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Valencia-Avellan, Magaly, Slack, Rebecca, Stockdale, Anthony and Mortimer, Robert ORCID logo ORCID: <https://orcid.org/0000-0003-1292-8861> (2017) Understanding the mobilisation of metal pollution associated with historical mining in a carboniferous upland catchment. *Environmental Science: Processes & Impacts*, 19 (8). pp. 1061-1074.

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

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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.

Keywords: *neutral mine drainage, water quality, carboniferous catchment, metal mobility.*

1. Introduction

Anthropogenic activities have become an important driver of the global biogeochemical cycling of metals. Present day and historic 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, 2, 3, 4, 5, 6}. In the United Kingdom, old mines from the 18th and 19th centuries represent the major diffuse source of metals having an adverse effect in aquatic ecosystems^{7, 8, 9, 10}. Rivers draining these mining areas are heavily affected by metal

43 pollution as mineral veins present elevated concentrations of lead and zinc ores with variable
44 concentrations of cadmium, barium and fluorine¹¹.

45
46 Water chemistry in surface waters are particularly vulnerable to biogeochemical and
47 hydrological processes which are controlled by seasonality^{12, 13, 14}. In this context, knowledge
48 about metal mobility in natural water systems is extremely complex¹⁵. Biogeochemical
49 partitioning of metals results in a diversity of forms. Within the dissolved phase metals are
50 present as hydrated free ions, and associated with organic and inorganic complexes. Within
51 the suspended particulate phase, metals may be complexed with inorganic or organic particles
52 and biota or be present as discrete metal minerals. Adsorption and desorption of metals
53 depend on a number of factors including pH, redox conditions, mineral ore sources and the
54 composition of suspended particulate matter. For this reason, understanding the mechanisms
55 related to metal distribution is a key issue as they determine the mobility and toxicity of the
56 metals within aquatic ecosystems, which can support efforts to manage or mitigate pollution¹⁶.

57
58 Several countries have developed guidelines to obtain good ecological and chemical status of
59 and ground waters¹⁷. In the European Union (EU), the implementation of the Water Framework
60 Directive (WFD) obliges member states to assess surface waters through improved catchment
61 scale management (River Basin Management Plans, RBMPs). However, surface water bodies
62 such as headwater streams have been excluded from early RBMPs due to their small size.
63 Studies from Freeman et al.¹⁸, Dodds and Oakes¹⁹, and Meyer et al.²⁰ have shown the
64 importance of these waterbodies as biodiversity richness, migration corridors, origin of stream
65 networks and diffuse source of chemicals. Consequently, sound management is crucial for
66 maintaining ecosystem health in higher order streams that are targeted by the WFD aims.

67
68 A serious environmental hazard caused by mining is the generation of acid mine drainage
69 (AMD). Mine drainages, spoil wastes run-off and spoil erosion constantly discharge large
70 amounts of dissolved and particulate metals through AMD, representing a persistent and acute
71 pollution source and reducing water and sediment quality^{21, 13, 14}. Studies of mine wastes
72 chemistry have identified two types of mine effluents, acid mine drainage (low pH and high
73 concentration of dissolved sulphate) and circumneutral mine drainage (major ion
74 concentrations reflect the mineralogy of the catchment bedrock)^{22, 23}. Thus, mine drainage is
75 dependent on the geologic setting, local water chemistry, kinetic rates, and permeability of ore
76 and gangue minerals^{24, 25, 26, 27, 28}. Mine drainage flowing through Carboniferous limestone
77 host rock is consequently metal-rich but with a circumneutral pH^{13, 14}. Research from Lindsay
78 et al.²⁹ and Desbarats and Dirom³⁰ indicates that circumneutral mine drainage might support
79 natural attenuation of some metal-sulphides (e.g. ZnS, PbS) through the precipitation of

80 secondary minerals. Consequently, catchments under these conditions may be more
81 vulnerable to environmental harm due to changes in geochemical or hydrological conditions,
82 producing high pulses of dissolved metal concentrations or long leaching processes in
83 response to decades of chemical weathering^{31, 32}.

84

85 Another long-standing metal pollution problem is physical and chemical mobilisation of metals
86 through the passive dispersal and active transformation of abandoned tailings, spoil heaps,
87 bed sediments and contaminated floodplains. Studies on metal transportation from mine
88 wastes have reported the mobility of metals over long distances as free ions and complexed
89 forms within rivers. In addition, solid phases can be stored within floodplain deposits for
90 decades to millennia^{33, 34, 8, 35, 36, 37}. In an area of the UK with Carboniferous bedrock, the north
91 Pennines, historical metal mining has directly affected surface and subsurface floodplain soils
92 with heavy metal concentrations above background levels³⁸. Specifically, the Yorkshire Ouse
93 basin which drains the Pennine Orefield is estimated to contain 620 million tonnes of lead and
94 640 million tonnes of zinc stored within its floodplains³. Given the large differences in chemistry
95 between acid and circumneutral mine drainage, particularly in the concentrations of protons
96 and of Fe and Al whose solubility is controlled by pH, there will be significant differences in
97 the degree of availability of metal forms that can interact with aquatic organisms. This
98 necessitates dedicated studies of such Carboniferous catchments.

99

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

108

109 **2. Site characteristics of Hebden Beck**

110 2.1. Lithology and geology

111 Hebden Beck is a sub-catchment of the River Wharfe located in the northern Pennines region
112 of the United Kingdom and within the Yorkshire Dales National Park. Hebden Beck rises from
113 Grassington Moor and is joined by multiple tributaries including Coalgrove Beck, Bolton Gill
114 and Loss Gill before the confluence with the Wharfe. It is approximately 12 km long, with the

115 upper reach (6.4 km) of the main channel being the most heavily impacted by historic mine
116 working. It drains an area of 26 km² and subsequently flows into the River Wharfe which drains
117 the Wharfedale valley. The Wharfe flows into the River Ouse and ultimately reaches the sea
118 at the Humber Estuary which is one of the largest in the UK (24,750 km²). The geology of
119 Hebden Beck is dominated by Millstone Grit sandstone (approx. 20 km²) but crucially also
120 contains bands of Carboniferous limestone (approx. 6 km²) (Figure 1). The catchment cover
121 comprises 46% peatlands, predominantly in the upstream areas, 35% Carboniferous
122 limestone, mainly in the south and 19% glacial sediment, predominantly in the west³⁹.

123 2.2. Ore processing and mine wastes

124 Hebden's orefield comprised coal and lead-zinc mineral deposits, where galena (PbS) is the
125 most common mineral, but with associated sphalerite (ZnS), chalcopyrite (CuFeS₂), barite
126 (BaSO₄), fluorite (CaF₂) calcite (CaCO₃) and witherite (BaCO₃)³⁹. These minerals occur mostly
127 in vertical veins along fault planes. Early mine workings were open cuts and shafts to extract
128 deeper layers of lead ore. In later years until around 1850, the hushing method was used to
129 scour away the soil using the erosive power of water to expose mineral veins. This method
130 required the construction of dams to control streams, and manmade channels to divert water.
131 Horizontal drainage levels (adits) were driven from the valley bottoms to enable deeper
132 working and easier removal of minerals. Lead ores were crushed, classified and bagged at
133 the dressing floors located at the surface close to the mines, then transported to the smelting
134 mills to be processed. Water power was also applied at the dressing floors and smelt mills,
135 therefore spoil tips or mine wastes are located next to rivers. Approximately, 124 mining
136 features exist in the Hebden Beck catchment area, however main features are 5 lead-zinc
137 mines, 15 adits, 7 spoil tips and 4 smelters. From 1700-1900, 1686.5 tonnes of lead were
138 extracted from these mines⁴⁰.

139 **3. Methods**

140 3.1. Sampling strategy

141 Sites were selected from the most impacted area, covering an area of 5 km² including point
142 and diffuse sources flowing downstream from mine sites. A total of sixteen sites were chosen
143 for water sampling including the main channel, minor and major tributaries, including a source
144 pool feeding a tributary (Table 1). Eight of these sites (about 3.3 km) were part of a water
145 quality monitoring programme performed by the Environment Agency³⁹. The other eleven sites
146 were selected based on their proximity to mine wastes (e.g. tailings, spoils). Monthly sampling
147 campaigns were carried out from November 2013 to December 2014.

148 3.1.1. Water sampling

149 Samples were taken from downstream to upstream (H1 to H15) in order to minimise
150 contamination of other sites by disturbance⁴¹. At each site, a sample was taken with a pre acid
151 washed (10% HNO₃, Nitric acid-Sigma Aldrich 69% and Milli-Q water) 750 ml polypropylene
152 bottle attached to a plastic pole. Four subsamples were then extracted from this bottle. For
153 total metals, unfiltered samples were placed individually into a pre-weighted 50 ml tube
154 (polypropylene) containing 1 ml of preservation solution (10% HNO₃) to reach 1% v/v of the
155 final volume and pH ≤ 2^{41, 42}. For dissolved metals analysis, samples filtered through syringe
156 filters (0.45 µm, polyethersulfone-hydrophilic, Sartorius) were placed individually into a pre-
157 weighted 50 ml tube (polypropylene). Then preservation solution (10% HNO₃) was added as
158 used for total metals. For quantifying major anions, the sample was filtered (Sartorius syringe
159 filters 0.45 µm, polyethersulfone-hydrophilic) and placed into polypropylene tubes. For
160 inorganic and organic carbon analysis the samples were passed through syringe filters (0.45
161 µm, nylon-polypropylene, Avonchem) and placed into polypropylene tubes. All samples were
162 kept in a cool box during sampling and transported the same day to the laboratory for storage.
163 Samples for major anions analysis were stored frozen at -20°C while samples for all other
164 analyses were refrigerated at 4°C.

165 A carbon Analyser (Analytik Jena Multi N/C2100) was used for measuring carbon compounds
166 (dissolved inorganic carbon-DIC and dissolved organic carbon-DOC), Ion Chromatographer
167 for major cations (Ca, Mg) and anions (Cl⁻, NO₃²⁻, SO₄²⁻) (Dionex ICS-3000), and SEAL
168 Analytical AA3 was used for orthophosphate quantification. For metal analysis, nine elements
169 were measured (Pb, Ba, Cd, Sr, Zn, Cu, Fe, Mn, Al), using inductively coupled plasma mass
170 spectrometry (ICP-MS; Thermo Fisher iCAPQc) with specific limits of detection (Pb: 0.0001
171 µg/l, Ba: 0.06 µg/l, Cd: 0.0001 µg/l, Sr: 0.08 µg/l, Zn: 67 µg/l, Cu: 0.05 µg/l, Fe: 0.11 µg/l, Mn:
172 0.04 µg/l, Al: 0.16 µg/l). Field blanks (n=3) and replicates (n=3) were collected at each
173 sampling campaign.

174 3.1.2. Sediment and spoil sampling

175 Most sites were dominated by large rocks and coarse sediment. Sediment samples were
176 collected during a single campaign at specific sites (H14, H12, H10 and H1) to assess the
177 evolution of mineral composition. Plastic scoops were used for their collection by wading along
178 a cross-section of the stream, sediments were sieved through a <250 µm stainless steel mesh
179 and transferred into 50ml polypropylene tubes. Spoil sampling was carried out at single spoil
180 heaps at Grassington Moor (GM) and the Beaver spoil area (B1), in addition a further sample

181 was collected at the Beaver spoil area that represented material that had been subjected to
182 movement and size sorting by the actions of rainfall events (B2).

183 In the laboratory, sediment samples were centrifuged at 3200 rpm for 10 mins to allow removal
184 of the supernatant. The supernatant was decanted and the resulting slurries were placed in a
185 petri dish to air dry. After drying, sediments were placed into zip log bags for disaggregation.
186 Spoil samples (B1, B2, and GM) were dried to calculate percentage water composition. The
187 surface area was also measured to estimate the mineral area available for dissolution
188 reactions. This was performed using the Brunauer, Emmett and Teller method (BET;
189 Micromeritics Gemini VII 2390a) on 2 g of sample dried overnight under N₂ gas at 75 °C. In
190 addition, both sediment and spoil samples were analysed by X-ray Diffraction (XRD, Bruker
191 D8-Discover instrument) for determining mineralogy of the major constituents and X-ray
192 Fluorescence (XRF, Innovex X-5000) for chemical composition. The minimum mineral
193 fractions required for detection on this instrument is 2-3%. The standard reference material
194 STSD-3 (stream sediment) was used as XRF quality control.

195 3.1.3. In situ measurements

196 Pre-calibrated multiple sensor probes (Model HQ30d flexi 1032) were used in the field to
197 measure pH, dissolved oxygen (DO: mg/l) and conductivity (EC: μS/cm). Flow rate (m³/s) was
198 calculated from in situ flow velocity measurements (m/s) (flow meter: Global 800-876) together
199 with data from river depth (m) and width (m). Flow data from the UK Environment Agency
200 gauging station (H2) was also obtained from their continuous monitoring records. This flow
201 data together with metal concentrations were used for the calculation of annual metal loading
202 and comparison with Environmental quality standards (EQS) for freshwater in the UK³⁹.

203 3.2. Data analysis

204 3.2.1. Geochemical modelling

205 The PHREEQC code (version 3.)^{43, 44} was used for modelling main geochemical reactions
206 occurring in aqueous solutions. This software allows the prediction of mineral precipitation that
207 potentially controls the composition of the aqueous phase. Equilibrium reactions and
208 thermodynamic constants were retrieved from the built-in WATEQ4F database^{45, 46, 47}. Mineral
209 saturation indices and metal free ion activities for hydroxide, carbonate and sulphate minerals
210 were calculated for the pH range 3.5-9 and based on mean values across our field sites and
211 all sampling dates: temperature 10 °C, SO₄²⁻ (\bar{x} : 13592 μg/l) and Cl⁻ (\bar{x} : 7730 μg/l). With
212 calculations for carbonate minerals the $p\text{CO}_2$ was fixed at 3 times the atmospheric
213 concentration (0.0012 atm), consistent with typical supersaturation of this gas in streams.

214 These model predictions are compared with metal free ion activities calculated for each
215 sampling site and date to investigate the controlling mineral phases.

216 3.2.2. Principal Component Analysis

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

223 4. Results

224 4.1. Characterising metal pollution in the catchment

225 In water samples, metal concentrations occurred in the following order for total:
226 Zn>Fe>Sr>Ba>Pb>Al>Mn>Cd>Cu and dissolved forms: Zn>Fe>Sr>Ba>Al>Pb>Mn>Cd>Cu
227 (Table 1-SI). Two metals, Zn and Pb were chosen as the focus for this study based on their
228 significant concentrations derived from mining activities (Table 2). Annual pH averages
229 reflected the considerable contribution of the underlying limestone bedrock showing a
230 dominant circumneutral pH (mean= 6.8) in 80% of the studied sites. Some sites (e.g. H4 and
231 H13) represent moorland runoff with little interaction with underlying rock, thus pH is lower
232 (<6.3) due to high DOC and no carbonate buffering.

233 Across the catchment, Zn_D was the most abundant pollutant with concentrations ranging from
234 95.7 to 3220.5 µg/l in perennial tributaries. Ephemeral tributaries also showed high
235 concentrations up to 4252.3 µg/l while sites along the main channel had Zn_D concentrations
236 from 158.9 to 510.2 µg/l. The second toxic pollutant of concern was Pb_D, where main
237 contributions were observed in ephemeral tributaries with ranges from 4.4 to 284.2 µg/l, and
238 perennial tributaries ranged from 1.9 to 157.6 µg/l. The main river channel showed
239 concentrations of Pb from 16.6 to 80.7 µg/l. Major cations were dominated by calcium, with
240 concentrations from 2.6-54.9 mg/l, and major anions comprised sulphate (3-24.9 mg/l), nitrate
241 (1-17.8 mg/l), phosphate (0.002 to 0.1 mg/l) and chloride (7.2-10.5 mg/l). Dissolved inorganic
242 carbon concentrations ranged from 0.9 to 42.7 mg/l and dissolved organic carbon from 1.2 to
243 16.8 mg/l (Table 2-SI). Field blanks measurements shown concentrations below limit for all
244 the elements and replicates a standard deviation of ≤ ±0.5 µg/l (Cd and Cu), ≤ ±3.6 µg/l (Mn
245 and Sr), ≤ ±12 µg/l (Pb, Al, Ba).

246 From mineralogical analysis of spoil and sediment samples, the most abundant minerals were
247 quartz (SiO_2) and fluorite (CaF_2). Spoil samples (B1, B2 and GM) included barite (BaSO_4) as
248 an additional dominant mineral, at B1 and GM other secondary minerals like muscovite
249 ($\text{KAl}_2(\text{Si}_3\text{AlO}_{10})(\text{OH})_2$) and kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) were present, furthermore at B1 the
250 mineral cerussite (PbCO_3) was detected. In sediments (H14, H12, H10, H1), the mineralogy
251 of H14 was similar to B2 (principally the presence of quartz, fluorite and barite) whereas H12
252 and H10 contained calcite (CaCO_3), and H1 (140 m from the confluence with the River Wharfe)
253 presented mainly quartz and calcite. Chemical composition analysis detected significant
254 fractions of Pb in spoils B1 (35.1 g/kg) and Zn in GM (34.2 g/kg), while for sediments, major
255 Pb concentrations were present in H12 (15.3 g/kg) and Zn in H14 (11.9 g/kg). Total Pb plus
256 Zn in the sediment samples showed a decrease the further downstream the sample origin
257 (Figure 2). Analysis of water composition and surface area in spoil samples showed higher
258 percentages of water composition in GM (34.29%) followed by B2 (18.77%) and B1 (18.6%),
259 while for surface area values were: GM (20.6 m^2/g), B1 (5.82 m^2/g), B2 (1.34 m^2/g).

260 4.2. Mineral phases controlling dissolved metal concentrations

261 The metals Zn and Pb are the most significant toxic pollutants derived from mining activities.
262 However, we modelled the geochemical behaviour of the additional metals Al, Fe, Ba and Sr
263 as they are present in significant concentrations in the catchment. Geochemical modelling
264 predicted that kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) may account for the Al source with the solubility being
265 controlled mainly by amorphous Al oxide phases ($\text{Al}(\text{OH})_3$). Similar to aluminium, Fe
266 concentrations are more likely derived from complex minerals such as jarosite
267 ($\text{KFe}^{3+}_3(\text{OH})_6(\text{SO}_4)_2$), which is a secondary source of Fe commonly associated with mining
268 areas. Iron solubility is controlled by amorphous phases such as ferrihydrite ($\text{Fe}(\text{OH})_3$). The
269 supersaturation of the Al and Fe phases may suggest the presence of some colloidal metal
270 measured as part of the dissolved fraction. Barium concentrations are controlled by barite
271 (BaSO_4), while Sr activity was too low to infer a controlling phase, perhaps being controlled by
272 a mineral where it is present as a secondary metal. Lead and Zn concentrations are largely
273 regulated by secondary minerals as metal-carbonates, cerussite (PbCO_3) and smithsonite
274 (ZnCO_3), respectively (Figure 3).

275 4.3. Key chemical relationships

276 Table 3 summarises correlation analysis of metals derived from mining activities (Pb, Zn) and
277 bedrock weathering (Ca) with major water chemistry parameters (pH, SO_4^{2-} , DIC and DOC).
278 Zinc presented good correlation with SO_4^{2-} ($r=0.6$), Ca showed very strong association with
279 DIC ($r=0.9$), while Pb presented poor correlations ($r\leq 0.3$). Principal component analysis (PCA)

280 shows key geochemical processes in influencing the water chemistry of Hebden Beck (Figure
281 4). The first component (PC1) with a 32% of variance indicates strong correlations between
282 dissolved and particulate forms of calcium, magnesium, with DIC, EC and pH, reflecting
283 weathering of the bedrock, while moderate correlation between iron with DOC refers to the
284 transport of metals through colloidal matter in aquatic systems. Furthermore, the second
285 component (PC2) with 21% of variance shows good correlations between strontium, zinc and
286 cadmium with SO_4^{2-} , reflecting the oxidation of sulphide minerals. Other in situ parameters like
287 temperature, DO, flow and anions (NO_3^{2-} and Cl^-) were not significantly associated to metals
288 when considering all sites.

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

296 4.4. Seasonality and trends

297 Across the sampling campaigns, water temperature ranged from 3.6 to 15.6 °C, with higher
298 values in summer (July) and lowest in winter (February). Consistent with temperature, low
299 monthly average of EC values were recorded in winter (78 $\mu\text{S}/\text{cm}$) and high average values
300 during summer (209 $\mu\text{S}/\text{cm}$). Dissolved oxygen levels showed similar values, ranging from
301 10.2-14.0 mg/l, with lower concentrations recorded in winter (December) and highest levels in
302 autumn (September). For flow, highest annual rates were recorded in November (2666.1 l/s)
303 and lowest rates in July (54.0 l/s) (Table 3-SI).

304 Fluctuations were also dependent on the type of tributaries (e.g. perennial and ephemeral)
305 (Table 4-SI). Flow values in perennial tributaries ranged from 3.0 to 192.7 l/s and in ephemeral
306 from 9.0 to 57.0 l/s when flow was measurable, as some tributaries were dry for 5 or 6 months.
307 Across all tributaries, two significant sites were identified as metal contributors of Zn_D (H12:
308 4252.3 $\mu\text{g}/\text{l}$ and H7: 3220.5 $\mu\text{g}/\text{l}$) and Pb_D (H12: 284.2 $\mu\text{g}/\text{l}$) (Table 1). Across all sites, mean
309 values of pH were highest in September (7.1) and lowest in November 2013 (5.6) (Table 3-
310 SI). In individual sites, pH means ranged from 3.9 to 7.5, showing large monthly variations
311 ($\text{SD} \geq \pm 0.7$) in sites H15, H11, H9, and H1P. Despite these variances a circumneutral pH (6.2-
312 7.4) was predominant in the catchment.

313 Trends of flow and pH were considered to analyse their influence on metals concentration.
314 Regression analysis was performed using all sampling sites. However, the results
315 demonstrate the site specific nature of trends, with no catchment wide trends revealed (Figure
316 2-SI). We investigate further the trends for H2, as the chemistry is representative of a
317 significant distance of the downstream reach and it has limited dilution before entering the
318 River Wharfe. Strong positive relationships were present for Pb_D -flow ($R^2= 0.51$) and Zn_D -pH
319 ($R^2= 0.58$) and no clear relationships for Pb_D -pH ($R^2= 0.06$) and Zn_D -flow ($R^2= 0.02$) (Figure
320 7).

321 4.5. Annual metal load

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

328

329 **5. Discussion**

330 In the catchment, biogeochemical actions such as weathering and erosion are significant
331 processes in the generation of dissolved metals, which are likely derived from bedrock
332 weathering and oxidation or dissolution of mineral ores. Carboniferous limestone bedrock,
333 mainly composed of calcite ($CaCO_3$) is weathered, releasing significant amounts of calcium
334 and carbonate, and creating a neutralizing capacity and circumneutral pH in environments
335 surrounded by sulphide ore wastes. The influence of the geology in the catchment was shown
336 by strong relationships between Ca_D with DIC ($r=0.9$, $p<0.001$) and pH ($r= 0.6$, $p<0.001$). For
337 metals derived from mining activities, a potential primary source of Zn_D is the oxidation of
338 sphalerite (ZnS) as good correlation is observed between Zn_D and SO_4^{2-} ($r= 0.6$, $p<0.001$)
339 (Table 3), however, additional Zn_D concentrations may be attributed to the presence of
340 secondary zinc minerals (e.g. smithsonite)⁴⁸. Contributions of Pb_D are associated with
341 dissolution of metal-carbonate compounds (cerussite) rather than oxidation of metal-sulphide
342 as no correlation between Pb_D with SO_4^{2-} was identified ($r\leq -0.1$, $p<0.001$) (Table 3). The
343 presence of secondary minerals such as metal-carbonate might affect the solubility and
344 mobility of metals as they present slower dissolution kinetics than primary minerals^{49, 50, 51, 52}.

345

346 Geochemical modelling has revealed the importance of secondary minerals such as
347 carbonates, sulphates and hydroxides in the control of dissolved metals (Figure 3). For
348 instance, Pb and Zn concentrations are greatly influenced by the dissolution of metal-
349 carbonate forms (e.g. cerussite and smithsonite)^{53, 49}. Carbonates released from the
350 dissolution of metal-carbonate also contribute to the river alkalinity, enhancing the buffering
351 capacity of the system. In addition, the source of Al can be associated to the presence of
352 kaolinite which was identified by the XRD analysis in most of the spoil/sediment. The presence
353 of Fe concentrations can be associated to jarosite although this mineral was not detected by
354 XRD analysis, it is a common secondary Fe mineral in mining areas^{27, 28}. Aluminium and Fe
355 solubility are controlled by amorphous phases, specifically Al(OH)₃ and Fe(OH)₃ (known as
356 ferrihydrite). The presence of hydroxide compounds in the catchment could affect metal
357 mobility, as they might sorb or co-precipitate with metals like Pb and Zn, acting as natural
358 scavengers of these toxic elements⁵⁴. Nordstrom⁵⁵ indicated that hydrology is another factor
359 influencing metals mobility as concentrations of constituents in natural waters depend to a
360 large extent on the rate of dissolution relative to flow rate. This condition was observed in the
361 upper site of the catchment (a pond) as concentrations of metals were closer to saturation due
362 to longer residence time of the water than under stream flow conditions (Figure 1-SI).
363 Clustered sites with high metal free ion activities were identified and associated to sites with
364 low pH values (<5) possible caused by high DOC concentrations (>8 mg/l), which are not
365 considered in the modelling. The presence of metal-organic complexes will reduce the
366 activities of metal free ions.

367

368 Analysis from sediments and spoils were consistent with water chemistry results showing Zn
369 (11.9 and 34.2 g/kg) and Pb (15.3 and 35.1 g/kg) as major metals present in spoil due to lower
370 extraction efficiency methods common in historical mining⁴⁰. Preliminary sequential batch
371 leaching experiments of spoil samples into deionised water showed consistent Zn and Pb
372 concentrations of at least one order of magnitude above other metals across several leaching
373 cycles (except Pb in GM where it is not present in significant concentrations). For leaching
374 with acid (0.1 M HCl) most Zn was solubilised in the first two batches. Similar concentrations
375 of Pb and Ca were leached but over five acid addition cycles, suggesting different dissociation
376 kinetics of Pb and Zn minerals⁵⁶. Future work will explore further the kinetics of leaching from
377 the mineral forms in the spoils and sediments. Mineralogical results revealed the presence of
378 secondary minerals such as cerussite (PbCO₃) as a source of Pb. Current chemical
379 characterisation is in agreement with previous studies of water quality, metal composition and
380 flux in the Yorkshire Pennine Orefield¹⁴.

381

382 The impact of former metal mining on water quality has been evidenced by Pb, Zn and Cd
383 pollution in the Yorkshire Pennine region, particularly in Hebden Beck^{14, 39}. In expanding the
384 range of Hebden Beck tributaries from earlier works, we have included sites close to mine
385 wastes (e.g. tailings, spoils) for the identification of principal sources of metals. Major
386 contributions of Zn_D and Pb_D were identified from mine water discharges (H7) and spoil wastes
387 (H12)¹⁴. For these two sites there are statistically significant relationships between Zn and Pb
388 with SO₄²⁻ and DIC inferring the composition of their respective mineral sources. At site H12,
389 an extended area covered by spoil wastes from Yarnbury mines, moderate correlations were
390 identified between Zn_D with SO₄²⁻ (R²= 0.4), and Pb_D with DIC (R²= 0.5) reflecting the Zn_D
391 contribution from the oxidation of sphalerite and Pb_D contribution from the dissolution of
392 cerussite (Figure 6). These correlations revealed the type and grade of ores mined during the
393 eighteenth and nineteenth century, producing spoils with different particle size and permeability,
394 influencing their capacity to form secondary minerals⁵⁷. At site H7, a mine channel from Bolton
395 Haw, strong correlations were observed between Zn with SO₄²⁻ (R²= 0.93) and DIC (R²= 0.95)
396 (Figure 5). Both correlations suggest the oxidation of sphalerite as main Zn source, however,
397 if all sulphate was from ZnS the expected molar ratio between Zn_D and SO₄²⁻ should be 1:1
398 instead of the observed value of 5:1. Furthermore, the mineralogical and geochemical results
399 did not show extensive evidence of pyrite mixed in mineral veins (correlation of Fe/SO₄²⁻ r= -
400 0.5; p= 0.076). Thus, secondary zinc minerals such as smithsonite (ZnCO₃), hydrozincite
401 (5ZnO.2CO₂.3H₂O) and hercynite (Zn₂[Si₂O₇](OH)₂.H₂O), should be considered as
402 possible sinks⁴⁹. No correlation for Pb was observed in this site, probable due to the presence
403 of low concentrations (4.3 µg/l) as consequence of aging⁵⁸ or the sorption effect of biofilms,
404 becoming a significant sink for Pb⁵⁹.

405

406 In Hebden Beck, flow events can alter the river water chemistry and metal concentrations¹⁴.
407 During base flow conditions, the circumneutral pH and buffering capacity are maintained by
408 groundwater rather than surface water. This condition contributes with the presence of
409 secondary zinc minerals and other carbonate minerals that sequester zinc, also influence the
410 complexation of Pb with carbonate and organic matter, as well as its transformation in other
411 forms like hydroxide, oxyhydroxide, hydroxysulfate minerals, limiting solubility and further
412 weathering^{49, 60, 55, 52}. Flow fluctuations caused by drought or heavy rainfall allowed the
413 identification of major point and diffuse sources (H7 and H12) and their metal contributions
414 under different flow events. At the point source H7 (mine adit-Bolton Haw), metal
415 concentrations were generally constant at both flow conditions, therefore this site can be
416 considered as a continuous source of metals (particularly for Zn: 3220.5 µg/l). At the diffuse
417 source H12 (ephemeral tributary-draining spoil wastes from Yarnbury mine), metal

418 concentrations become more significant during high flow, but greater contributions were
419 observed after dry period (e.g. July [0 l/s, Zn_D and Pb_D below detection limits], August [8.4 l/s,
420 5709.0 µg Zn_D/l, 419.2 µg Pb_D/l]). This might be explained by the capacity of soluble sulphate
421 minerals to store metals (e.g. Zn) during dry seasons and release them into the environment
422 during wet seasons⁶¹. In addition, Byrne et al. ⁶² and Canovas et al. ⁶³ have indicated the
423 influence of runoff produced by storms in increasing metals dissolved from weathered metal
424 salts (smithsonite, cerussite) located in superficial mine spoils. Rothwell et al. ⁶⁴ showed
425 differences in metal concentrations not only between base and high flow conditions but also
426 within and between storm events. Thus, further studies of metal concentrations and fluxes
427 under a range of hydrological conditions are pertinent since the frequency and magnitude of
428 floods are increasing the transport of dissolved and particulate metal forms from sources to
429 river channels and floodplain soils, which are often used for agriculture⁶⁵.

430 Seasonal variations of pH and flow were considered to assess metal mobility. In the main
431 channel (H2) strong correspondence occurred between pH-Zn_D (r= 0.7) and flow- Pb_D (r= 0.6)
432 while relationships for Pb_D-pH and Zn_D-flow were unclear. The absence of a relationship of
433 Zn with flow suggests that dissolution of zinc minerals is not kinetically limited (Figure 7),
434 although solubility been shown to depend on mineral composition in some cases⁵⁷. The Pb
435 relationship with flow may be related to greater flushing of areas where minerals have had
436 longer to leach Pb into waters (e.g., H15 or the ephemeral pond feeding H12) (Figure 2-SI).
437 Sims et al.⁶⁶ have also reported the role of flow in the generation of suspended matter,
438 affecting the transport Pb forms. Once they enter into the aquatic system they tend to be
439 adsorbed to suspended matter, while for the case of carbonate minerals they are likely to break
440 down in acid waters, liberating significant quantities of Pb to sediments further down the river⁶⁷.
441 Thus, understanding the chemical tendencies of Zn and Pb under local pH and flow conditions
442 is extremely important for estimating the potential fate and extent of pollutants.

443 Metal contributions from point and diffuse sources decreased downstream (H2) (Zn_D: 479.4
444 µg/l, Pb_D: 35.1 µg/l), indicating a dilution effect from non-mine affected tributaries. Two dilution
445 behaviours were observed in the main river, an abrupt reduction of Zn_D after high
446 concentrations were converged with relatively clean tributaries (from 3220.5µg/l (H7) and
447 4252.3µg/l (H12) to 444.4µg/l (H10)), and a gradual decrease of Pb_D (284.2µg/l (H12) to
448 80.7µg/l (H10)) as dilution is likely to be related to the distribution of particulate matter from
449 sediments⁶⁸. Pb forms showed a higher fraction present as particulate (≥50%) in certain
450 tributaries (e.g. H12, H11, H8, H3, H1) where dissolved organic carbon (H12 and H11>16
451 mg/l) and other complexing compounds like bicarbonates (DIC in H8, H3 and H1>22 mg/l) or

452 hydroxides (e.g. $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$) may bind Pb. Thus, knowing solubility and speciation
453 properties of Zn and Pb could help in the explanation of their mobility. Low solubility of Pb
454 conceals high concentrations released at diffuse sources, due to binding to particulates⁶⁹. In
455 addition, sorption properties also affect metal dynamics, for instance, Pb has a greater affinity
456 for binding to dissolved organic matter and surface reactive mineral complexes, as reflected
457 in higher fractions present as particulate forms. These mechanisms are fundamentally
458 associated with metal speciation, bioavailability and toxicity. The bioavailability of Zn and Pb
459 in Hebden Beck has been assessed, revealing quality standard failures of Pb and Zn
460 throughout the catchment at all monitoring sites³⁹.

461 Calculations of the dissolved Zn and Pb being transported downstream to the River Wharfe
462 indicate annual loads of 0.2 tonnes/year of Pb and 2.9 tonnes/year of Zn. Although, these
463 loads might increase depending on physical or chemical conditions caused by seasonal
464 variations or particular flow conditions. Several studies in river systems have reported that
465 metals associated with suspended sediments can make a major contribution to the total load
466 of metals^{70, 71}. Horowitz⁷² compared and contrasted metal concentrations in suspended and
467 bottom sediments versus dissolved levels, results indicated that bottom sediment
468 concentrations were more than 100,000 (5 orders of magnitude) times higher than dissolved
469 levels. Applying this approach in a downstream site (H1), higher results were observed for Pb
470 (>430,000) and to a lesser extent for Zn (>17,000). Considering the importance of sediments
471 in the transport and cycling of metals further work is needed in Hebden Beck. Comparisons
472 between maximum measured concentrations of total dissolved metal concentrations in the
473 main channel (site H2) with established regulatory limits for metals indicated that maximum
474 annual concentrations of Al_D (188 $\mu\text{g/l}$), Fe_D (657 $\mu\text{g/l}$), Ba_D (306 $\mu\text{g/l}$) and Sr_D (356.4 $\mu\text{g/l}$)
475 were within established regulatory limits (e.g. Al: 200 $\mu\text{g/l}$; Fe: 1000 $\mu\text{g/l}$; Ba: 1000 $\mu\text{g/l}$; Sr:
476 1500 $\mu\text{g/l}$). Conversely, maximum annual concentrations of Pb_D (87 $\mu\text{g/l}$) and Zn_D (607 $\mu\text{g/l}$),
477 when compared with environmental quality standards (EQS) showed maximum exceedances
478 of 1200% with likely ecological effects^{73, 74} (Table 4).

479 Studies on the effects of geochemical parameters on a number of parameters associated to
480 plant and microbial communities have indicated geochemical parameters exert strongest
481 effect on these biotic communities and therefore is of greatest concern from the perspective
482 of restoration.

483 Metal toxicity and bioavailability are mainly controlled by metal concentrations, pH conditions
484 and concentration of organic matter. Although each of these factors might have a stronger
485 effect on biotic communities. For example, Ramsey⁷⁵ reported that soil acidity and organic

486 matter concentration exerted stronger effects on plant and microbial community than metals.
487 Thus, discriminating the influence of these key factors in biological processes is important
488 from the perspective of dealing ecotoxicological effects of metals and potential restoration
489 efforts^{5, 76}. In this context, environmentally friendly and cost-effective techniques such as
490 bioremediation has been developed for heavy metal removal/recovery where microbial
491 remediation is particularly used in mine drainages due to the ability of microorganisms to
492 generate alkalinity and immobilise metals⁷⁷. For instance, in the UK the sulphur-reducing
493 bacteria (e.g. *Desulfovibrio vulgaris*) has been used in the treatment of mine drainage due to
494 its diverse metabolic strategies to reduce sulphate (SO_4^{2-}) to hydrogen sulphide (H_2S) and
495 other elements like iron (Fe(III)), oxygen or compounds like nitrate and nitrite and fumarate⁷⁸.
496 Aquatic organisms such as diatoms and invertebrates have an important role as biomonitors
497 and bioindicators for assessing the impact of metal pollution. These organisms together with
498 established EU-WFD classification tools and diversity indices (e.g. ASPT, N-TAXA) were used
499 in a preliminary research in this catchment, however the effects of elevated metal levels were
500 unclear⁷⁹. Studies in neutral mine drainage carried out by Byrne et al.⁸⁰ indicated that the use
501 of standard macroinvertebrate biotic and diversity indices (EU-WFD tools) could lead to
502 erroneous classifications of aquatic ecosystem health. These results revealed that failure in
503 the interpretation of biogeochemical interactions could lead to inaccurate analysis of
504 organisms at risk of exposure, hence ineffective management decisions. Thus, the
505 assessment of metal effects in living organisms is complex since biota might have different
506 responses according to physiological processes and metals are subject to a range of factors
507 affecting their level of reactivity, toxicity and bioavailability¹⁵. Considering WFD goals, more
508 nuanced approaches are needed for assessing metals and their ecological effects. In this
509 context, current chemistry data and updated chemical speciation tools will be used in future
510 work to assess metal availability and toxicity and advising improvements to river basin
511 management plans.

512 **6. Conclusions**

- 513 • Underlying limestone bedrock controls pH and weathering reactions, and therefore metal
514 mobility within such catchments.
- 515 • Mobilisation of Zn and Pb have a strong dependence on site specific biogeochemistry and
516 hydrological conditions. No dependence of Zn with flow suggests that Zn_D has no kinetic
517 limitations on Zn mineral dissolution, whereas Pb_D varied according with flow variations,
518 reflecting its tendency to be complexed with colloidal or particulate forms.

- 519 • Point sources are regular contributors of Zn_D despite flow fluctuations, diffuse sources like
520 spoil wastes produced higher contribution of Zn_D and Pb_D in overflow conditions after dry
521 periods.
- 522 • Not all contributions of Zn_D and Pb_D are derived directly from oxidation of sphalerite and
523 galena. Mineralogical and geochemical analysis revealed the contribution of secondary
524 minerals such as smithsonite and cerussite, which are continuously leaching into the river
525 and represent an added complexity for future remediation.
- 526 • Metal pollution results in a large area of catchment having a depleted chemical status with
527 likely effects on the aquatic ecology.

528 **Acknowledgements**

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

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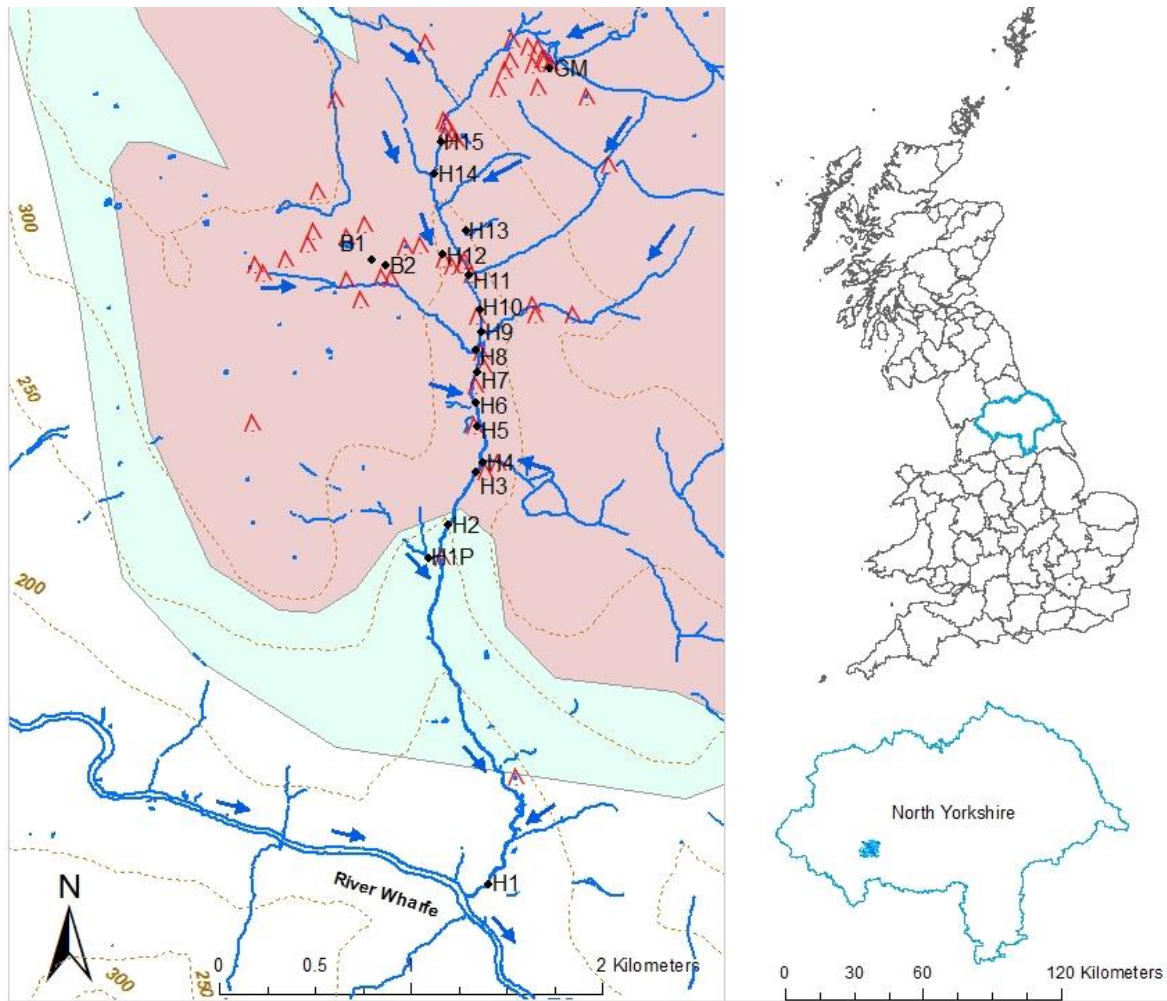
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701 **Figures and Tables**



Legend

- Sampling sites
- ▲ Mine structures (e.g. dressing floors, adits, shafts, smelt mills)
- Waterways
- - - Elevation (m)

Geology-Bedrock

- Millstone grit (mudstone, siltstone, sandstone)
- Liddesdale-Yoredale (limestone, sandstone, siltstone, mudstone)

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

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706 Table 1. Sampling sites along Hebden Beck. Table indicates type of sample, site elevation, coordinates,
 707 and distance from River Wharfe. Sites are listed from upstream to downstream. Locations adopted from
 708 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

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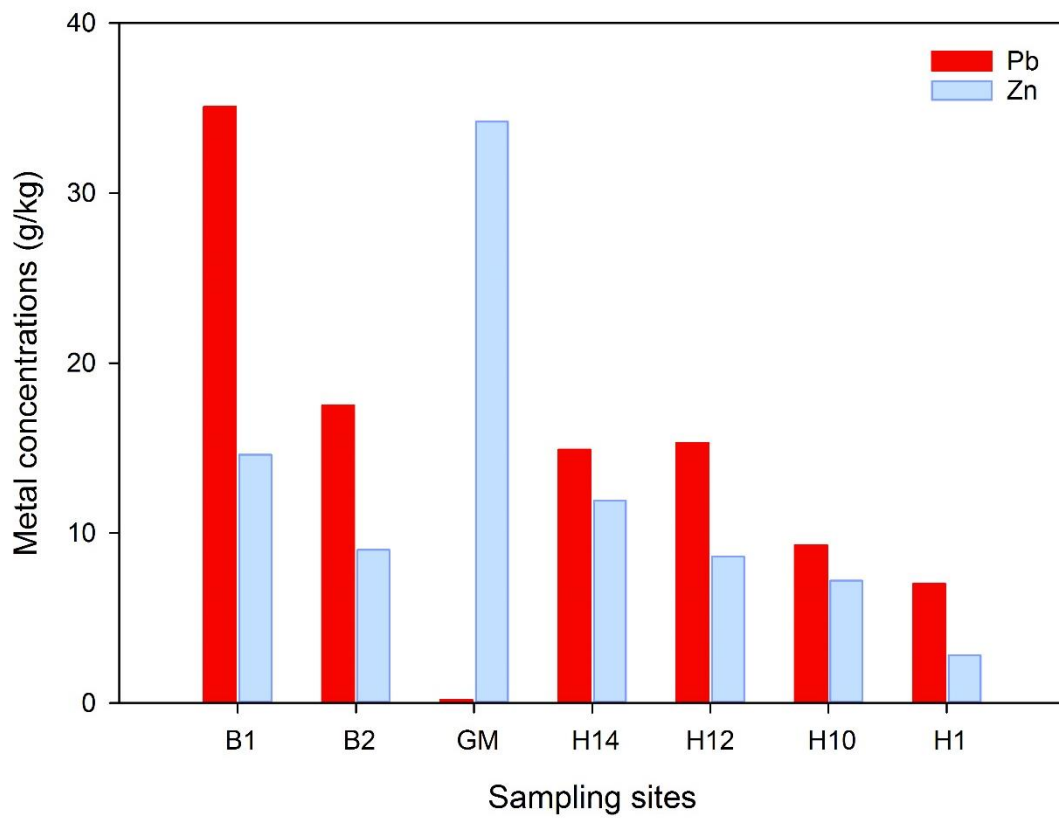
711 Table 2. Mean, maxima and minima from water chemical analysis. Metal forms are denoted as total (T)
 712 and dissolved (D). Description of sites are indicated as main channel (MC), ephemeral tributaries (ET)
 713 and perennial tributaries (PT). Units are in µg/l. Values below the detection limit are represented by
 714 (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

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

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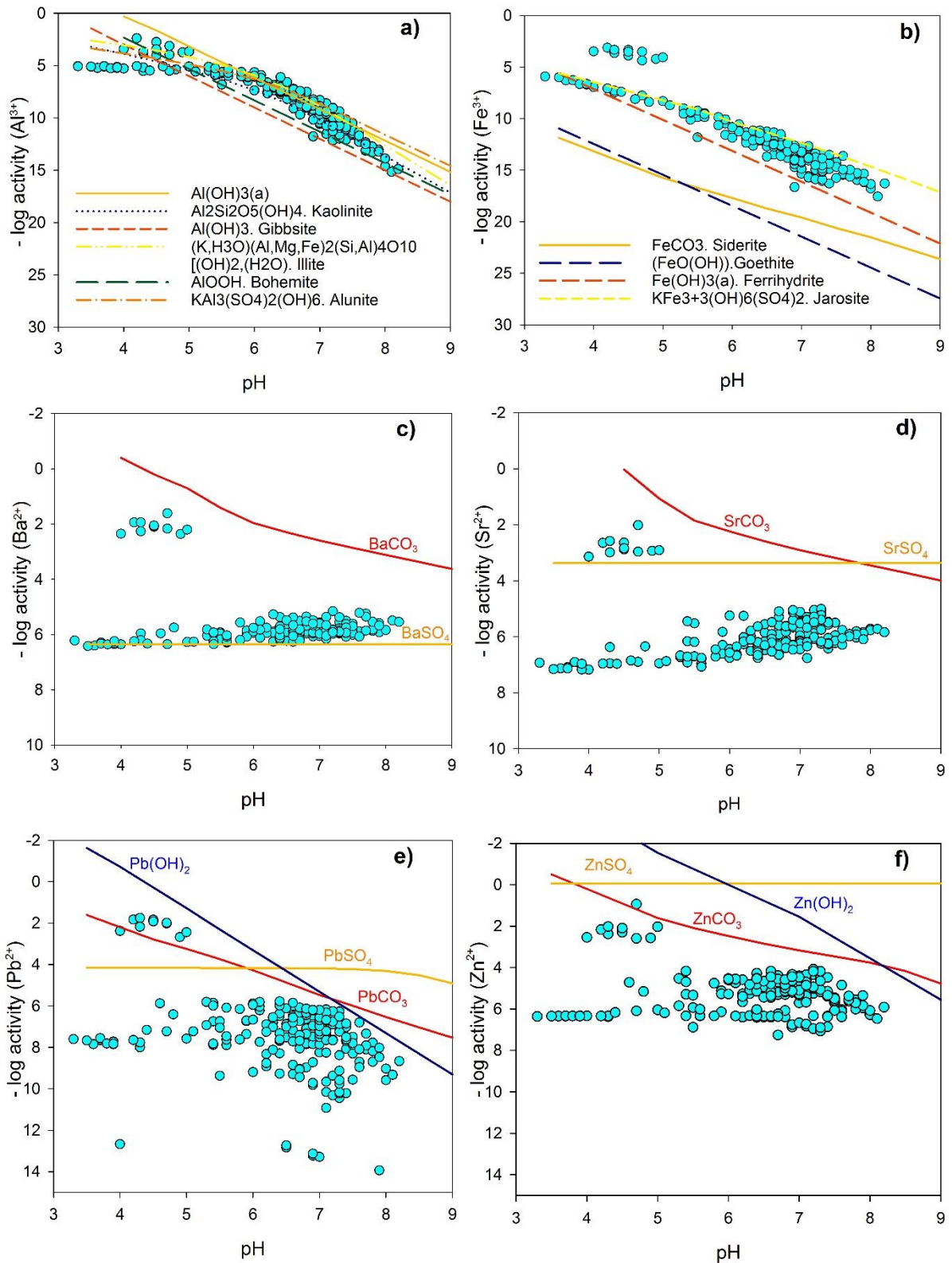
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739 Figure 3. Aluminium, Fe, Ba, Sr, Pb and Zn activity as a function of pH, SO_4^{2-} (13592 $\mu\text{g/l}$), Cl^- (7730
 740 $\mu\text{g/l}$) and $p\text{CO}_2 = 0.0012 \text{ atm}$. Theoretical saturation of mineral forms are represented by solid lines
 741 and calculated metal free ion activity of experimental data by dots.

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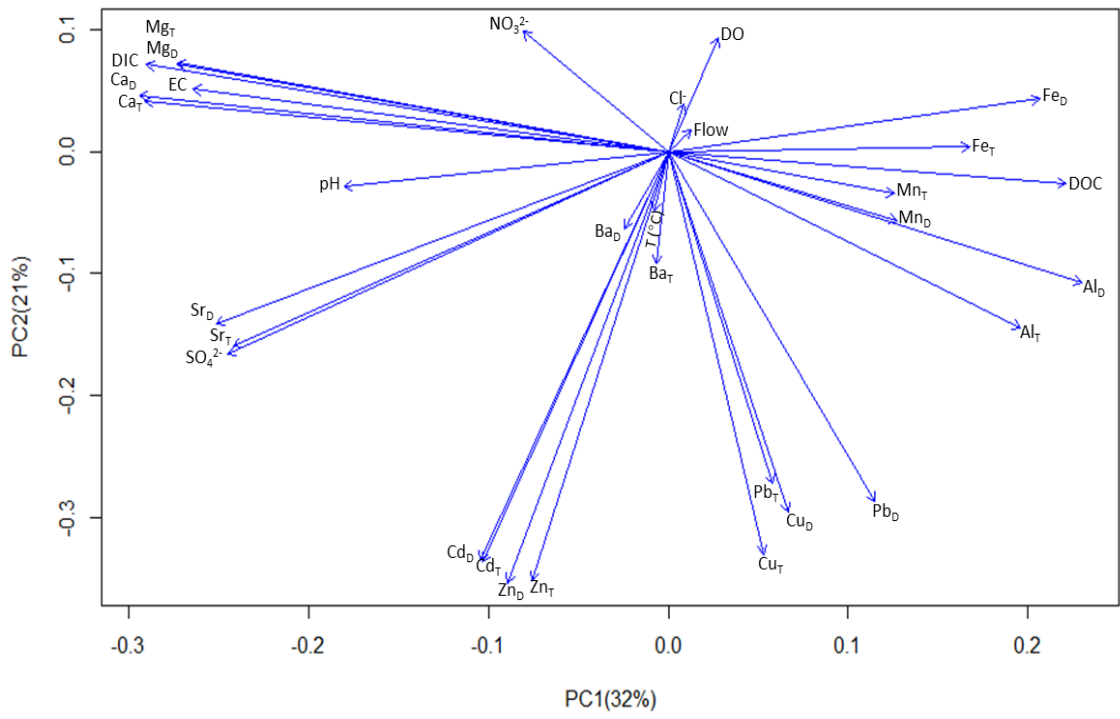
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Table 3. Relationships between metals (Pb, Zn, and Ca) with pH, SO₄²⁻, DIC and DOC. Pearson correlation coefficient is denoted as r, p-value as p and confidence interval (95%) as CI.

	Stats	pH	SO ₄ 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]

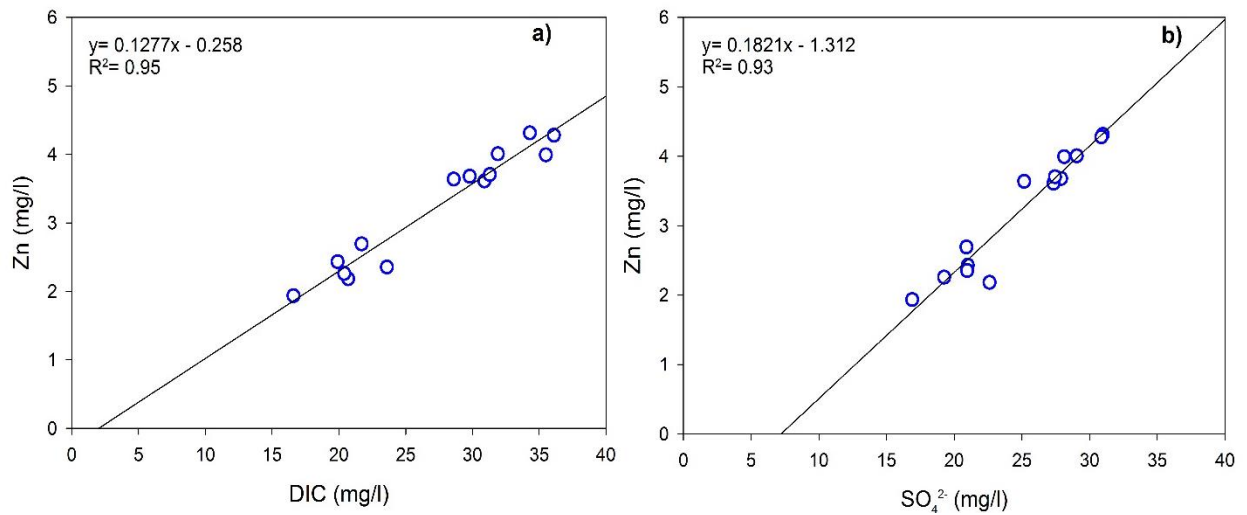
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765 Figure 4. Scree plot from PCA analysis, horizontal axis shows projections of the first principal
766 component PC1 which represents 32% of the total variance and the vertical axis the second component
767 PC2 representing the 21% of variance.

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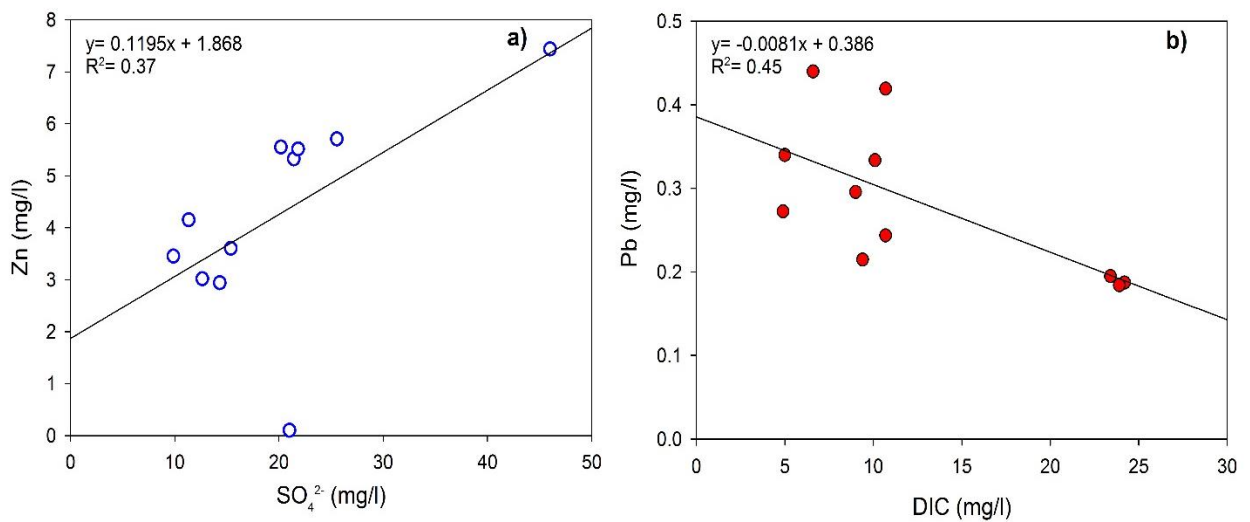


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771 Figure 5. Relationships in tributary H7 between Zn_D and DIC (left panel) and SO₄²⁻ (right panel).

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774 Figure 6. Relationships in tributary H12 between Zn_D with SO₄²⁻ and Pb_D with DIC.

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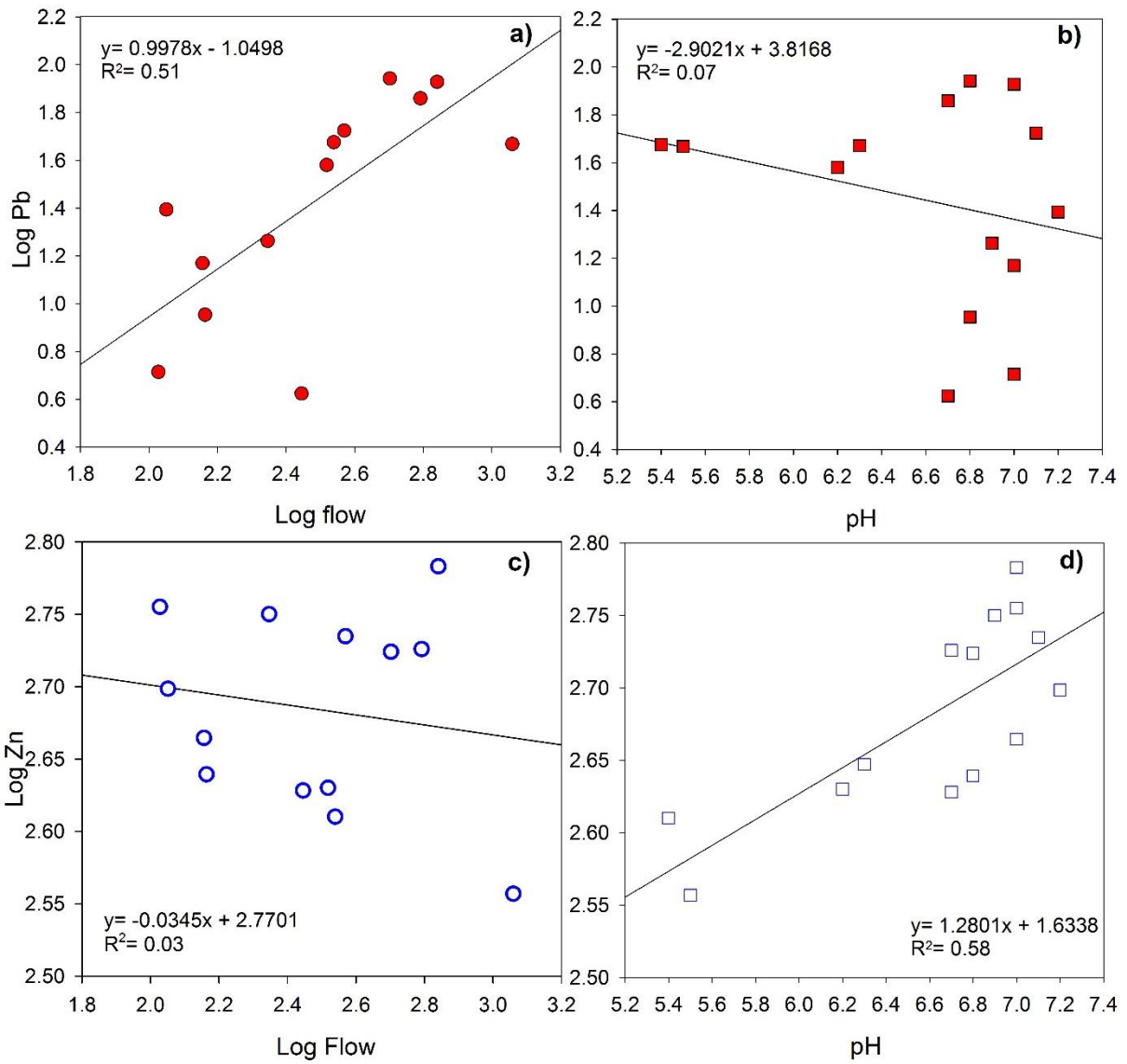
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788 Figure 7. Trends of metals in function of flow and pH in H2. Panel a and b show trends of Pb and panel
789 c and d indicate Zn trends. Solid lines represent regression lines.

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791 Table 4. Estimation of annual Pb and Zn load by using flow records from Environment Agency (EA)
 792 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
<i>EQS-Hardness based</i>		7.2		50.0	

793 a) Maximum values recorded in February 2014.

794 b) Minimum values recorded in July 2014.