **320**, 189-209.
6. G. W. Fernandes, F. F. Goulart, B. D. Ranieri, M. S. Coelho, K. Dales, N. Boesche, M. Bustamante, F. A. Carvalho, D. C. Carvalho, R. Dirzo, S. Fernandes, P. M. Galetti Jr, V. E. G. Millan, C. Mielke, J. L. Ramirez, A. Neves, C. Rogass, S. P. Ribeiro, A. Scariot and B. Soares-Filho, *Natureza & Conservação*, 2016, **14**, 35-45.
7. M. G. Macklin, in *Gregory, K. J. Fluvial Geomorphology of Great Britain*, ed. J. N. C. Committee, Chapman and Hall, London, 1997, vol. 201-238.
8. K. A. Hudson-Edwards, *Mineralogical Magazine*, 2003, **67**, 205-217.
9. M. Olías, J. M. Nieto, A. M. Sarmiento, J. C. Cerón and C. R. Cánovas, *Science of The Total Environment*, 2004, **333**, 267-281.
10. L. J. Oulton, M. P. Taylor, G. C. Hose and C. Brown, *Ecotoxicology*, 2014, **23**, 1022-1029.
11. K. Hudson-Edwards, M. Macklin and M. Taylor, *Science of The Total Environment*, 1997, **194**, 437-445.
12. L. A. Warren and E. A. Haack, *Earth-Science Reviews*, 2001, **54**, 261-320.
13. P. Byrne, P. J. Wood and I. Reid, *Critical Reviews in Environmental Science and Technology*, 2012, **42**, 2017-2077.

14. A. Jones, M. Rogerson, G. Greenway, H. A. B. Potter and W. M. Mayes, *Environmental Science and Pollution Research*, 2013, **20**, 7570-7581.

15. S. Luoma, Rainbow, P., *Metal contamination in Aquatic Environments: Science and Lateral Management*, Cambridge University Press, New York, United States., 2008.

16. J. F. Elder, *Metal biogeochemistry in surface-water systems; a review of principles and concepts*, Report 1013, 1988.

17. S. E. Apitz, M. Elliott, M. Fountain and T. S. Galloway, *Integrated environmental assessment and management*, 2006, **2**, 80-85.

18. M. C. Freeman, C. M. Pringle and C. R. Jackson, *JAWRA Journal of the American Water Resources Association*, 2007, **43 (1)**, 5-14.

19. W. K. Dodds and R. M. Oakes, *Environmental Management*, 2008, **41**, 367-377.

20. J. L. Meyer, D. L. Strayer, J. B. Wallace, S. L. Eggert, G. S. Helfman and N. E. Leonard, *JAWRA Journal of the American Water Resources Association*, 2007, **43 (1)**, 86-103.

21. W. M. Mayes, D. Johnston, H. A. B. Potter and A. P. Jarvis, *Science of The Total Environment*, 2009, **407**, 5435-5447.

22. D. Banks, V. P. Parnachev, B. Frengstad, W. Holden, A. A. Vedernikov and O. V. Karnachuk, *Alkaline mine drainage from metal sulphide and coal mines: examples from Svalbard and Siberia*, Geological Society, London, Special Publications, 2002, vol. 198, pp. 287-296.

23. A. Akcil and S. Koldas, *Journal of Cleaner Production*, 2006, **14**, 1139-1145.

24. A. Navarro, X. Font and M. Viladevall, *Mine Water and the Environment*, 2015, **34**, 329-342.

25. G. Plumlee, K. Smith, M. Montour, W. Ficklin and E. Mosier, *The environmental geochemistry of mineral deposits. Part B: case studies and research topics*, 1999, **6**, 373-432.

26. C. A. Cravotta Iii, *Applied Geochemistry*, 2008, **23**, 166-202.

27. C. A. Cravotta Iii, *Applied Geochemistry*, 2008, **23**, 203-226.

28. J. Sánchez España, E. López Pamo, E. Santofimia, O. Aduvire, J. Reyes and D. Barettino, *Applied Geochemistry*, 2005, **20**, 1320-1356.

29. M. B. J. Lindsay, P. D. Condon, J. L. Jambor, K. G. Lear, D. W. Blowes and C. J. Ptacek, *Applied Geochemistry*, 2009, **24**, 2212-2221.

30. A. J. Desbarats and G. C. Dirom, *Applied Geochemistry*, 2007, **22**, 415-435.

31. P. M. Heikkinen, M. L. Räisänen and R. H. Johnson, *Mine Water and the Environment*, 2009, **28**, 30-49.

32. B. Lottermoser, *Mine Wastes: Charaterization, Treatment and Environmental Impacts. 3rd Edition*, Springer-Verlag Berlin Heidelberg, Germany, 2010.

33. J. R. Miller, *Journal of Geochemical Exploration*, 1997, **58**, 101-118.

34. M. Gosar, S. Pirc and M. Bidovec, *Journal of Geochemical Exploration*, 1997, **58**, 125-131.

35. K. A. Hudson-Edwards, H. E. Jamieson, J. M. Charnock and M. G. Macklin, *Chemical Geology*, 2005, **219**, 175-192.

36. R. R. Cave, J. E. Andrews, T. Jickells and E. G. Coombes, *Estuarine, Coastal and Shelf Science*, 2005, **62**, 547-557.

37. M. P. Taylor and K. A. Hudson-Edwards, *Environmental Pollution*, 2008, **152**, 193-204.

38. D. Johnston, H. Potter, C. Jones, S. Rolley, I. Watson and J. Pritchard, *Abandoned mines and the water environment. Science project: SC030136-41*, UK-Environment Agency, Bristol, UK, 2008.

39. J. Barber, *Humber River Basin District: Hebden Beck: WFD Investigation. Mining Pollution: Catchment Characterisation Report*, UK-Environment Agency, pp(37). 2014.

40. M. C. Gill, *The Grassington Mines*, Northern Mine Research Society, 1993.

41. A. Apha, *Standard methods for the Examination of Water and Wastewater*, 1995.

42. US Environmental Protection Agency and Office of Research and Development, *Environmental Monitoring and Support Laboratory: Handbook for sampling and sample preservation of water and wastewater*, Ohio, United States, 1982.

43. U.S. Geological Survey (USGS), PHREEQC (Version 3) - A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations https://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/, (accessed June 2, 2017).

44. D. L. Parkhurst and C. A. J. Appelo, *User's guide to PHREEQC (Version 2) : a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations*, Report 99-4259, U.S. Geological Survey : Earth Science Information Center, Open-File Reports Section. http://pubs.er.usgs.gov/publication/wri994259, 1999.

45. D. K. Nordstrom, L. N. Plummer, D. Langmuir, E. Busenberg, H. M. May, B. F. Jones and D. L. Parkhurst, *Revised chemical equilibrium data for major water—mineral reactions and their limitations*, ACS Publications, 1990.

46. J. W. Ball and D. K. Nordstrom, *User's manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural waters*, U.S. GEOLOGICAL SURVEY, California, USA, 1991.

47. J. I. Drever, *The Geochemistry of Natural Waters: Surface and Groundwater Environments, 436 pp*, third ed. Prentice Hall, Englewood Cliffs, NJ., 1997.

48. C. Tame, K. A. Hudson-Edwards and H. A. B. Potter, *Procedia Earth and Planetary Science*, 2017, **17**, 284-287.

49. C. A. Nuttall and P. L. Younger, *Secondary minerals in the abandoned mines of Nenthead, Cumbria as sinks for pollutant metals.*, Geological Society, London, Special Publications, 2002, vol. 198, pp. 241-250.

50. S. A. Carroll, P. A. O'Day and M. Piechowski, *Environmental Science & Technology*, 1998, **32**, 956-965.

51. D. M. Carmona, Á. Faz Cano and J. M. Arocena, *Geoderma*, 2009, **150**, 150-157.

52. H. E. Jamieson, *Elements*, 2011, **7**, 381-386.

53. X. Li and I. Thornton, *Applied Geochemistry*, 2001, **16**, 1693-1706.

54. V. Ettler, Z. Johan and D. Hradil, *Comptes Rendus Geoscience*, 2003, **335**, 1013-1020.

55. L. S. Balistrieri, S. E. Box, A. A. Bookstrom and M. Ikramuddin, *Environmental Science & Technology*, 1999, **33**, 3347-3353.

56. D. K. Nordstrom, *Applied Geochemistry*, 2011, **26**, 1777-1791.

57. B. Osbourn and A. Stockdale, unpublished work.

58. B. Palumbo-Roe, J. Wragg, M. R. Cave and D. Wagner, *Environmental Science and Pollution Research*, 2013, **20**, 7699-7710.

59. K. C. Dunham and A. A. Wilson, *Geology of the Northern Pennine orefield, Stainmore to Craven. Economic Memoir of British Geological Survey*, H.M. Stationery Off., London, 1st edn., 1985.

60. P. Iavazzo, P. Adamo, M. Boni, S. Hillier and M. Zampella, *Journal of Geochemical Exploration*, 2012, **113**, 56-67.

61. A. S. Templeton, T. P. Trainor, S. J. Traina, A. M. Spormann and G. E. Brown, *Proceedings of the National Academy of Sciences of the United States of America*, 2001, **98**, 11897-11902.

62. D. K. Nordstrom, *Aqueous pyrite oxidation and the consequent formation of secondary iron minerals*, Soil Science Society of America, 1982.

63. H. E. Jamieson, C. Robinson, C. N. Alpers, R. B. McCleskey, D. K. Nordstrom and R. C. Peterson, *Chemical Geology*, 2005, **215**, 387-405.

64. P. Byrne, I. Reid and P. J. Wood, *In: Proceedings of the International Mine Water Conference, 19-23 October 2009, Pretoria, South Africa, ISBN 978-0-09802623-5-3, 124-129.*, 2009.

65. C. Cánovas, C. Hubbard, M. Olías, J. Nieto, S. Black and M. L. Coleman, *Journal of Hydrology*, 2008, **350**, 25-40.

66. J. J. Rothwell, M. G. Evans, S. M. Daniels and T. E. H. Allott, *Journal of Hydrology*, 2007, **341**, 90-104.

67. S. F. Lynch, L. C. Batty and P. Byrne, *Minerals*, 2014, **4**, 52-73.

68. D. B. Sims, P. S. Hooda and G. K. Gillmore, *Environment and Pollution*, 2013, **2**, 22.

69. K. A. Hudson-Edwards, M. G. Macklin, C. D. Curtis and D. J. Vaughan, *Environmental Science & Technology*, 1996, **30**, 72-80.

70. P. E. T. Douben, *Environmental Pollution*, 1989, **61**, 211-226.

71. D. Langmuir, *Aqueous environmental geochemistry*, Prentice Hall, Upper Saddle River, N.J, 1997.

72. I. D. L. Foster and S. M. Charlesworth, *Hydrol. Process.*, 1996, **10**, 227-261.

73. A. J. Horowitz, K. A. Elrick, J. A. Robbins and R. B. Cook, *Journal of Geochemical Exploration*, 1995, **52**, 135-144.

74. A. J. Horowitz, *A primer on sediment-trace element chemistry*, Report 2331-1258, US Geological Survey; Books and Open-File Reports Section [distributor], 1991.

75. UK-Environment Agency, Chemical Standards Data Base. http://evidence.environment-agency.gov.uk/ChemicalStandards/Home.aspx, (accessed June 5, 2017).

76. Department of Environmental Protection and State of New Jersey, Division of Water Monitoring and Standards, http://www.state.nj.us/dep/wms/, (accessed June 2, 2017).

77. P. W. Ramsey, The relationship between microbial communities processes and mine waste contamination in upper Clark Fork River alluvial soils. University of Montana. Theses, Dissertations, Professional Papers. 9582, 2006.

78. I. A. Dennis, T. J. Coulthard, P. Brewer and M. G. Macklin, *Earth Surface Processes and Landforms*, 2009, **34**, 453-466.

79. C. N. Mulligan, R. N. Yong and B. F. Gibbs, *Engineering Geology*, 2001, **60**, 193-207.

80. A. Jarvis, C. Gandy, M. Bailey, J. Davis, P. Orme, J. Malley, H. Potter and A. Moorhouse, 2015.

81. Environment Agency, *Report on ecological sampling to assess the impacts of metal pollution: Hebden Beck and Ashfoldside Beck*, UK-Environment Agency, Bristol, United Kingdom, 2014.

82. P. Byrne, I. Reid and P. J. Wood, *Environmental Science: Processes & Impacts*, 2013, **15**, 393-404.