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3 **Lead mobilisation in the hyporheic zone and river bank sediments of a contaminated stream:**
4 **contribution to diffuse pollution**

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18 **Abstract**

19 *Purpose* Past metal mining has left a legacy of highly contaminated sediments representing a significant diffuse
20 source of contamination to water bodies in the UK and worldwide. This paper presents the results of an
21 integrated approach used to define the role of sediments in contributing to the dissolved lead (Pb) loading to
22 surface water in a mining-impacted catchment.

23 *Materials and methods* The Rookhope Burn catchment, northern England, UK, is affected by historical mining
24 and processing of lead ore. Quantitative geochemical loading determinations, measurements of interstitial water
25 chemistry from the stream hyporheic zone, and inundation tests of bank sediments were carried out.

26 *Results and discussion* High concentrations of Pb in the sediments from the catchment, identified from the
27 British Geological Survey (BGS) Geochemical Baseline Survey of the Environment (GBASE) data, demonstrate
28 both the impact of mineralisation and widespread historical mining. The results from stream water show that the
29 stream Pb load increased in the lower part of the catchment, without any apparent or significant contribution of
30 point sources of Pb to the stream. Relative to surface water, the interstitial water of the hyporheic zone
31 contained high concentrations of dissolved Pb in the lower reaches of the Rookhope Burn catchment,
32 downstream of a former mine washing plant. Concentrations of 56 $\mu\text{g l}^{-1}$ of dissolved Pb in the interstitial water
33 of the hyporheic zone may be a major cause of the deterioration of fish habitats in the stream and be regarded as
34 a serious risk to the target of good ecological status as defined in the European Water Framework Directive.
35 Inundation tests provide an indication that bank sediments have the potential to contribute dissolved Pb to
36 surface water.

37 *Conclusions* The determination of Pb in the interstitial water and in the inundation water, taken with water Pb
38 mass balance and sediment Pb distribution maps at the catchment scale, implicate the contaminated sediments as
39 a large Pb supply to surface water. Assessment of these diffuse contaminant sources is critical for the successful
40 management of mining-impacted catchments.

41

42 **Keywords** Abandoned mines • Diffuse pollution • G-BASE • Hyporheic zone • Inundation test • Northern
43 Pennines, UK • Pb • Sediments

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45

46 **1 Introduction**

47 The importance of diffuse pollution sources in abandoned mine-impacted river catchments and their potential to
48 affect water quality and ecology has been fully recognised (Caruso and Ward 1998; Kimball et al. 2002;
49 Balistrieri et al. 2007; Mayes et al. 2008; Mighanetara et al. 2009; Banks and Palumbo-Roe 2010; Gozzard et al.
50 2011). These dispersed sources of acidity and dissolved metal load to surface water arise from seepage and
51 runoff from mine waste, contaminated groundwater inputs through the hyporheic zone and remobilization of
52 previously deposited metal-rich particles in stream channels and floodplains. As such, they pose considerable
53 barriers to compliance with the demands of the EU Water Framework Directive (WFD) and represent a major
54 management issue for the mining industry worldwide (Baresel et al. 2007; Coetser et al. 2007). Failing to
55 account for these dispersed sources of pollutant loading in a catchment can severely reduce the effectiveness of
56 point source remediation directed to the treatment of mine water discharges.

57 Past mining operations in England and Wales (UK) have left a substantial legacy of highly contaminated
58 sediments in rivers that extend many kilometres downstream of the mines (Macklin et al. 2006). The erosion,
59 transport and deposition of historically contaminated alluvium are very important sources of sediment-borne
60 metals in all mining-affected river systems in England and Wales (Hudson-Edwards et al. 2008). Re-suspension
61 of these sediments during floods has the potential to cause additional harm to aquatic life, and to contaminate
62 floodplain soils used for agriculture. Furthermore, the changes in water chemistry following the remediation of
63 mine drainage sources could result in an enhanced release and remobilisation of metals from the sediments
64 (Butler 2009). However, few attempts have been made to determine the fluxes of metals to surface water
65 associated with contaminated sediments. This paper describes the role of sediments in contributing to the
66 loading of dissolved Pb to surface water in the Rookhope catchment, northern England. The catchment has been
67 affected by historical mining and processing of lead (Pb) and zinc (Zn) ore and is representative of several
68 catchments affected by the environmental legacy related to mining in the Northern Pennine Orefield, northern
69 England. The catchment has recently been highlighted in a national review as one of the most severely mine-
70 impacted (in terms of water quality) in England and Wales (Mayes et al. 2009).

71

72 In order to estimate the sediment contribution to the diffuse dissolved Pb loading in the catchment waters, the
73 investigation consisted of three parts: i) quantification of the diffuse dissolved metal load along the stream using
74 a chemical mass balance approach; ii) collection of evidence of the sediment contribution to the diffuse load by
75 sampling bed sediments and sediment interstitial water in the hyporheic zone of the stream; and iii) laboratory
76 inundation tests of the river bank sediments.

77

78 **2 Study site**

79 The Rookhope Burn catchment in County Durham, Weardale, occupies an area in the order of 37 km². The
80 southerly flowing stream contributes a discharge ranging from 100 to 2300 l s⁻¹ to the River Wear at Eastgate

81 (Fig. 1). The annual effective rainfall is in the order of 1000 mm, with monthly contributions varying between
82 53 and 116 mm. Flow conditions in the stream give rise to a flashy hydrograph and storm events are transmitted
83 rapidly through the catchment.

84

85 The upper part of the Rookhope Burn catchment has been incised in Namurian sandstones and mudstones of the
86 Stainmore Formation (Yoredale Group). Its source is in grouse moorlands at an elevation of about 600 m
87 Ordnance Datum (OD). The middle portion of the catchment comprises a relatively treeless landscape
88 characteristic of the mining heritage of the area and is largely utilised for hill farming. The bedrock in this part
89 of the catchment comprises the interbedded shales and sandstones of the lower part of the Stainmore Formation.
90 Evidence of the former mining comes from: the scars of abandoned quarries, formerly exploited for iron ore and
91 building stone; galena and fluorspar mines, that occur in the rakes and flats; piles of mine waste; abandoned
92 mine buildings; and former tailings lagoons. The mine workings extend into the lower part of the catchment, but
93 here they are interspersed with karst features including dolines and springs, which have developed in the
94 limestones of the basal part of the Stainmore Formation. The more resistant Alston Formation bedrock (basal
95 formation of the Yoredale Group) gives rise to a number of waterfalls towards the base of the catchment, which
96 contrasts with the karstic nature of the till-covered limestones immediately to the north.

97

98 Superficial deposits and mine-reworked sediments are distributed widely throughout the channel, with only
99 local outcrops of bedrock in the bed of the stream. To date, no detailed geomorphological studies of the
100 catchment have been undertaken. However, both field evidence and studies of historic maps of an adjacent
101 catchment (Swinhope Burn; Warburton et al. 2003) would suggest that stretches of the stream channel with a
102 low gradient may change in response to floods and changes in sediment supply. There is also evidence of bank
103 instability alongside specific stretches of the stream. Another source of potential instability is mine outbursts,
104 resulting from underground collapse. Sediment mobilisation can be important in exposing fresh minerals to
105 weathering (Hudson-Edwards et al. 2008)

106

107 **3 Methods**

108 **3.1 Surface water sampling and mass balance calculations**

109 The surface water data include flow monitoring and chemical data for inflows and instream waters throughout
110 the catchment (Fig. 1). Full description of the water sampling can be found in Banks and Palumbo-Roe (2010).
111 Results from Banks and Palumbo-Roe (2010) are supplemented by a further sampling event (April 2009) and re-
112 analysis of waters for Pb by Inductively Coupled Plasma Atomic Mass Spectrometry (ICP-MS). Re-analysis
113 was undertaken as previous results by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)
114 were reported at or around the ICP-AES method detection limit (0.010 mg l^{-1}). Chemical data and major
115 physico-chemical parameters were used to calculate saturation indices (SI) for relevant mineral phases using
116 PHREEQC (Parkhurst and Appello 1999) and the WATEQ4f database (Ball and Nordstrom 1991).

117 The surface water metal load distribution along the Rookhope Burn was calculated from the product of the flow
118 and element concentration. Sources and sinks of dissolved Pb along the Rookhope Burn were determined using
119 a mass balance approach. A mass balance determines the element that is gained or lost in a stream stretch by
120 comparing the amount of the element that enters a stream segment with the amount that leaves the same

121 segment, based on the assumption that the load at the end of a stream segment includes the load from the point
122 upstream plus the contribution from all surface and subsurface inflows along the stream segment.

123

124 **3.2 Sediments and sediment interstitial water sampling and analysis**

125 The sampling locations were selected from the findings of the first phase of investigation (Banks and Palumbo-
126 Roe 2010). Specific features associated with these locations are summarised in Table 1. Bed sediment samples
127 were collected along the Rookhope Burn (see Fig. 1) during the week of May 11-15 2009, during low river flow
128 conditions. Points HZ-0 and HZ-A0 represent two sampling sites not impacted by mining activities and each is
129 characterised by a different underlying geology. Sediment chemical analysis on the <150µm fraction was carried
130 out using mixed acid digestion (HF/HClO₄/HNO₃) and ICP-AES. The pH was analysed by a CaCl₂/slurry
131 method, organic matter content by loss-on-ignition (LOI) at 450°C, and mineralogical analysis using X-ray
132 Diffraction (XRD).

133 At each location, the interstitial water from the hyporheic zone of the stream was collected using a low-flow
134 inertial pump from a 50 mm diameter stainless-steel piezometer inserted 30 cm into the streambed sediments.
135 The overlying surface water was also sampled at each sampling point. 0.45 µm filtered water samples, acidified
136 to 1% HNO₃, were analysed by ICP-MS. The water pH and Eh were measured in the field using hand-held
137 Hannah combination HI 9125 meters with associated probes. The Pt electrode Eh measured values were
138 corrected to the Standard Hydrogen Electrode.

139 Additionally, 41 sediment Pb analyses were retrieved from the British Geological Survey (BGS) Geochemical
140 Baseline Survey of the Environment (GBASE) database. Sediments were collected from the active drainage
141 channel of first or second order streams as part of a national geochemical survey at a sampling density of one
142 sample every 1-2 km² on average. G-BASE field procedures and sediment analysis are documented in Johnson
143 et al. (2005).

144

145 **3.3 Bank sediment inundation test**

146 Duplicate samples of bank sediments were collected for sites HZ-11, HZ-16 and HZ-23. The Rookhope Burn
147 stream water collected at the footbridge in the Rookhope village (co-ordinates 393750 542840) at the time of the
148 sediment sampling was used to flood the sediments. The organic carbon concentration of the stream water
149 sample, measured as non-purgeable organic carbon, was 2.57 mg l⁻¹, the pH was 7.82 and the Pb concentration
150 was 0.7 µg l⁻¹.

151 About 50 g of each sediment sample was submerged with 500 ml of Rookhope stream water and inundated for a
152 3 month (88 day) period in a laboratory-scale inundation test. Filtered (0.45µm) samples of the overlying water
153 column were collected at 1, 7, 28 60 and 88 days of inundation after gently stirring the inundation water without
154 disturbing the sediment at the interface. These were analysed for major and trace anions and cations by ICP-MS.
155 The pH and Eh of the inundation water were measured at the same time. The porewater for each replicate was
156 collected for analysis by centrifugation at 3000 G at the conclusion of the 88 day inundation period.

157

158 **4 Results and discussion**

159 **4.1 Surface water lead load distribution**

160 Fig. 2 shows the Pb concentration profile along Rookhope Burn as dissolved Pb concentration in the surface
161 water ($\mu\text{g l}^{-1}$) and Pb load (mg s^{-1}) for three sampling events. There were large differences in concentrations in
162 the three sampling events, but similar patterns across the catchment. The greatest increase in the dissolved Pb
163 concentration (see Fig. 2) occurred from the headwaters to point 3, downstream of Grove Rake Mine (the last
164 lead and fluorspar workings to close in 1999; Johnson and Younger 2002). Farther down the catchment,
165 dissolved Pb displayed lower concentrations.

166 The Pb load profile displayed discrete peaks, for all three sampling events, partly in response to visible point
167 contributions from mine waters and seepage from mine spoils (see Fig. 2). In contrast with a commonly
168 observed attenuation of dissolved metals downstream from the pollution source – due to dilution, dispersion,
169 precipitation and adsorption processes (Chapman et al. 1983) – the Pb load steadily increased, generally from
170 point 16 towards the lower part of the catchment. From sampling points 23 to 25, mass balance calculations
171 (Table 2) indicated a net load increase ranging from 27% to 97% in the three sampling events (the variability of
172 the load increase is attributed to antecedent conditions prior to the sampling events, with greater load increases
173 occurring in response to rainfall events). In this lower part of the catchment, the influence of tributaries or point
174 sources was found negligible in terms of metal load contribution, strongly suggesting a dispersed input of Pb.

175

176 **4.2 Lead concentrations in bed sediments**

177 The sediment mineralogical composition was dominated by the presence of quartz (c. 58–76%), with additional
178 contributions from mica (c. 9–14%), fluorite (c. 2–12%), kaolin (c. 2–5%) and chlorite (c. 2–3%). Bank and bed
179 sediment samples at location HZ-21 and HZ-23 were noticeably different, because of the presence of a small
180 percentage (<3%) of calcite, cerussite (PbCO_3), dolomite, galena (PbS), and sphalerite (ZnS). The Pb carbonate
181 mineral phase cerussite is a common weathering product of Pb-sulphides in high pH/ pCO_2 limestone-dominated
182 source terrains, as evidenced by Hudson-Edwards et al. (1996).

183 The pH of the sediment samples ranged between 5.90 and 7.34. The organic matter content, as measured by
184 LOI, was low, with concentrations ranging between 3.0% and 4.2%. The two control sites – point HZ-0 and
185 point HZ-A0, located, respectively, in the head of the Rookhope catchment and in the lower part of the
186 catchment in a tributary not impacted by mining – had Pb concentrations of 97 and 825 mg kg^{-1} , respectively
187 (Table 3). Lead concentrations in the sediment samples along the burn increased from 1610 to 15,350 mg kg^{-1} .
188 Commonly, sediment contamination is noticeable immediately downstream from discrete point sources and
189 decreases in a downstream direction, due to the effect of hydraulic sorting and dilution by uncontaminated
190 sediment from tributaries (Pulford et al. 2009). However, in the Rookhope catchment, as illustrated in the
191 GBASE sediment Pb distribution map (see Fig. 1), many tributaries, some of which are unaffected by mining,
192 had elevated Pb contents in the sediments. The observed increased concentrations in a downstream direction,
193 therefore, reflected both the impact of the widespread historical mining and of mineralisation. The high Pb
194 concentrations at the control site HZ-A0 can also be related to high background values of mineralised areas.

195

196 **4.3 Lead concentrations in the interstitial water of the hyporheic zone**

197 The pore water from the stream hyporheic zone had near neutral pH except for site HZ-0, where the low pH of
198 4.83 reflected the peaty upland location and the more acidic bed sediments (Table 3). Full chemical analysis and
199 selected physico-chemical parameters of the hyporheic zone pore water and overlying surface water are reported

200 in [Online Resource 1](#). Redox measurements indicated prevailing oxidising conditions in the hyporheic zone at
201 the time of the sampling. This is common for bed sediments in upland reaches, where surface water–hyporheic
202 zone exchanges are maximised due to sediment with larger particle sizes and hence higher permeability,
203 compared to lowland rivers (Bencala 2011).

204 Lower concentrations of Zn together with Mn and Fe were measured in the hyporheic zone compared to surface
205 water ([Online Resource 1](#)). This has been attributed to natural attenuation of dissolved Zn through a mechanism
206 of precipitation/adsorption onto newly-formed manganese (Mn) and iron (Fe) oxyhydroxides on the stream bed
207 sediments of the Rookhope Burn (Palumbo-Roe et al. 2010). Vice versa, dissolved Pb concentrations were
208 enriched in the hyporheic zone compared to surface water and mine water samples ([Fig. 3](#)), clearly showing a
209 distinct pattern from dissolved Mn, Fe and Zn, and possibly reflecting different metal–sediment association
210 and/or release models. Because both surface water and mine water Pb concentrations were lower than those in
211 the hyporheic zone, only the contaminated sediments could act as a source of dissolved Pb and account for the
212 observed metal enrichment in the interstitial water of the hyporheic zone.

213
214 Many studies of mining-affected river sediments, both in UK and elsewhere in the world (Filipek et al. 1981;
215 Macklin and Dowsett 1989; Byrne et al. 2010), highlight the association of Pb with Mn and Fe oxyhydroxides
216 and indicate remobilisation of sediment-bound metals as governed by chemical sorption-desorption processes or
217 reductive dissolution. The hyporheic zone, in particular, can be characterised by steep physico-chemical
218 gradients highly favouring biogeochemical processes including oxidation-reduction (Benner et al. 1995).
219 However, in this study the hyporheic zone redox conditions were shown to be too high for the Mn and Fe
220 oxyhydroxides to become unstable ([Online Resource 1](#)) and reductive dissolution cannot be invoked to explain
221 the high pore water Pb concentrations (up to $56 \mu\text{g l}^{-1}$) at point HZ-21 and HZ-23 in the lower reaches of the
222 Rookhope catchment, in contrast to the control sites and upstream points HZ-11 and HZ-16 ($<9 \mu\text{g l}^{-1}$). The lack
223 of a similar enrichment in dissolved Mn and/or Fe in the pore water supports this conclusion.

224 The pore water Pb concentration of HZ-21 and HZ-23 was found close to saturation with respect to cerussite
225 ($SI_{\text{PbCO}_3} = -0.56$ and -0.77 for HZ-21 and HZ-23, respectively) and the mineral phase was identified by
226 mineralogical analysis, suggesting that the Pb carbonate mineral may control the pore water concentration.
227 Physical factors in affecting solute composition, such as the importance of particle size, need to be evaluated in
228 future work.

229
230 The hyporheic water composition can affect downstream water quality and be significant at the catchment scale
231 providing that sufficient connectivity between surface water and the hyporheic zone exists to allow stream–
232 hyporheic solute exchanges (Harvey and Fuller 1998). Stream water infiltrates the shallow channel bed and
233 banks, flows following the general gradient, and then returns to the stream with flow patterns variable in time
234 and scale depending on variation in stream and catchment geomorphic and geologic features, such as hydraulic
235 conductivity, alluvial volume, and streambed slope (Bencala 1984). In the case of our study catchment, the
236 poorly sorted sandy, gravelly stream sediment would favour hyporheic flows and solute exchanges.

237

238 **4.4 Lead behaviour during river bank sediment flooding**

239 Bank sediments from sites HZ-11, HZ-16 and HZ-23 had total Pb concentrations of 1350, 975 and 29,515 mg
240 kg⁻¹, respectively. The rate of release curve for Pb during the 88 days sediment flooding is shown in Fig. 4, with
241 the Rookhope Burn Pb concentration used as inundation water at time zero as the starting point. The overlying
242 water column remained oxidised during the entire period of inundation. The Eh increased with time and ranged
243 between c. 465-550, 410-560 and 425-535 mV, for samples HZ-11, HZ-16 and HZ-23, respectively. The pH of
244 the inundation water was immediately reduced, by c. 0.2 to 0.8 pH units, by the introduction of the Rookhope
245 stream sediments over the first 24 hours of the study. Over the first 28 days of the inundation test, the pH of the
246 flood water became more acidic, in general reaching a plateau after a 28 day inundation period. Sample HZ-11
247 had the greatest impact on the pH of the Rookhope stream water, reducing the pH by the largest amount, c. 1 pH
248 unit in total, and maintaining a solution pH below 7 after the 28 day inundation period. Samples HZ-16 and HZ-
249 23 maintained a pH above 7 throughout the inundation period.

250 The laboratory simulated flooding of river bank sediment samples from sites HZ-11, HZ-16 and HZ-23 caused a
251 substantial increase in dissolved Pb in the overlying water column during the first day of inundation. Sediment
252 from site HZ-23 continued to release Pb throughout. The final Pb average concentration in the water column for
253 this sampling point was 395±12.5 µg l⁻¹. For the other sediment samples, after an initial solubilisation, a distinct
254 dip in the amount of dissolved Pb was observed at around 28 to 60 days, after which point a further
255 solubilisation of Pb was noted, reaching 1.1±0.1 µg l⁻¹ for Point HZ-11 and 2.05±0.05 µg l⁻¹ for Point HZ-16 at
256 the end of the inundation period. The sediment pore water sampled at the end of the experiment contained Pb
257 concentrations of 15±0.01 µg l⁻¹ for Point HZ-11, 5.35±0.6 µg l⁻¹ for Point HZ-16 and 491±0.1 µg l⁻¹ for Point
258 HZ-23. XRD evidence of the presence of cerussite in the sediment from sampling site HZ-23 coupled with the
259 saturation index (close to saturation with respect to cerussite), suggested that this phase may control Pb
260 solubility during the sediment flooding.

261 It is worth noticing that temporal changes in surface water pH can be substantial in metal mining-impacted
262 catchments, as shown in the case of the adjacent Allen catchment with a fall in instream pH of approximately 1
263 unit between baseflow and highflow conditions (Gozzard et al. 2010), and of the Afon Twymyn in central
264 Wales, UK, with a decreased river water pH during rain-fed flood events (Byrne et al. 2009). When estimating
265 sediment bound-metal mobilisation during flooding, this potential decrease in surface water pH should be
266 accounted for, due to the inverse pH-dependency of solubility of metal-bearing phases. The results of the
267 inundation test using baseflow river water samples may underestimate the potential Pb remobilisation under
268 field conditions. Nevertheless, these results demonstrate that the sediments can act as a significant source of
269 dissolved Pb to the overlying water column through a diffusion mechanism, simulated in the experiment, driven
270 by the element concentration gradients across the sediment–water interface.

271

272 **5 Conclusions**

273 In contaminated rivers and streams, reductions in surface water contamination due to metal dilution and
274 dispersal are often observed downstream of point sources of contamination, particularly in circum-neutral and
275 alkaline waters, such as the Rookhope Burn waters, where natural attenuation processes through chemical
276 sorption or co-precipitation of metals like Pb are enhanced. Deviations from these decreasing trends downstream
277 of point source pollution are due to inputs of contaminants from diffuse sources. This is the case in the

278 Rookhope Burn where the Pb load increased steadily down the catchment, without any apparent contribution of
279 point sources of Pb to the stream.

280 The widespread contaminated bed sediments and hyporheic zone Pb-enriched pore water are considered
281 important as a source of Pb to the water column. This study also shows the potential for diffuse flux of Pb out of
282 the contaminated bank sediments during simulated flooding or stagnant conditions.

283 Characterising these diffuse contaminant sources is important for managing basins to achieve good ecological
284 status and to optimise remediation strategies. Despite the relatively low Pb concentrations in surface water, the
285 measured concentrations in the sediment interstitial water introduce toxic levels into the habitat for aquatic
286 invertebrates and may thereby be a major cause of the deterioration of fish habitats in the stream, representing a
287 significant barrier to the target of good ecological status as defined in the European Water Framework Directive.

288

289

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372 **Table 1** Hydrological setting of the sampling locations, Rookhope Burn catchment, northern England, UK

Locality Reference	National Grid Reference	Description
HZ-0	387597-545057	Peat upland. Boulders in river bed.
HZ-11	391661-542747	Alluvium. Broad stretch of river, meandering. Cobble and boulder grade gravel.
HZ-16	392747-542957	Alluvium. Straight stretch of river; minor steps in channel cobbles and boulders.
HZ-21	393809-542627	Alluvium over till. Downstream of Boltsburn Mine washing plant. Cobbles and boulders in bed. Anthropogenic influence evident. Broad.
HZ-23	394203-542016	Alluvium over till. Channel more constrained. Tree cover. Boulders in bed.
HZ-A0	394410-541554	Till over limestone. Tributary stream. Cobbles and boulders in bed of stream.

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375 **Table 2** Mass balance of dissolved lead (Pb) loads for Rookhope stream segments to the base of the
376 catchment for the sampling events from years 2007-2009 inclusive

Stream stretch	Net change in Pb load		
	Jun-07 (mg s ⁻¹)	Jan-08 (mg s ⁻¹)	Apr-09 (mg s ⁻¹)
1-3	10.3	1.6	0.2
3-5	-2.9	0.6	0.3
5-6	2.0	1.8	-0.4
6-9	8.4	-0.5	0.2
9-11	0.8	3.3	0.1
11-13	2.9	-0.9	-0.1
13-16	-8.1	-0.9	0.3
16-19	10.5	2.9	-0.3
19-21	4.8	4.1	0.5
21-23	5.9	-3.9	0.6
23-25	9.7	8.0	0.6

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380 **Table 3** Analysis of lead (Pb) and pH of surface water, hyporheic zone pore water and bed sediments
 381 along the Rookhope Burn catchment

	Point HZ-0	Point 11/HZ-11	Point 16/HZ-16	Point 21/HZ-21	Point 23/HZ-23	Point HZ-A0
Surface water						
pH	6.22	7.02	6.87	7.33	7.25	6.88
Pb $\mu\text{g l}^{-1}$	0.96	6.15	3.78	2.80	4.56	1.37
Hyporheic zone water						
pH	4.83	7.07	6.77	7.16	6.84	6.87
Pb $\mu\text{g l}^{-1}$	4.91	8.89	4.51	55.6	43.0	3.53
Bed sediments						
pH	5.89	7.01	7.27	7.34	7.33	7.18
Pb mg kg^{-1}	96.5	1610	1978	2086	15346	825

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386 **Figure captions**

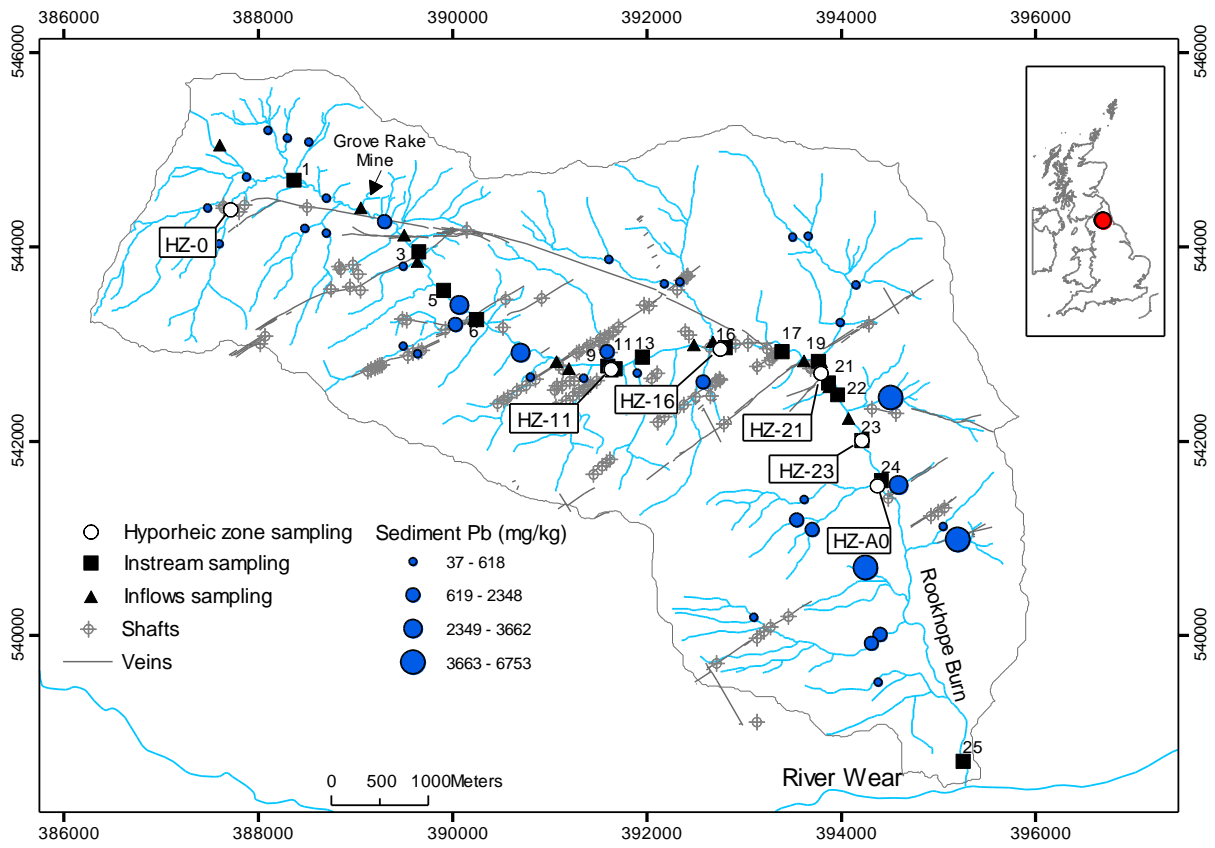
387 **Fig. 1** Location map of sampling points and spatial distribution of lead (Pb) in sediments of the Rookhope Burn
388 catchment, UK (data from British Geological Survey (BGS) Geochemical Baseline Survey of the Environment –
389 GBASE database).

390 **Fig. 2** Distribution of dissolved lead (Pb) concentration ($\mu\text{g l}^{-1}$) and Pb loads (mg s^{-1}) along the Rookhope Burn
391 for three sampling events over years 2007-2009. The x-axis shows the distance from the headwaters down the
392 catchment. Sampling points along the catchment are identified by closed square symbols. Inputs from visible
393 point sources of Pb from contributing tributaries and mine adits are identified by closed triangles (high Pb
394 concentrations of tributary stream receiving mine spoil seepage for June 2007 and Jan 2008 sampling events are
395 reported against secondary y-axis with open triangle symbol).

396 **Fig. 3** Lead (Pb) concentration distribution in the hyporheic zone (HZ) pore water (n=6), in surface water (SW)
397 (n=6) and in mine waters (MW) (n=4) sampled in the Rookhope Burn catchment. Mine water data as reported in
398 Banks and Palumbo-Roe (2010).

399 **Fig. 4** Lead (Pb) release rate curves and pore water concentrations for river bank sediments at sampling points
400 HZ-11, HZ-16 and HZ-23, with data for sample at point HZ-23 plotted on the secondary y-axis. The error bars
401 displayed were calculated as the absolute difference between the duplicates, where the data point is the mean
402 duplicate value.

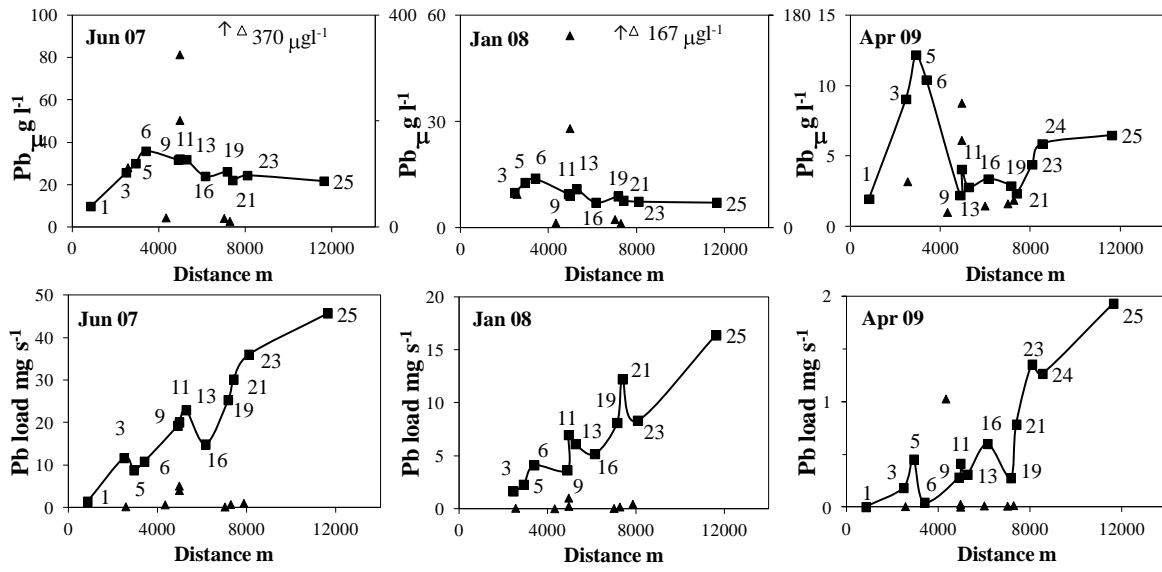
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406 **Figure 1**

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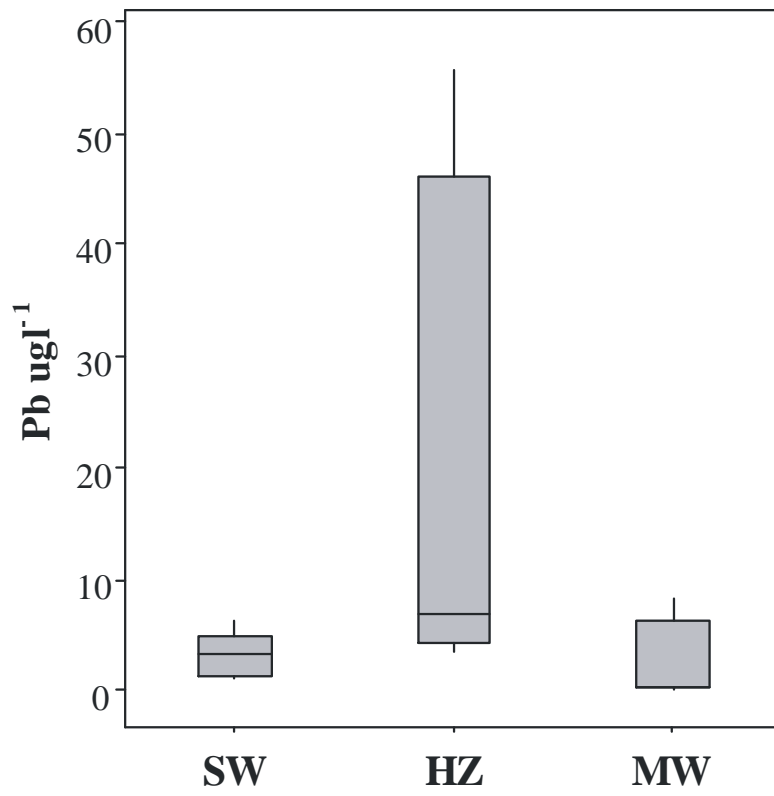


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410 **Figure 2**

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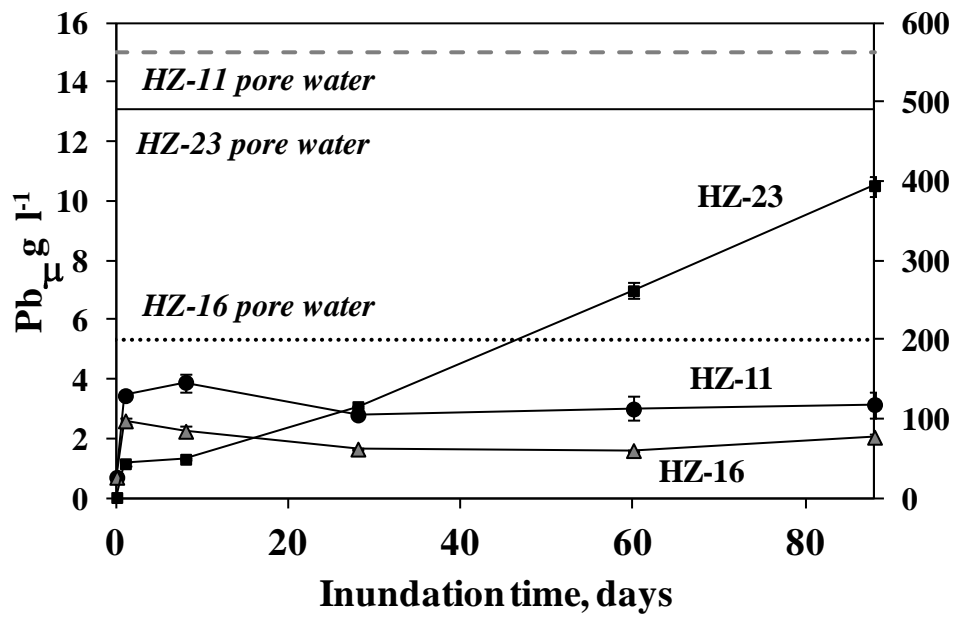
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414 **Figure 3**

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ELECTRONIC SUPPLEMENTARY MATERIAL

IASWS 2011: THE INTERACTIONS BETWEEN SEDIMENTS AND WATER

Lead mobilisation in the hyporheic zone and river bank sediments of a contaminated stream: contribution to diffuse pollution

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Table ESM 1 Chemical analysis and physico-chemical parameters of hyporheic zone pore water (HZ) and overlying surface water (SW) along the Rookhope Burn on 11th May 2009

Point		T	Eh	pH	Cond	HCO ₃ ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	F ⁻	NPOC	Total P	Si	Ba	Sr	Mn	Total Fe	As	Cd	Cu	Ni	Pb	Zn
		°C	mV		µS cm ⁻¹	mg l ⁻¹															µg l ⁻¹					
HZ-0	SW	9.68	349	6.22	52.0	9.68	4.58	1.27	3.74	0.557	4.91	2.78	0.051	8.82	<0.003	1.27	0.013	0.020	0.067	0.558	0.396	0.024	1.69	2.37	0.956	10.7
	HZ	10.4	406	4.83	48.0	<5.00	3.20	1.12	4.36	0.913	5.25	4.21	0.076	8.52	0.010	1.30	0.014	0.015	0.757	1.14	0.511	0.057	8.30	5.28	4.91	45.9
HZ-11	SW	9.13	268	7.02	333	65.4	43.0	7.79	7.17	3.60	9.97	75.4	2.19	3.14	<0.003	2.10	0.014	0.154	1.44	0.419	0.391	0.549	2.59	17.9	6.15	566
	HZ	9.44	257	7.07	333	71.4	42.9	8.01	7.38	4.05	10.0	73.9	2.22	2.84	0.041	2.01	0.011	0.155	0.366	0.149	0.360	0.459	3.39	12.5	8.89	472
HZ-16	SW	14.6	560	6.87	331	80.2	41.1	7.22	7.53	3.23	10.9	62.8	1.78	2.59	<0.003	1.99	0.015	0.156	0.890	0.276	0.274	0.323	1.08	10.9	3.78	269
	HZ	14.6	483	6.77	340	87.0	49.4	7.29	8.61	4.47	12.4	62.4	2.18	4.77	0.006	2.12	0.014	0.193	0.008	0.030	0.332	0.061	2.22	2.87	4.51	28.9
HZ-21	SW	9.53	456	7.33	341	96.5	45.1	7.38	9.53	3.39	11.2	60.3	1.62	2.24	<0.003	2.25	0.016	0.186	0.610	0.165	0.333	0.220	1.33	7.64	2.80	196
	HZ	10.1	423	7.16	348	99.0	45.7	7.18	9.80	3.69	12.1	62.5	1.78	2.35	0.004	2.28	0.016	0.198	0.091	0.299	0.645	0.178	4.25	4.97	55.6	82.3
HZ-23	SW	14.1	440	7.25	365	107	47.0	8.24	8.99	3.20	10.8	61.9	1.43	2.30	<0.003	2.23	0.015	0.217	0.352	0.157	0.323	0.181	1.24	5.41	4.56	117
	HZ	16.2	381	6.84	355	174	59.5	4.41	5.46	1.59	6.30	17.8	1.64	1.25	0.001	2.30	0.023	0.286	0.198	0.031	0.269	0.360	8.12	4.23	43.0	71.1
HZ-A0	SW	9.76	368	6.88	162	72.3	21.7	4.06	5.72	1.77	7.31	8.26	0.154	2.72	0.010	2.23	0.015	0.093	0.004	0.112	0.200	0.012	1.40	1.04	1.37	2.73
	HZ	10.2	471	6.87	175	70.8	22.5	3.87	5.56	1.90	7.52	8.38	0.176	2.72	0.015	2.18	0.015	0.089	0.003	0.069	0.228	0.008	2.04	1.42	3.53	2.13