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Environmental risk of severely Pb-contaminated riverbank sediment as a consequence of hydrometeorological perturbation

S.F.L. Lynch^{a,*}, L.C. Batty^a, P. Byrne^b

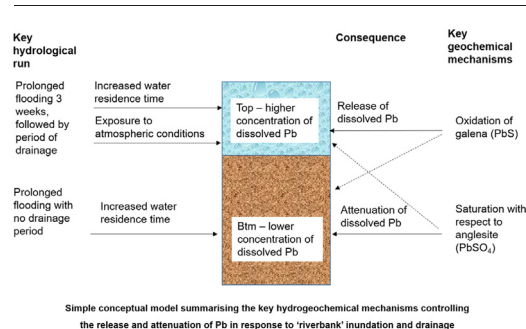
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HIGHLIGHTS

- Environmental factors controlling diffuse pollution are currently seen as a “black box”.
- Two mesocosm experiments were designed to mimic the riverbank environment.
- High concentrations of dissolved Pb were released, due to the oxidation of galena.
- Solubility of Pb sulphate mineral anglesite had little control over dissolved Pb concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

Metal mining activities have resulted in the widespread metal pollution of soils and sediments and are a worldwide health concern. Pb is often prolific in metal-mining impacted systems and has acute and chronic toxic effects. Environmental factors controlling diffuse pollution from contaminated riverbank sediment are currently seen as a “black box” from a process perspective. This limits our ability to accurately predict and model releases of dissolved Pb. Previous work by the authors uncovered key mechanisms responsible for the mobilisation of dissolved Zn. The current study identifies key mechanisms controlling the mobilisation of dissolved Pb, and the environmental risk these releases pose, in response to various sequences of “riverbank” inundation/drainage. Mesocosm experiments designed to mimic the riverbank environment were run using sediment severely contaminated with Pb, from a mining-impacted site. Results indicated that, although Pb is generally reported as less mobile than Zn, high concentrations of dissolved Pb are released in response to longer or more frequent flood events. Furthermore, the geochemical mechanisms of release for Zn and Pb were different. For Zn, mechanisms were related to reductive dissolution of Mn (hydr)oxides with higher concentrations released, at depth, over prolonged flood periods. For Pb, key mechanisms of release were related to the solubility of anglesite and the oxidation of primary mineral galena, where periodic drainage events serve to keep sediments oxic, particularly at the surface. The results are concerning because climate projections for the UK indicate a rise in the occurrence of localized heavy rainfall events that could increase flood frequency and/or duration. This study is unique in that it is the first to uncover key mechanisms responsible for dissolved Pb mobilisation from riverbank sediments. The mineralogy at the mining-impacted site is common to many sites worldwide and it is likely the mechanisms identified in this study are widespread.

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1. Introduction

Metal mining activities including mineral extraction, processing and dumping of contaminated waste alongside river channels has resulted in the widespread metal pollution of soils and sediments and is a world-wide health concern (Foulds et al., 2014; Frau et al., 2018; Zhang et al., 2012; Zadnik, 2010). The impacts of these activities have been reported internationally; Coeur d'Alene River Valley, Idaho (USGS, 2001), San Luis, Argentina (Tripole et al., 2006) and throughout Europe, Upper Silesia in southern Poland (Ullrich et al., 1999), Iberian Pyrite Belt, south west Spain (Torres et al., 2013). In England and Wales, mining impacted catchments play a critical role in the distribution of metals through fluvial systems with the highest metal flux arising from mineralised catchments with a history of metal mining (Mayes et al., 2013). Contrary to the traditional focus on point sources of pollution from adits and shafts, a greater emphasis has been placed on dealing with diffuse forms, primarily due to the EU Water Framework Directive 2000/60/EC requirement that management of water quality should be at a catchment scale delivered through the river basin management plans (Collins et al., 2012). There are 226 waterbodies categorised as “impacted” by non-coal mine water pollution in England and Wales and over 50% show evidence of diffuse pollution (Environment Agency, 2010). That could serve as a barrier to achieving “good” surface water chemical status for all water bodies by 2021 (EU amending directives 2000/60/EC and 2008/105/EC). Identifying the exact sources, and understanding pollution dynamics, within a catchment are listed as key priorities for effective management and remediation efforts (Environment Agency, 2012a).

Pb is listed as a priority substance in EU amending directives 2000/60/EC and 2008/105/EC in the field of water policy because of its known toxic effects. Unlike elements, such as Cu and Zn, Pb has no known biological function and therefore can be harmful to flora and fauna at very low levels (Chibuike and Obiora, 2014). Pb is bioaccumulative, passing through trophic levels of the food chain and increasing in concentration at each level. Bioavailable forms of Pb can be taken up and stored in tolerant plants (Sharma and Dubey, 2005) and macroinvertebrates (Cid et al., 2010), accumulate in earthworms (Wijayawardena et al., 2017) and high concentrations can be stored in liver, kidneys and muscles of cattle due to the consumption of contaminated forage (Zadnik, 2010). In severely contaminated mining catchments such as Coeur d'Alene river Basin, USA, levels of Pb in children's blood have been found to far exceed federal intervention levels (USGS, 2001). Pb can have chronic and acute toxicity effects that include detrimentally impacting macroinvertebrate community structure (Montserrat, 2010; Byrne et al., 2013), phytotoxicity resulting in riverbank instability (Environment Agency, 2008), chronic effects in cattle such as osteoporosis and anaemia with high exposure resulting in ataxia and death (Zadnik, 2010) and neurotoxic effects in children such as behaviour problems, lower IQ and learning disabilities (Wijayawardena et al., 2017).

In mining impacted catchments Pb can be introduced into the environment when primary sulphide mineral galena (PbS) is brought to the surface and oxidised through exposure to atmospheric conditions. High concentrations of Pb and sulphate can be released into fluvial systems in this way. Once introduced to the river system Pb can be transported downstream as a free ion, aqueous complex, or in particulate form sorbed to sediment particles (vanLoon and Duffy, 2011). Where physical, chemical and hydrological changes within the river allow, Pb associated sediment would be deposited on riverbanks and floodplains, the location depending on factors such as particle size, flood magnitude and morphology of the river (Macklin and Dowsett, 1989; Bradley, 1995; Dennis et al., 2003). The partitioning of Pb in sediment is dependent on the chemical environmental conditions and the geology, for example formations high in quartz or carbonates that would influence mineralogy. Where Pb is associated with mineral forms impervious to weathering, environmental changes would not influence the

mobilisation of dissolved Pb and this contaminant would remain unavailable for uptake. However in mining impacted catchments Pb is often associated with Fe and Mn (hydr)oxide and sulphur minerals in the sediment (Tripole et al., 2006; Buekers et al., 2008; Zakir and Shikazono, 2011). These minerals can undergo dissolution and precipitation reactions in response to dynamic changes in redox potential, pH (Nordstrom and Alpers, 1999) and levels of moisture (Buckby et al., 2003) – processes that commonly occur within the riverbank environment (Byrne et al., 2013; Krause et al., 2010; Du Laing et al., 2009). As a result the sediment can become a source of dissolved Pb to river systems (Charlatchka and Cambier, 2000; Torres et al., 2013).

Climate projections based on UKCP09 river basin regions in West Wales and North West England (Met Office, 2017) indicate a shift towards aridity by 2020. Summer river flows are expected to decline and Q95 (flow that is exceeded 95% of the time) may reduce 26% by 2050 and 35% by 2080 in western Wales, using medium emissions (P50) scenarios (DEFRA, 2012a). Furthermore projections indicate a rise in the occurrence of localized heavy rainfall events, particularly in winter. Peak river flows are expected to increase 13% by 2020, 20.8% by 2050 and 27.6% by 2080 in Wales, using medium (P50) scenarios (DEFRA, 2012b). Changes in river flow alter river stage and expose river bank sediments to variable water saturation regimes, periods of inundation are followed by periods of drainage. If climate change projections are correct, patterns of inundation and drainage are likely to become more pronounced. The focus of the current research is within the UK, however it is important to note that climate driven changes in distribution of rainfall and the resulting increase in peak flow events within mining impacted systems, is an issue experienced internationally (Ciszewski and Grygar, 2016).

The current research is intended to add to the work of Lynch et al. (2017) in which the geochemical mechanisms controlling dissolved Zn release from riverbank sediments were determined (Lynch et al., 2017). Key Zn control mechanisms were: the (co)precipitation of Zn with Mn (hydroxides), followed by the reductive dissolution and release of Zn in response to prolonged flooding and; Precipitation of Zn sulphate salts over long dry antecedent periods followed by the immediate dissolution of these salts and release of dissolved Zn on sediment flood wetting.

In the current study the same mesocosm experiments are run to allow the authors to determine the control that different sequential patterns of flooding and drainage have on the mobilisation of dissolved Pb. Pb is reported as less mobile than Zn under oxic conditions (Galan et al., 2003; Carroll et al., 1998) with a greater affinity for Fe (hydr)oxide surfaces (Evans, 1991; Wang et al., 2010) and a lower sorption edge (Lee et al., 2002; Appelo and Postma, 2010). However, in severely polluted catchments contaminated sediments have been identified as an important source of dissolved Pb contamination to surface water (Palumbo-Roe et al., 2012; Byrne et al., 2013) and it is hypothesised that certain flood/drain sequences will control the mobilisation of dissolved Pb from contaminated riverbank sediment.

Key hydrogeochemical mechanisms may include: (i) Pb co-precipitation with and sorption to Fe/Mn (hydr)oxides under oxidised (drained) periods followed by reductive dissolution and release of dissolved Pb due to a fall in redox potential conditions over prolonged flood periods; (ii) the oxidation of the primary mineral galena and release of dissolved Pb and sulphate where previously reduced sediment is exposed to oxic conditions (Wragg and Palumbo-Roe, 2011) (iii) the precipitation of insoluble Pb sulphides due to a fall in redox potential conditions over prolonged flood periods (Lynch et al., 2014); (iv) control of dissolved Pb concentrations to low levels through saturation with respect to anglesite (PbSO₄) over flooded periods (Palumbo-Roe et al., 2013; Appelo and Postma, 2010); (v) hydrological saturation and precipitation of soluble sulphate salts over long dry periods followed by dissolution of these salts, and a “flush” of dissolved Pb and sulphate, in response to flood wetting (Byrne et al., 2013).

Previous studies have investigated the effects of alternately flooding and drying contaminated soil for different frequencies and durations on the mobilisation of toxic trace elements such as Cd and Zn (Lynch et al., 2017; Shaheen et al., 2014; Du Laing et al., 2007). This study is unique in that experiments examine the patterns of dissolved Pb release from coarse grained riverbank sediment collected from a mining impacted catchment highly contaminated with Pb. Understanding the mechanisms of release for this toxic metal under varying hydrometeorological perturbations is crucial information for environmental monitoring and the development of successful pollution control measures.

To establish the environmental risk Pb-contaminated riverbank sediment may pose in light of UK climate projections, the results of two laboratory mesocosm experiments are examined. The objectives were to: (i) investigate if flooding and draining sequences influence the patterns of dissolved Pb release from severely contaminated river bank sediment; (ii) identify key hydrogeochemical processes responsible for controlling the mobilisation of dissolved Pb and if they differ from the mechanisms of control for dissolved Zn; (iii) establish if Pb contaminated riverbank sediment poses an environmental risk when exposed to alternate flooding and draining sequences.

2. Introduction

A summary of the sample site data and mesocosm treatment methods is provided below. Please see (Lynch et al., 2017) for detailed information on the methodology.

2.1. Sediment sample site

The sample site at Cwmystwyth (SN799743) is located in central Wales, at an elevation of 250 m above sea level (ASL). The mine site is drained by the Afon Ystwyth River which runs from east to west, draining into the Irish Sea at Aberystwyth (approximately 25 km north east of Cwmystwyth) (Fig. 1). The north side of the river is marked by spoil heaps rising to 500 m ASL and on the south side grass banks,

used primarily for grazing, rise steeply to 450 m ASL. Mining ceased at Cwmystwyth in 1921 (Bick, 1976). The country rock dates from the Silurian period with alternating bedrock of hard coarse sandstones and shales that form the upper Llandovery Series (British Geological Survey, 2007). Rivers that rise on this type of geology have been described as “Base Poor” having a low alkalinity, so less able to buffer acidic inputs (Natural Resources Wales, 2004).

2.2. Rainfall and river flow characteristics

Detailed information on rainfall and flow at the sample site can be found in Lynch et al. (2017). Generally flow rises and recedes quickly, however extended periods (greater than a week) of flow well above the mean value (1.989 m³/s) (leading to riverbank and floodplain inundation) and extended periods well below the mean value (leading to drainage and exposure of riverbank and floodplain), are common (Centre for Ecology and Hydrology, 2015). Changes in river flow are known to cause a rise and fall in river stage that can influence patterns of hyporheic exchange flow (Byrne et al., 2013).

2.3. Sediment collection

Sediment was collected on two occasions, July 2012 and December 2013 for analysis in two separate mesocosm treatments. Visual inspection of the northern riverbank indicated that sediment was made up of predominantly sandy gravel interspersed with some finer silt particles and larger pebbles and boulders. The sediment samples were collected from the north bank of the river at the same site, but different locations. On the first visit, sediment was taken from waste piles running along the side of the river channel. This material would have been dumped along the side of the river during active mining and was therefore likely to contain high concentrations of primary and secondary minerals. On the second visit, material was taken from the base of the mining waste piles, on a lateral flow path, so was likely to contain lower concentrations of the primary waste and material eroded from the waste piles.



Fig. 1. Location of sample site, grid reference SN799743 (denoted by a star) at the Cwmystwyth abandoned mine complex in the River Ystwyth catchment in mid-Wales (inset).

This site was closer to the active river channel and therefore would be more susceptible to hydrometeorological perturbations. A stainless steel shovel was used to collect sediment from the top 10 cm.

2.4. Laboratory analysis

2.4.1. Mesocosm experiments

Two mesocosm experiments were conducted in order to meet the objectives. The first experiment was run to determine the effect alternately wetting and drying contaminated sediment for different durations and frequencies had on the release of dissolved Pb and establish whether the sediment posed an environmental risk. The second experiment focused on runs where patterns of dissolved Pb release were pronounced allowing a (i) comparison of concentration and lability of Pb in the sediment at the two different sampling locations; (ii) comparison of the environmental risk the sediment posed at each location (iii) determination of the repeatability of the results. For both experiments water and sediment analysis enabled the elucidation of the key geochemical mechanisms of dissolved Pb mobilisation.

The sediment was homogenised by hand and larger pebbles were removed. The sediment was then packed into each mesocosm to a depth of 24 cm using a plastic trowel (Fig. 2). An extended experimental timeframe for each column of 20 days at field capacity, to equilibrate the sediment, followed by a maximum of 11 weeks treatment period promoted the removal of any artefacts and allowed time for systems to settle into a steady pattern. Artificial Rainwater (ARW) was created based on Plynlimon rainwater chemistry (pH 4.9–5.2), found in the uplands of mid-Wales (Neal et al., 2001). For field capacity, twice a week, 500 ml of ARW was added via the top of the mesocosm until water percolated through the bottom tap (Fig. 2). Following field capacity, mesocosms were divided into 7 different treatments. 5 were variable wet and dry runs and 2 constant controls. The Cwmystwyth gauged daily flow (grid reference SN790737), taken from the UK National River Flow Archive (Centre for Ecology and Hydrology, 2015), provided guidance regarding the length of time riverbank sediment may be exposed to atmosphere or submerged (Section 2.2). Variable runs were designed to include longer wet runs, longer dry runs and wet and dry run of same duration and frequency. Control runs were non-variable and either constant wet (flood) or unsaturated and oxidised (field capacity). This allowed a comparison between variable and non-variable wet and dry runs. Constant flood and field capacity were sampled

every week. Variable run samples were taken only at the start and end of a wet period. Runs were: 1 week wet followed by 1 week dry (1wwet), 1 week wet followed by 2 weeks dry (2wdry), 1 week wet followed by 3 weeks dry (3wdry), 2 weeks wet followed by 1 week dry (2wwet), 3 weeks wet followed by 1 week dry (3wwet), Flood (Flood) and field capacity (F/C). The temperature was maintained at 22–23 °C for the 1st mesocosm experiment and ~18 °C for the 2nd mesocosm experiment.

Water samples were taken from the top of the mesocosm using a plastic syringe and from the bottom via a tap, in that order to avoid mixing between levels and filtered through a 0.45 µm PTFE syringe filter. A Hanna Combo pH/EC and temperature hand held stick meter model No 98129, recorded pH, conductivity and temperature for each sample. An Aquaread Aquameter multiparameter water quality probe was used to measure dissolved oxygen (DO) and redox potential (ORP) (2nd mesocosm experiment only). The ORP reference electrode was type 3MPK1 AgCl and ORP readings were converted to the hydrogen scale (Eh) as instructed by Aquaread. For further detail regarding mesocosm methodology, please see Lynch et al. (2017).

2.4.2. Trace metal and anion analysis

Flame Atomic Absorption Spectroscopy (FAAS) (Perkin Elmer Analyst 300) was used to measure Fe, Mn, Pb, Ca, Ni, Cu (mg L^{-1}) in filtered pore water samples from the 1st mesocosm experiment. Detection limits were: Ca, 0.06; Fe, 0.03; Cu, 0.01; Mn, 0.01; Pb, 0.04 and Ni, 0.01 (mg L^{-1}). Inductively Coupled Plasma with Optical Emission Spectroscopy (ICP/OES) (iCAP 6500 Duo) was used to measure dissolved Fe, Mn and Pb in (i) filtered pore water samples of the 2nd mesocosm experiment and (ii) sequential extraction samples from the 1st and 2nd mesocosm experiments. Detection limits were: Fe, 0.005; Mn, 0.001; Pb, 0.05 (mg L^{-1}). Ion Chromatography (Dionex ICS2000) was used to measure dissolved sulphate, nitrate, chloride and phosphate in pore water samples of the 1st mesocosm experiment and the 2nd mesocosm experiment. Detection limits were: sulphate, 0.07; nitrate, 0.04; chloride, 0.06; phosphate, 0.06 (mg L^{-1}). Flame photometer BWB technologies was used for detection of Na, K and Ca in filtered pore water of the 2nd mesocosm experiment. For all analysis quality control standards and blanks, either de-ionised water, or matrix matched solutions for sequential extractions, were used throughout. The results were considered acceptable if the data were within 5% of the expected concentration.

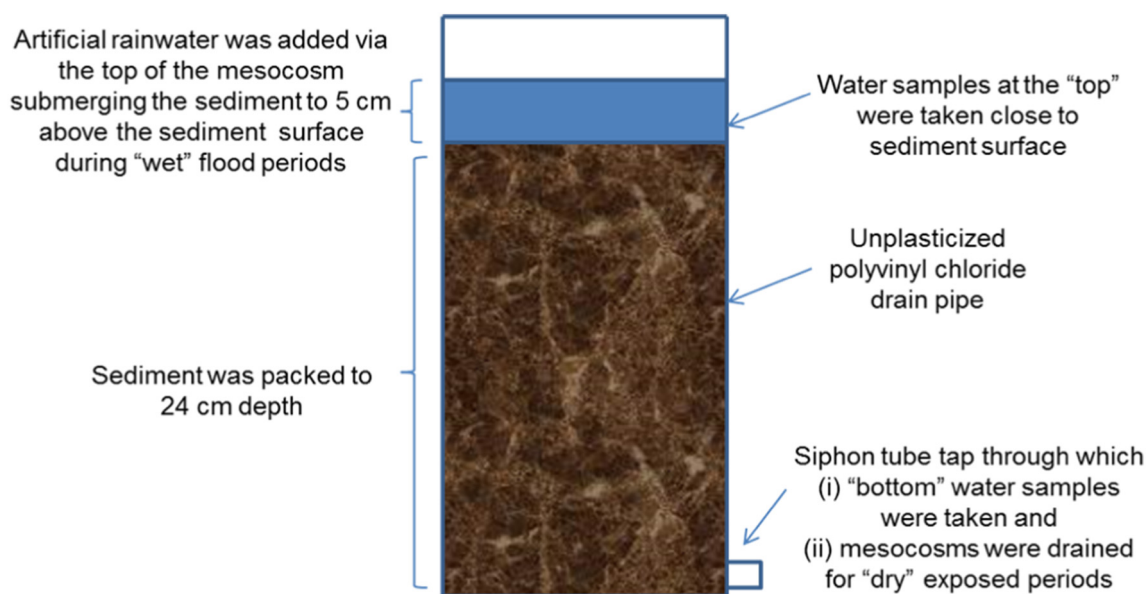


Fig. 2. Outline of mesocosm including sampling points. Note: Filtered samples are referred to as "dissolved" concentrations. However, this is operationally defined and the authors acknowledge that the samples may contain colloidal and/or nano-sized particles.

2.4.3. Alkalinity and inorganic carbon analysis (water and sediments)

Unfiltered water samples from both mesocosm treatment runs were analysed for alkalinity (as calcium carbonate) using the standard operating procedure for Great Lakes National Program office total alkalinity titration method (US EPA, 1992). Filtered pore water samples were tested for total carbon (TC) and non purgeable organic carbon (NPOC) using a carbon analyser (Shimadzu TOC-V CSN). Inorganic Carbon = Total Carbon – Non Purgeable Organic carbon. For non purgeable organic carbon the sample was first acidified to pH 2 to transform inorganic carbon to CO₂. The CO₂ was removed via sparging with a carrier gas. During this process some purgeable organic carbon (benzene, toluene, cyclohexane and chloroform) may be partly removed. Although there tends to be negligible amounts of these in surface water samples, the remaining organic carbon is “non-purgeable” and is measured, as mg (of carbon) per litre of water, through CO₂ detection in the analyser using a non-dispersive infrared (NDIR) detector. Standards and blanks were used throughout. The results were considered acceptable if within 5% of the expected concentration. Sediment collected for the 2nd mesocosm experiment was analysed for total inorganic (IC) using a separate solid sample module of the Shimadzu instrument (SSM 5000A). A sub sample of sieved (2 mm) sediment was weighed (no >50 mg), and oven dried at 140 °C for 24 h. The sample was treated with phosphoric acid inside the Shimadzu instrument to produce CO₂ that was purged at 200 °C and detected using a non-dispersive infrared (NDIR) detector. Calibration was performed using different weights of sodium carbonate containing 11.3% carbon. The results provided % TIC (Shimadzu Scientific Instruments, 2014). The results were considered acceptable if within 5% of the expected concentration.

2.4.4. Statistical analysis

All calculations were performed using SPSS 20.0. Statistical tests revealed the data was not normally distributed therefore significant differences in pore water data were identified through non-parametric Wilcoxon rank sum test. Relationships between Pb and pore water variables were determined using Spearman's rho 2-tailed non-directional tests.

To determine key factors linked to the mobilisation of dissolved Pb for selected variable runs at the bottom of the mesocosms, Principal Component Analysis (PCA) was carried out. Data was assessed to ensure (i) that underlying variables correlated (Bartlett's test of sphericity) and (ii) sampling adequacy (Kaiser-Meyer-Olkin). Factor rotation was chosen based on whether the factors (principal components (PC)) were thought to be unrelated (orthogonal) or related (oblique). For further information on PCA see Supplementary information D.

2.4.5. PHREEQC (Ph-Redox-Equilibrium in “C”)

The geochemical computer program PHREEQC was used for speciation and saturation index (SI) calculations using the WATEQ4F.dat database distributed with the PHREEQC program. The saturation state of various minerals were calculated using input data derived from pore water measurements for selected runs (Tables A1 and A2). Data was considered acceptable if charge balance was ≤5%.

In some cases the control of trace metal solutes by equilibrium with a mineral can be demonstrated (Appelo and Postma, 2010). The keyword “equilibrium_phases” was used to calculate the concentration of anglesite that would precipitate and subsequent dissolved Pb concentrations in pore and surface water if conditions were brought to equilibrium and reached saturation with respect to anglesite.

2.4.6. Sequential extraction of sediment samples

Dynamic changes in redox potential conditions can occur within river bank sediment due to flooding/draining sequences (Lynch et al., 2017; Lynch et al., 2014; Du Laing et al., 2009). Different Fe phases display a wide range of reactivity (adsorption capacity and susceptibility to reduction). A fall in redox potential conditions can result in the microbially mediated reductive dissolution of Fe and Mn (hydroxides) (Stumm and Sulzberger, 1992; Lynch et al., 2014). This can serve to remobilize partitioned contaminants such as Pb (Torres et al., 2013). When flood waters subside the exposure of previously reduced sediment surfaces to atmospheric conditions may result in the oxidation and hydrolysis of previously reduced Fe and Mn (Lovley and Phillips, 1989; Grundl and Delwiche, 1993). Fe and Mn (hydr)oxides can rapidly (minutes to hours) scavenge high concentrations of dissolved trace metal contaminants such as Pb (Burton, 2010; Caetano et al., 2003). In order to understand the reactivity of Fe and Mn minerals in the sediment along with partitioned Pb and therefore the potential for the sediment to control the mobilisation of Pb in response to dynamic changes in redox potential a modified 4 step sequential extraction procedure was carried out in triplicate on sediments samples collected for 1st and 2nd mesocosm experiments. The sequential extraction procedure focused primarily on Fe and Mn minerals with steps run sequentially from ‘most reactive’ to ‘least reactive’. Extractions were carried out on freeze dried –70 °C sediment (≤63 μm) (Table 1). Please see Supplementary information ‘E’ for full extraction methodology.

2.4.7. Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX)

A combination of SEM/EDX was carried out to create images of and identify elements at the surface of the sediment samples for areas at micron scale. Freeze dried sediment was dusted lightly onto carbon stubs and coated in carbon to encourage conductivity. Samples were analysed with a Philips XL30 FEG ESEM fitted with an Oxford Instruments X-Sight EDS ATW X-Ray detector. Please see Supplementary data ‘F’ for full methodology.

3. Results and discussion

3.1. Factors influencing the mobilisation of dissolved Pb

A key objective of the current study was to determine whether mining contaminated sediments became a source of dissolved Pb in response to flooding and draining sequences. The results indicated that these perturbations did influence the mobilisation of dissolved Pb, although patterns in the release of dissolved Pb were found to vary

Table 1
Sequential extraction steps.

Step #	Extractant	Extraction details	References
1	0.5 M HCl ^a	Rotational shaker for 1 h, centrifuged, supernatant filtered (0.45 μm)	Lovley and Phillips (1986)
2	0.25 M hydroxylamine hydrochloride in 0.25 M HCl	Rotational shaker for 1 h, centrifuged, supernatant filtered (0.45 μm)	Poulton and Canfield (2005)
3	50 g L ⁻¹ sodium dithionate with 0.2 M in 0.35 M acetic acid	Rotational shaker for 2 h, centrifuged, supernatant filtered (0.45 μm)	Poulton and Canfield (2005)
4	Aqua Regia cHCl and cHNO ₃ (3:1 molar ratio)	Agitated gently overnight. Following day heated 80 °C for 2 h. Filtered Whatman no 42	Wilson and Pyatt (2007), Montserrat (2010)

^a 0.5 M HCl is a moderately corrosive first step and therefore it is not possible to differentiate the release of divalent ions from loosely sorbed/exchangeable phase or as a result of dissolution of amorphous or soluble phases. Furthermore, the first step was originally used for analysis of Fe from within a different sediment environment. The implications regarding these points are included in the results/discussion section as the authors consider the results provide valuable supporting data.

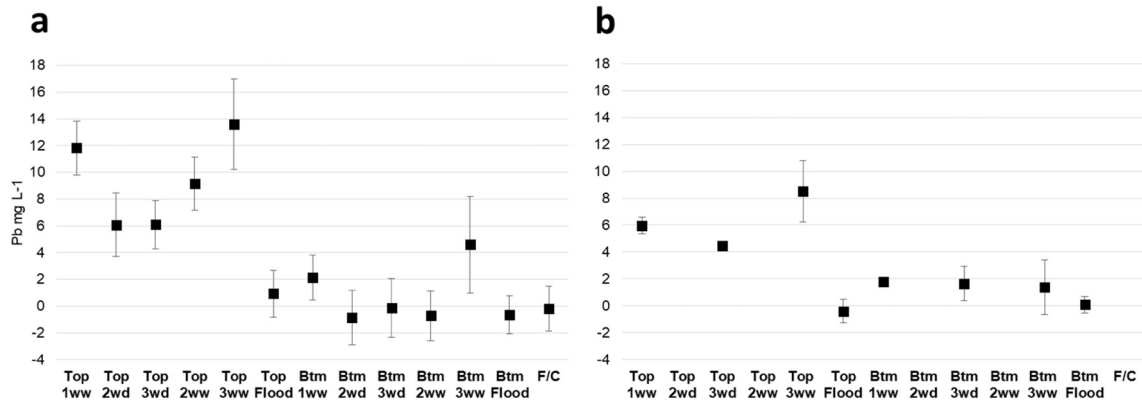


Fig. 3. Average concentration of dissolved Pb released over a flood period (mg L^{-1}) (concentration at the end of a flood minus concentration at the start) for all runs, top and bottom of the mesocosm for (a) 1st mesocosm experiment, bars indicate standard error ($n = 9$ for 3wwet and 3wd, $n = 18$ for 1ww, flood and F/C) (b) 2nd mesocosm experiment bars indicate standard error ($n = 3$ for 3wwet and 3wd, $n = 5$ for 1ww, flood).

depending on the flood/drain sequence and the location (top/bottom) within the mesocosms.

The average concentration of dissolved Pb released over a flood period was significantly higher at the top of the mesocosm compared to the bottom ($z = -7.3$, $p \leq 0.001$), ($z = -2.525$, $p \leq 0.05$), 1st and 2nd mesocosm experiments respectively. At the top of the mesocosm, within surface water, the concentration of dissolved Pb increased over the duration of the flood. All variable wet and dry runs displayed significantly higher concentrations of dissolved Pb at the end of a flood compared to the start ($z \leq -1.96$, $p \leq 0.05$) (Fig. 3a and b). In contrast, at the bottom of the mesocosm almost all of the dissolved Pb was released at the start of a flood (within 2–3 h) and concentrations remained relatively constant, or declined over the flood period. There was no significant increase in dissolved Pb between the start and end of a flood period at the bottom of the mesocosm for the 2wdry, 3wdry, 2wwet and F/C runs ($z \geq -1.96$, $p \geq 0.05$), nor for the constant flood runs at the top ($z = -0.73$, $p = 0.465$) ($z = -1.424$, $p = 0.155$) and bottom ($z = -0.63$, $p = 0.53$) ($z = -0.316$, $p = 0.752$) of the 1st and 2nd mesocosm experiments respectively (Fig. 3a and b). Similarities in the patterns of dissolved Pb release were apparent between the two mesocosm experiments possibly indicating the key geochemical mechanisms controlling Pb mobilisation were the same.

Principal components analysis was conducted on 8 items with orthogonal rotation (varimax) to determine the underlying factors influencing the mobilisation of Pb. Two PCs had eigenvalues greater than “1”: PC1 explained 62.7% and PC2 explained 14.9% of the variance. PC1 showed a high positive loading for sulphate (0.958) and Ca (0.897) and a negative loading for Pb (-0.527). At the bottom of the mesocosms, runs with longer flood periods, particularly the constant flood run, scored highly against this component (Fig. 4). Pore and surface water chemical analysis found that average concentrations of dissolved sulphate and Ca were higher at the bottom of the mesocosms compared to the top (Tables 2 and 3) and correlation analysis for the flood run at the bottom of the mesocosm showed a significant negative relationship between Pb and sulphate ($r = -0.889$, $p \leq 0.01$) and Pb and Ca ($r = -0.605$, $p \leq 0.01$). These results could indicate that underlying factors contributing to the release of sulphate and Ca over flooded periods may be linked to the lower concentrations of Pb at the bottom of the mesocosms. Inorganic carbon (IC) in the sediment was below detection in the current study both prior to treatment and at the end of the run. Pore and surface water analysis indicated that bicarbonate concentrations were undetectable. Furthermore, it can be seen, Section 3.2, Table 4, geochemical modelling, that no carbonate minerals were predicted to precipitate. Therefore it is unlikely the substitution of Ca for Pb in carbonate minerals such as calcite (CaCO_3), aragonite ($\text{CaMg}(\text{CO}_3)_2$), and ankerite ($\text{Ca}(\text{Fe,Mg})\text{CO}_3$) (Cravotta, 2008; Fairchild et al., 2010) or the precipitation of Pb carbonate minerals such as cerussite

(VanLoon and Duffy, 2011) were key geochemical mechanisms controlling the mobilisation of dissolved Pb. Sulphate was present at higher concentrations than the other anions (nitrate, chloride and phosphate). In waters with high sulphate concentrations the production of hydrogen sulphide and precipitation of insoluble metal sulphide galena (PbS) can serve as a sink for dissolved Pb (Du Laing et al., 2009). However, although redox potential measurements were lower at the bottom of the mesocosms than at the top (Table 3), they did not decline low enough for the production of hydrogen sulphide (<120 mV) (Ross, 1989; Gambrell et al., 1991; Bartlett, 1999). Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is often present in mining impacted catchments (Younger, 1998; Harris et al., 2003; Kuechler et al., 2004). Piper analysis indicated that the water samples were Ca-sulphate water type - typical of mine drainage. Dissolution of this mineral could account for the presence of sulphate and Ca in pore water and processes relating to the dissolution of this mineral could be linked to the attenuation of dissolved Pb. This is discussed further in Section 3.2.

High negative loadings for DO (-0.814) and redox potential (-0.942) were recorded against PC1 and 2. This is in line with the negative loading for Pb (-0.527) against PC1. Runs, at the top of the

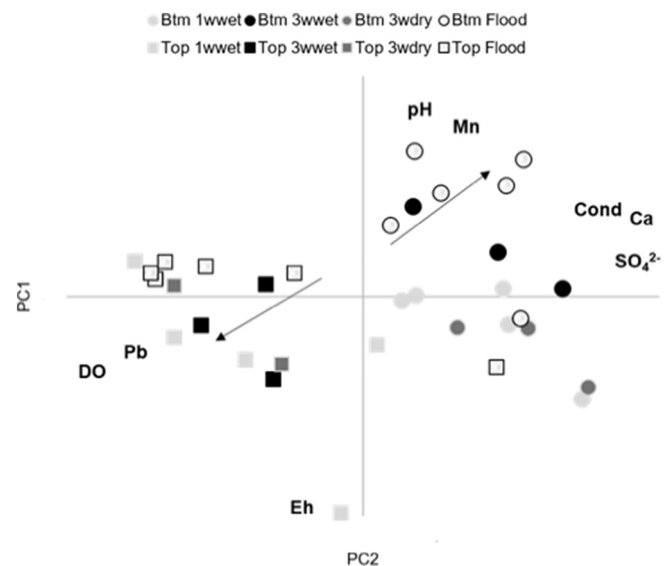


Fig. 4. Principal component analysis showing the distribution of pore water chemical samples along the first two principal components includes runs 1wwet, 3wwet, 3wdry, flood at the top (squares) and bottom (circles) of the mesocosms. Arrows indicate general trend for longer flooded runs (bottom) compared to 1wwet and 3wwet runs (top) (2nd mesocosm experiment).

Table 2
1st mesocosm experiment, mean and range (in parenthesis) of dissolved (<0.45 µm) metals and anions (mg L⁻¹), pH, conductivity (µS/cm), temperature (°C) at the end of a flood, by run, top (T) and bottom (B) of the mesocosm, key average values (bold and underlined), n = #.

Run Location	1wwet (T) n = 18	1wwet (B) n = 18	2wdry (T) n = 12	2wdry (B) n = 12	3wdry (T) n = 9	3wdry (B) n = 9	2wwet (T) n = 12	2wwet (B) n = 12	3wwet (T) n = 9	3wwet (B) n = 9	Flood (T) n = 33	Flood (B) n = 33	F/C (B) n = 33
pH (Range)	5.2 (5–5.6)	5.3 (5.1–5.5)	5.1 (5–5.3)	5.2 (5.1–5.5)	5.1 (4.8–5.3)	5.2 (5–5.3)	5.1 (4.9–5.4)	5.3 (5.1–5.5)	5.2 (4.9–5.7)	5.4 (5.2–5.7)	5.3 (5–5.8)	5.5 (5–5.7)	5.2 (5.1–5.4)
Temp (Range)	22.3 (20.9–24.2)	23.1 (21.9–24.8)	22.3 (21.2–23.3)	23.0 (21.7–23.9)	23.0 (21.4–24.4)	23.8 (22.3–25.1)	22.6 (20.4–24.5)	23.3 (20.9–25.1)	22.0 (21.4–22.6)	22.7 (22.1–23.2)	22.4 (19.9–24.5)	23.1 (22.1–23.2)	22.9 (21–25)
Cond (Range)	110.6 (87–144)	183.2 (155–204)	100.2 (88–116)	188.4 (152–214)	110.9 (94–136)	208.3 (164–250)	134.2 (107–156)	208.1 (188–224)	156.4 (146–169)	230.4 (218–264)	105.8 (46–126)	248.6 (140–339)	77.9 (50–130)
Fe (Range)	0.0 (0–0.4)	0.4 (0–1.7)	0.0 (0–0.2)	0.6 (0–1.6)	0.0 (0–0.8)	0.2 (0–0.8)	0.0 (0–0.8)	3.0 (2.2–3.9)	0.0 (0–0.7)	6.0 (3.6–10)	0.0 (0–0.5)	8.9 (0–27.7)	0.0 (0–0.5)
Mn (Range)	0.2 (0.1–0.4)	1.6 (1.2–1.8)	0.2 (0.1–0.2)	1.6 (1.1–2.2)	0.2 (0.1–0.3)	1.4 (0.6–2.9)	0.3 (0–0.7)	5.3 (3.5–6.4)	1.5 (0.7–3.1)	7.7 (6.7–9.6)	0.5 (0–1.3)	9.6 (0.4–16.6)	0.4 (0–1)
Pb (Range)	17.1 (9.8–22.3)	14.1 (8.6–24.3)	15.4 (13.2–17.2)	13.9 (12.5–15.2)	14.3 (10.8–16.8)	12.6 (10.6–16.1)	18.5 (14.7–24.4)	13.2 (10.1–13.2)	21.5 (16.7–30.6)	14.4 (9.7–24.7)	17.2 (5.2–27.2)	10.8 (3.9–28.5)	10.2 (4.2–23.7)
Ca (Range)	2.4 (1.7–3.4)	3.9 (2.6–5)	1.7 (1.4–2.1)	3.4 (2.1–4.5)	2.1 (1.9–2.9)	4.1 (2.7–5.9)	2.3 (1.6–2.6)	3.9 (2.6–5)	3.3 (2.8–3.8)	4.2 (3.9–4.7)	2.6 (1.5–3.6)	4.5 (2.8–6.8)	1.9 (1.3–2.8)
NO ₃ ⁻ (Range)	2.3 (0–5.7)	0.5 (0–1.5)	3.3 (2–4.9)	2.6 (0–4.8)	4.1 (2.6–5.7)	2.5 (0–6)	1.9 (0.9–3)	0.0 (0–0.3)	1.5 (0–3.2)	0.0 (0–1.9)	1.4 (0–4.2)	0.6 (0–8.7)	2.3 (0.7–4.2)
Cl ⁻ (Range)	1.5 (0.3–2.9)	1.2 (0–2.5)	1.5 (0.9–2.8)	1.3 (0.8–2.4)	2.3 (1.6–3.2)	1.9 (1.3–2.7)	2.0 (0.9–3.1)	1.3 (0.5–2.2)	2.0 (0.9–2.5)	1.3 (0.7–1.9)	2.0 (1.1–3)	2.0 (0.8–3.9)	1.8 (0–17.8)
SO ₄ ²⁻ (Range)	38.9 (10.8–65)	71.2 (60.2–100.8)	44.5 (25.3–90.9)	84.1 (57.3–142.8)	42.7 (25.4–63.3)	87.9 (61.2–129.5)	48.6 (34.7–63.4)	82.9 (65.3–94.2)	61.8 (47.2–85)	95.0 (79.6–121.2)	46.5 (13.5–106.4)	119.7 (47.6–277.7)	36.2 (16.9–90.5)

^a Note: "n" relates to number of samples taken at the end of a flood period. The "n" varied between runs because certain runs had more flood periods than others over the treatment period. Includes replicates.

mesocosms, scored negatively against PC1 and in some cases PC2 (3wwet run) (Fig. 4). DO and redox potential measurements showed conditions were oxic ~99.5% DO, Eh 494 mV at the top of the mesocosms (Table 3). These results indicate that underlying factors linked to high DO and redox potential conditions, may have contributed to releases of dissolved Pb over flood periods at the top of the mesocosms. Correlation analysis for the 3wwet run indicated a significant positive relationship between dissolved Pb and sulphate ($r = 0.605$, $p \leq 0.01$) and dissolved Pb and Ca ($r = 0.828$, $p \leq 0.01$). The oxidation of Pb sulphide minerals such as galena in mine tailings and contaminated sediment has been linked to the release of high concentrations of dissolved Pb into surface water during laboratory inundation experiments (Wragg and Palumbo-Roe, 2011) and in the field, in response to storm events (Byrne et al., 2012). The oxidation of galena would not necessarily produce excess acidity however, any subsequent hydrolysis (Younger, 1998) or adsorption reaction (Dzombak and Morel, 1987) would result in proton release. Therefore, the slightly acidic pH observed (pH 5.3, range 4.8–5.8), (pH 5.7, range 5.1–5.8) during the 1st and 2nd mesocosm experiments respectively could be linked to these acid producing processes and the poor buffering capacity of the water.

3.2. Solubility control of dissolved Pb concentrations in pore and surface water by equilibrium with anglesite

Anglesite has been reported to form as a weathering product from the oxidation of galena in mine drainage environments (Harris et al., 2003; Palumbo-Roe et al., 2013). To assess how close to saturation the flood water solutions were with respect to mineral phases, particularly anglesite, that may have formed over the treatment period, saturation indices (SI) were calculated using PHREEQC (Ball and Nordstrom, 2001).

The three week wet run (top) and flood run (bottom) were selected for analysis because the highest average concentration of dissolved Pb was observed for the 3wwet run at the top of the mesocosm (21.5 ± 2.9 mg L⁻¹), (10 ± 2.1 mg L⁻¹) and the lowest average concentration was observed for the constant flood run at the bottom (10.8 ± 2 mg L⁻¹), (3.8 ± 0.3 mg L⁻¹) (Tables 2 and 3). Mineral phases and SI's were calculated from input data (Table A1) and are listed (Table 4).

For both the 3 week wet (top) and constant flood (bottom) runs, surface and pore water conditions reached supersaturation with respect to anglesite by the end of the first 3 week flood (week D) (Table 4). For the constant flood run, pore water conditions then changed from supersaturated to saturated by weeks H and L. This was not the case for the 3 week wet run where conditions remained supersaturated over the entire treatment period.

The flood run, unlike the variable runs, was not periodically drained and exposed to atmospheric conditions. The sediment, to a large extent, remained saturated and the water stagnant so it is possible that this system could have moved towards an equilibrium state.

To test that theory, a simple script was run using PHREEQC to calculate the anglesite precipitation that would occur if the input data (Table A1) for sample weeks D, H, L reached saturation with respect to anglesite. The program also calculated the concentration of dissolved Pb that would be expected in pore water under these new saturated conditions (Fig. 5). The script was run for both the flood run (btm) and 3wwet run (top) for comparison.

In theory, if pore water conditions reach supersaturation with respect to anglesite, as was found to occur for the 3 week wet and constant flood run (week D), according to Le Châtelier's principle anglesite precipitation would occur and result in the decline in dissolved Pb and sulphate concentrations.

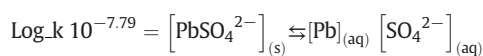


Table 3

2nd mesocosm experiment, mean and range (in parenthesis) of dissolved (<0.45 µm) metals and anions (mg L⁻¹), pH, conductivity (µS/cm), temperature (°C), DOC (mg L⁻¹), TIC (mg L⁻¹) at the end of a flood, by run, top (T) and bottom (B) of the mesocosm, key average values (bold and underlined), n = #^a.

	1wwet (T)	1wwet (B)	3wdry (T)	3wdry (B)	3wwet (T)	3wwet (B)	flood (T)	Flood (B)
	n = 5	n = 5	n = 3	n = 3	n = 3	n = 3	n = 10	n = 10
pH	5.5	5.7	5.6	5.7	5.6	5.8	5.7	5.8
(Range)	(5.1–5.7)	(5.6–5.8)	(5.5–5.7)	(5.6–5.7)	(5.4–5.7)	(5.7–5.8)	(5.4–5.8)	(5.6–5.8)
Temp	17.5	17.8	17.7	17.7	18.4	18.9	17.9	18.2
(Range)	(16–20)	(16.4–20.1)	(16.2–20.3)	(16.3–20.3)	(17–19.6)	(17.5–20)	(16–20.3)	(16.5–20.3)
Cond	225.2	392	175.3333	382	230.6667	405	264.9	408.4
(Range)	(148–373)	(336–435)	(170–186)	(338–415)	(206–276)	(359–436)	(162–416)	(342–452)
D.O. %	100	34	102	37	94	18	102	12
(Range)	(78–109)	(10.4–43.2)	(99–105)	(13.1–52.7)	(80.5–101)	(8.3–28.1)	(80.5–111)	(7.8–23)
Eh	509	482	499	491	483	428	485	423
(Range)	(459–603)	(456.9–530)	(479–525)	(478.9–509)	(468–504)	(412.7–436)	(446–555)	(381–485)
Fe	0.0	0.1	0.0	0.1	0.7	0.1	0.0	0.3
(Range)	(0–0)	(0–0.1)	(0–0.1)	(0–0.2)	(0–2)	(0.1–0.2)	(0–0.2)	(0.1–0.6)
Mn	0.1	0.1	0.0	0.1	0.1	3.5	0.2	5.8
(Range)	(0–0.1)	(0.1–0.2)	(0–0)	(0–0.2)	(0–0.1)	(2.2–5.3)	(0–0.7)	(1–10.1)
Pb	8.3	4.9	6.1	5.8	10.0	4.9	8.6	3.8
(Range)	(8–9.2)	(3.8–5.6)	(5–6.7)	(4.3–7)	(7.5–14.2)	(2.3–6.9)	(5–15)	(1.7–4.8)
Ca	2.4	11.8	2.0	13.7	4.7	15.7	5.7	13.6
(Range)	(0–8)	(8–14)	(0–4)	(16–12)	(3–7)	(14–17)	(0–18)	(4–19)
Nitrate	1.6	1.4	0.6	1.9	1.1	0.1	0.7	0.0
(Range)	(0.2–2.8)	(0.6–2.3)	(0–1.2)	(1–2.5)	(0.4–1.7)	(0–0.2)	(0–2.1)	(0–0.5)
Chloride	8.5	3.3	1.7	2.6	4.0	3.5	7.8	6.0
(Range)	(2.4–23.5)	(2.6–4.8)	(1.27–2.48)	(1.4–3.4)	(1.6–6.4)	(1.1–5.5)	(1.5–27.6)	(0.7–17.5)
Sulphate	25.3	95.2	17.7	120.3	36.0	110.3	35.5	94.6
(Range)	(8.5–64)	(121.9–47.7)	(8.8–35.2)	(90–145)	(19.3–52.9)	(66.6–147.7)	(7–115)	(46–138)
Na	2.2	4.8	3.0	4.7	5.3	14.3	7.3	8.8
(Range)	(0–4)	(3–7)	(1–6)	(3–7)	(4–7)	(9–19)	(1–22)	(2–18)
K	1.2	1.0	0.0	0.7	0.3	1.0	2.8	0.7
(Range)	(0–4)	(1.0–1.0)	(0–0)	(0–1)	(0–1)	(1.0–1.0)	(0–25)	(0–1)
DOC	2.5	3.1	1.9	3.1	2.6	4.3	2.6	3.6
(Range)	(2.1–3.2)	(2.4–3.5)	(1.9–2)	(2.6–3.8)	(1.9–3)	(3.7–4.9)	(1.9–4.9)	(2.5–4.8)
TIC	0.8	1.2	0.6	1.1	0.8	2.8	0.7	2.5
(Range)	(0.4–1.1)	(0.6–1.8)	(0.3–0.9)	(0.7–1.6)	(0.7–1.1)	(2.3–3.4)	(0.2–1.4)	(1.1–4.3)

^a Note: “n” relates to number of samples taken at the end of a flood period. The “n” varied between runs because certain runs had more flood periods than others over the treatment period.

For the flood run, week D, conditions were supersaturated with respect to anglesite (Table 4). Actual concentrations of Pb were higher in pore water than the concentrations predicted at equilibrium with respect to anglesite (Fig. 5). By week L pore water conditions were no longer supersaturated (Table 4) and actual Pb concentrations had declined to 5 mg L⁻¹ (Fig. 5). Predicted Pb concentrations at equilibrium for the flood run, weeks H and L were similar to actual Pb concentrations for these weeks (Fig. 5), indicating that conditions had moved towards an equilibrium state.

Table 4

Mineral phases, SI and charge balance (%) (first mesocosm run).

Week	D	H	L	D	H	L
Sample	3wwet	3wwet	3wwet	Flood	Flood	Flood
Location	Top	Top	Top	Bottom	Bottom	Bottom
Charge balance %	0.5	-0.8	-0.2	0.2	0	-0.1
Anglesite PbSO ₄	0.36	0.25	0.32	0.37	0.04	-0.07
Larnakite PbO:PbSO ₄	-1.58	-1.13	-1.52	-0.62	-1.41	-0.34
Pb(OH) ₂	-2.09	-2.05	-2.54	-1.65	-2.12	-1.95
Gypsum CaSO ₄ ·2H ₂ O	-2.96	-3.02	-2.88	-2.72	-2.56	-2.46
Zincite ZnO	-4.94	-4.58	-5.06	-4.2	-4.12	-3.9
ZnO(a)	-4.96	-4.61	-5.03	-4.26	-4.2	-3.93
Bianchite ZnSO ₄ ·6H ₂ O	-5.49	-5.28	-5.18	-5.18	-4.98	-5.02
ZnSO ₄ ·H ₂ O	-6.76	-6.54	-6.47	-6.43	-6.22	-6.28
Melanterite	ND	ND	ND	-5.15	-4.63	-4.44
FeSO ₄ ·7H ₂ O						
Pyrochroite Mn(OH) ₂	-9.89	-9.42	-9.77	-8.41	-8.17	-7.77
Birnessite MnO ₂	-20.09	-19.43	-20.17	-18.02	-17.77	-16.97

Note: All solution output results were checked for charge balance (within 5%). Small concentrations of Na were added to make up for any charge imbalance. Na was not measured in the pore water, however concentrations measured in previous studies at the sample site (Montserrat, 2010) were similar to the concentrations used to balance charges (7.5–32 mg L⁻¹). ND = no data/dissolved Fe was below detection. Anglesite SI in bold.

Predicted Pb concentrations for the 3wwet run at the top of the mesocosm were lower than actual Pb concentrations (Fig. 5). For this run, conditions reached supersaturation at the end of a three week flood and anglesite precipitation was predicted to occur but the actual Pb concentration data shows that this process did not result in a decline in dissolved Pb concentrations. The results indicate that the system was not in equilibrium and the solubility of anglesite had little control over dissolved Pb concentrations at the top of the mesocosms. For the 3wwet run long flood periods were followed by short drainage periods and re-flooded though addition of fresh artificial rain water. Sediment would therefore have been exposed to oxic conditions (particularly at the surface) that would have encouraged oxidation of Pb sulphide minerals and release of dissolved Pb during periods of inundation.

Concentrations of dissolved Pb were observed to be lower in the second mesocosm experiment however saturation indices calculated for the 2nd mesocosm experiment using information from input Table A2 showed that conditions at the bottom of the mesocosm were saturated with respect to anglesite (Table B1). The high concentration of sulphate measured at the bottom of the mesocosms during this experiment (Table 3) would have influenced saturation indices for anglesite. The dissolution of sulphate bearing minerals such as gypsum may have contributed to the high sulphate concentrations at the bottom of the mesocosms. SI calculations indicated gypsum was undersaturated, conditions that would favour the dissolution of this mineral. Batch-type experiments investigating the interaction of gypsum with Pb in aqueous solutions observed the rapid dissolution of gypsum and simultaneous formation of anglesite on the gypsum surface and in solution (Astillerosa et al., 2010). In the current study sulphate producing mechanisms such as dissolution of soluble sulphates would have encouraged the rapid precipitation of anglesite and provided a solubility control over dissolved Pb concentrations at the bottom of the mesocosm. Conditions

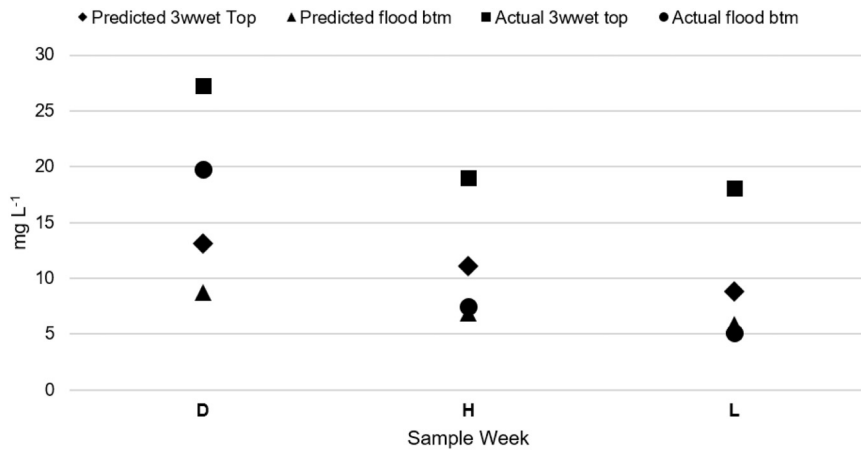


Fig. 5. Concentrations of dissolved Pb measured (actual) in pore and surface water and calculated (predicted) by bringing the system to saturation with respect to anglesite for the 3wwet (top) and flood run (bottom) of the mesocosms (1st mesocosm experiment).

were just below saturation with respect to anglesite at the top of the mesocosm (Table B1) and therefore it is likely the solubility of anglesite had little control over dissolved Pb concentrations at the top of the mesocosms for the 2nd mesocosm run.

3.3. Sediment analysis

Fe and Mn minerals have been reported as volumetrically the most important contaminant hosts in metal mining contaminated sediment in England and Wales (Hudson-Edwards, 2003). Reactive 'easily reducible' Fe and Mn (hydr)oxides have been found to reduce more quickly (Lovley and Phillips, 1987) at a higher redox potential (Du Laing et al., 2009) than older more crystalline forms such as goethite or hematite. Many studies have observed the partitioning of Pb with Fe and Mn hydroxides in metal contaminated sediments (Macklin and Dowsett, 1989; Evans, 1991; Hudson-Edwards, 2003; Burton et al., 2005; Byrne et al., 2010; Farnsworth and Hering, 2011). Dynamic changes in redox potential conditions and pH can bring about the reductive dissolution and precipitation of Fe and Mn hydroxides (Lovley and Phillips, 1986; Lee et al., 2002) and that can control the mobilisation of Pb (Charlatchka and Cambier, 2000; Lesven et al., 2010).

Extraction step 1 was intended to remove reduced Fe, Mn and Pb loosely sorbed to the sediment surface and extraction step 2 was expected to recover easily reducible Fe and Mn (hydr)oxides along with any partitioned Pb. The first two extractions therefore represented the most labile forms of Fe and Mn. A control standard of ferrihydrite was synthesised using Poulton and Canfield (2005) methodology and showed a 77% Fe recovery during extraction step 1. It is therefore likely that high concentrations of 'easily reducible' Fe were extracted during step 1. However, it can be seen from the results (Table 5) that relatively small concentrations of Fe and Mn were extracted from the sediment during the 1st and 2nd extractions compared to Pb. Almost all of the Pb (>90%) was extracted during the first 2 extraction steps (Fig. 6). The first extraction step was originally carried out on tidal river surface

sediment (Lovley and Phillips, 1986). Sediment was not severely Pb-contaminated and sulphate concentrations were in some cases an order of magnitude lower compared to the current study. Although chemical extractions are intended to be phase specific total specificity is highly unlikely (Leinz et al., 2000; Linge, 2008). Baba et al. (2011) reported that a 0.5 M HCl extraction resulted in 30% Pb removal from an anglesite sample (<63 μm) within 1 h. Leinz et al. (2000) carried out a series of Tessier et al. (1979) extractions and reported a 60,000 mg/kg recovery of Pb from anglesite using an extraction of 0.25 M hydroxylamine hydrochloride in 0.25 M HCl for 30 minutes at 50 °C. Furthermore, 0.5 M HCl produces a low pH extraction and galena dissolution has been found to increase as pH declines (Cama et al., 2005). It is possible therefore the high concentration of Pb released during the 1st and 2nd extraction may be due, in part, to the presence of other minerals, such as galena or anglesite in the sediment. The presence of these minerals was corroborated through SEM/EDX analysis (Figs. 8–10, Table 6).

In the current study concentrations of dissolved Fe were very low in surface and pore water compared to other metals (Tables 2 and 3). Gotoh and Patrick (1974) found that under flooded conditions Fe (hydr)oxide reductive dissolution occurred at 300 mV (pH 5), therefore this mechanism was unlikely to occur in the present study as redox potential measurements did not decline low enough, even at the bottom of the mesocosms. Furthermore microbial depletion of oxygen is limited by the availability of labile organic carbon (Gambrell et al., 1991) and the low-medium organic carbon measured in the current study would be unlikely to favour a large fall in redox potential conditions. The results of sediment and water analysis indicate that it is unlikely coprecipitation of Pb with Fe and Mn (hydr)oxides followed by reductive dissolution would have been a key mechanism controlling the mobilisation of Pb.

Higher concentrations of Pb were found in the 'easily reducible' fraction of the sediment sampled during the 1st mesocosm run, compared to the 2nd (Table 5) and it is likely that differences in Pb concentration in the sediment were reflected in pore water concentrations (Fig. 7).

Table 5
Mean concentrations (mg/kg) of metals in sediment (<63 μm grain size) collected in 2012 and 2014 (n = 3). Results are shown for pseudo-total metals and each geochemical phase of the sequential extraction.

	Pb (2012)	Pb (2014)	Fe (2012)	Fe (2014)	Mn (2012)	Mn (2014)
Loosely sorbed	59,463.9 ± 8589.6	59,807.2 ± 2015.1	2905.4 ± 242.3	4721.7 ± 49.2	146.9 ± 13.5	361.3 ± 2.3
Easily reducible	25,306.4 ± 3940.23	16,276.9 ± 911.9	1183.8 ± 76.7	1255.5 ± 111.3	59.9 ± 9.2	105.5 ± 10.8
Reducible	0	0	22,973.3 ± 1596.4	13,812.6 ± 248.1	68.8 ± 3.6	64.5 ± 0.8
Residual	2952.9 ± 1436.2	0	19,260.6 ± 1452.8	24,078.5 ± 990.6	330.9 ± 24.2	386.4 ± 15.1
Pseudo total	87,723.2	76,084.1	46,323.1	43,868.3	606.4	917.7
EA PEL guidelines*	91.3	91.3				

* Environment Agency Predicted Effect Level.

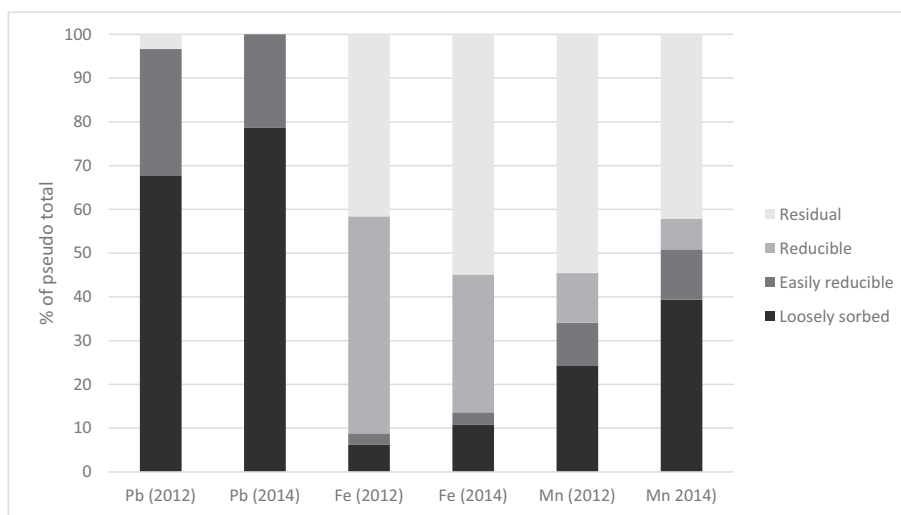


Fig. 6. Mean sequential extraction and residual Pb, Fe and Mn concentrations ($n = 3$) in the sediment ($<63 \mu\text{m}$ grain size) collected in 2012 and 2014. Results are shown as percentages associated with each phase.

The average concentration of “dissolved” Pb was significantly lower for 2nd mesocosm experiment in 2014 compared to the 1st experiment in 2012 for all runs at the top and bottom of the mesocosm ($z \leq -1.96$, $p \leq 0.05$). Average concentrations were approximately 2–3 times lower (Fig. 7). Sediment collected in 2012 was taken from piles of mine tailings that had been dumped along the side of the river due to inefficient processes at the time of extraction. This waste would contain high concentrations of the original ore minerals and their oxidised products. In 2014 sediment was collected from a different riverbank location closer to the river channel. This sediment may have been deposited during overbank flooding and as wash load transported from waste piles surrounding the site, this process has been described by (Merrington and Alloway, 1994). The spatial heterogeneity of the post mining landscape is problematic with regards to predicting diffuse pollution. The above results highlight the importance of characterising the sediment within a catchment prior to modelling pollutant releases.

SEM/EDX analysis was carried out to identify possible mineral associations of Pb in the sediment. Fig. 8 shows a back scattered electron image of the sediment (1st mesocosm run). Heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number) and therefore appear brighter in the image. As Pb is considered a heavier element, a bright grain was selected for analysis (spectrum 3) and a magnified back scattered electron image taken (Fig. 9).

EDX was carried out and the resulting quant specification (Table 6) shows an atomic % close to 1:1 ratio for Pb and S which could possibly indicate the presence of the mineral galena.

The smart map pattern (see Supplementary data ‘G’) for elements Pb, S and Fe shows that the grain in spectrum 3 is likely to be a Pb, S mineral. A similar pattern of Pb and S was found throughout the sediment indicating this mineral was widely distributed. Fe did not show the same pattern and was not found to be partitioned with Pb. Mn was difficult to quantify through SEM/EDS, possibly due to lower total concentrations of this element in the sediment.

Table 6

Quant specification for spectrum 3. Atomic % for S and Pb in bold.

Element	Weight%	Atomic%
S K	13.13	45.43
Mn K	−0.07	−0.14
Fe K	2.85	5.65
Zn L	3.46	5.87
Pb M	80.64	43.19
Totals	100.00	

3.4. Conceptual model for dissolved Pb mobilisation

The results from the current study were used to create a simple conceptual model showing the key geochemical mechanisms controlling the release and attenuation of Pb. The model contrasts two key hydrological runs, the prolonged 3wwet run with a short period of drainage and the constant flood (control) run. Both include a prolonged water residence time to allow reactions to occur at the sediment/water interface, however, the period of drainage for the 3wwet run allows exposure to atmospheric conditions, particularly at the surface. These conditions would promote the oxidation of galena and result in the release of dissolved Pb into surface water upon re-wetting. In contrast, for the prolonged flood period with no period of drainage there would be little exposure to atmospheric conditions and oxygen, particularly deeper in the sediment. This would serve to reduce the rate of galena oxidation and conditions may ‘stagnate’. High dissolved Pb concentrations and dissolution of sulphate bearing minerals such as gypsum may result in saturation with respect to anglesite leading to the attenuation of dissolved Pb. The 3wwet run is shown at the top of the mesocosm and the flood run at the bottom of mesocosm to highlight where the pattern of dissolved Pb mobilisation/attenuation is most pronounced for each run. The dashed arrows indicate the depth at which

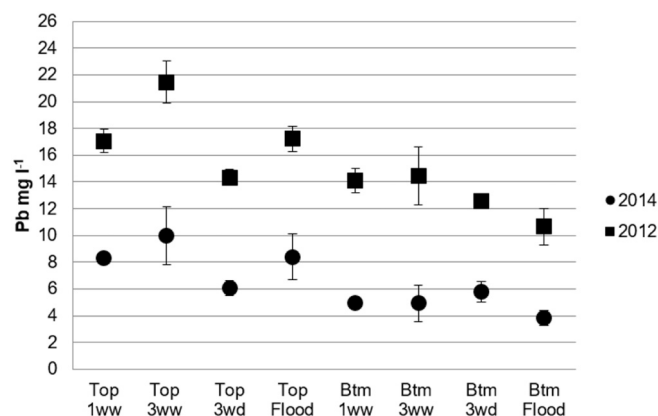


Fig. 7. Average concentration (mg L^{-1}) of dissolved Pb released at the end of a flood for mesocosm experiments in 2012 and 2014 by run at the top and bottom. Bars indicate standard error 1st mesocosm experiment $n = 9$ for 3wwet and 3wd, $n = 12$ for 2ww and 2wd, $n = 18$ for 1ww, flood and F/C; 2nd mesocosm experiment $n = 3$ for 3wwet and 3wd, $n = 5$ for 1ww, flood.

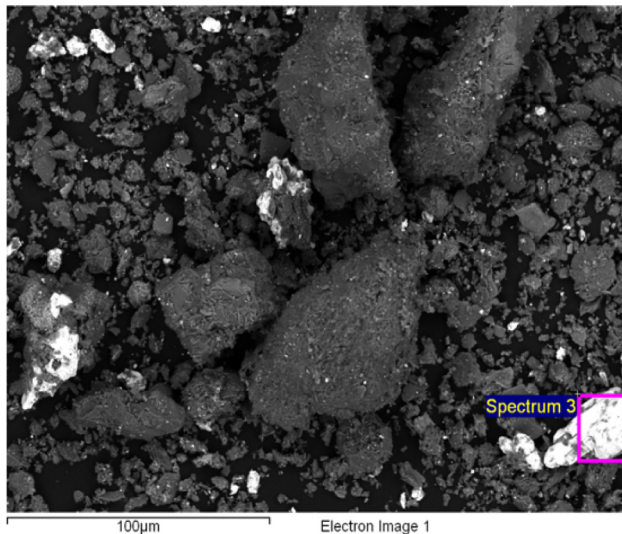


Fig. 8. Back scattered electron image of sediment (1st mesocosm run).

key mechanisms have less of an influence on the pattern of dissolved Pb release.

The environmental factors controlling diffuse pollution from contaminated riverbank sediment are currently seen as a “black box” from a process perspective. The current study is the first to uncover the key mechanisms responsible for dissolved Pb release into the riverine environment.

Compared to a previous study of Zn mobilisation in riverbank sediments (Lynch et al., 2017), the current research has found that the geochemical mechanisms controlling the release of dissolved Pb are dissimilar. Due to different geochemical mechanisms controlling mobilisation for Pb and Zn, the patterns of release were found to be different in response to the flood/drainage runs. High concentrations of dissolved Zn were released (i) immediately on flood wetting following a long dry antecedent period, and (ii) in response to prolonged flooding, at the bottom of the mesocosm, due to reductive dissolution processes. In the current study, the highest concentration of dissolved Pb release was observed at the surface, in response to longer/more frequent flood periods, with intermittent drainage episodes that promoted oxic conditions.

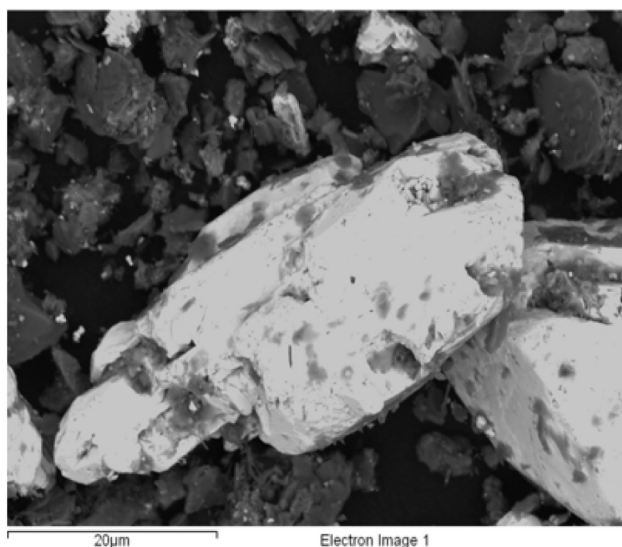


Fig. 9. Magnified Back scattered electron image of the grain in spectrum 3.

3.5. Environmental risk of contaminated sediments

Pb is listed as a priority substance in the Water Framework Directive 2013/39/EU, 12th August 2013, amending directives 2000/60/EC and 2008/105/EC in the field of water policy. These directives note that maximum allowable concentrations (MAC) should be taken into account in the river basin management plans covering period 2015 to 2021. For inland surface waters the annual average for Pb and its compounds is $1.2 \mu\text{g l}^{-1}$ (bioavailable). Where risk to, or via, the aquatic environment as a result of acute exposure has been identified, maximum allowable concentrations (MAC = $14 \mu\text{g l}^{-1}$) have been applied. The EU standard takes into the account the influence of DOC on the toxicity of Pb but unlike the standard for Zn it does not require consideration of Ca. A metal bioavailability assessment tool has been developed for Pb that takes into consideration the influence of DOC. Using the highest concentrations of DOC 4.9 mg l^{-1} measured in the current study the calculated predicted no effect concentration (PNEC) of Pb (the calculated dissolved concentration of Pb that is equivalent to the EQS available for local water conditions at the site) is $5.88 \mu\text{g l}^{-1}$.

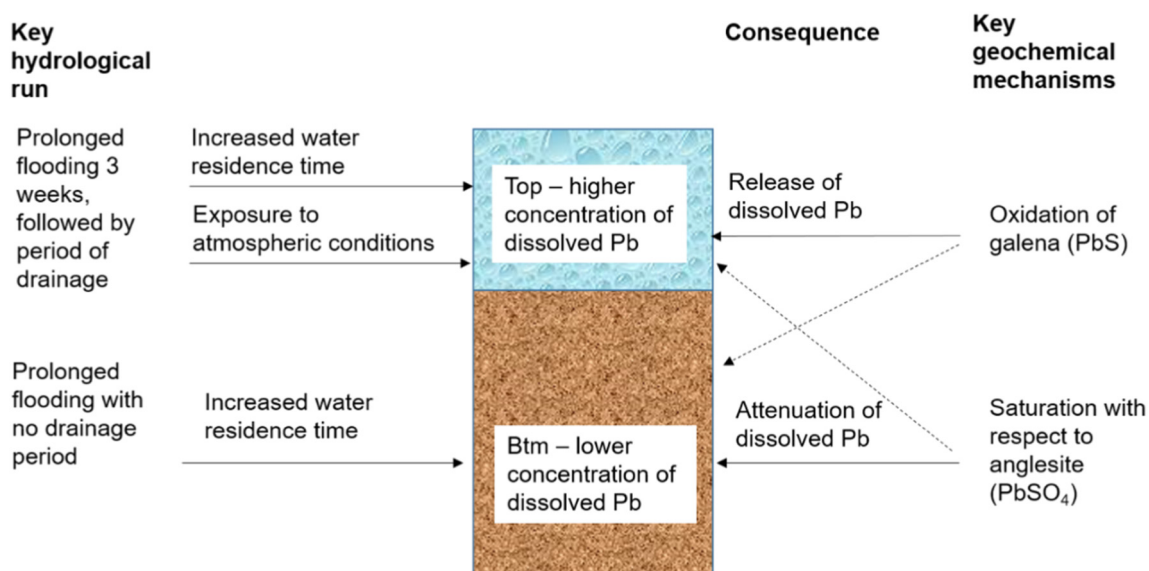
Comparing the above standards to the results from dilution calculations (Table 7) it can be seen that dissolved Pb concentrations for all runs exceed MAC and PNEC and therefore would be expected to cause adverse environmental effects and pose a significant environmental risk.

There are currently no mandatory threshold values for trace metal contaminants in river sediments in the UK and Europe. This is due to (i) the challenges of setting fixed standards in river systems where contamination is spatially highly variable and (ii) limited toxicological data (Environment Agency, 2008). Catchments with a long history of mining are often naturally highly mineralised and difficulties can arise when assessing the precise environmental risk contaminated soils and sediment may pose (Dennis et al., 2003). There are however interim sediment quality guideline values developed by the Environment Agency (Environment Agency, 2008) that are used to trigger further investigation. Predicted effect level (PEL) is the level above which adverse biological effects are expected to occur. It can be seen that sediment sampled for the 1st and 2nd mesocosm experiments contained high concentrations of Pb (Table 5). All samples far exceed predicted effect level (PEL) concentrations and therefore could pose a significant environmental risk. It should be noted that these interim standards relate to in-channel sediments, rather than river bank sediments, but in the absence of other standards relating to sediment they have been used as a guide.

PEL values relate to total metals (including residual forms) and therefore provide no indication of the potential bioavailability of trace metal contaminants. A recent study of Pb contaminated soil found that LC₅₀ values (concentration of Pb causing 50% mortality) for earth worms were far lower for acidic soils, pH 4.96 (1161 mg kg^{-1}) compared to neutral, pH 6.94 (4648 mg kg^{-1}) or alkaline, pH 8.45 (7851 mg kg^{-1}) soils and concluded that soil properties are important factors that modify bioavailability (Wijayawardena et al., 2017). In the current study the low inorganic carbon concentrations of the sediment indicate a slightly acidic environment that may favour increased bioavailability. Furthermore all concentrations of Pb measured in the current study exceeded all LC₅₀ values regardless of pH. The high concentration of Pb present in the most labile fractions of the sediment indicate that dissolved Pb could easily be released into pore and surface water in response to environmental perturbations with potentially serious adverse effects on water quality, aquatic flora and fauna and the surrounding agricultural and grazing land (Walling et al., 2003; Foulds et al., 2014).

4. Conclusions

The Cwmystwyth mine has been identified as a top 30 priority mining “impacted” waterbody in western Wales river basin district



Simple conceptual model summarising the key hydrogeochemical mechanisms controlling the release and attenuation of Pb in response to 'riverbank' inundation and drainage

Fig. 10. Simple conceptual model showing the key geochemical mechanisms controlling the release and attenuation of Pb.

(Environment Agency, 2012b). Although mining has ceased at the site the sediment remains severely Pb-contaminated. Results of the current study indicate the sediment is likely to act as source of dissolved Pb pollution to the Afon Ystwyth. Historical studies have found high concentrations of Pb ($68 \mu\text{g l}^{-1}$) in the river water half a km below the Cwmystwyth mine area with concentrations remaining high ($58 \mu\text{g l}^{-1}$) up to 7.5 km downstream although more recent studies found concentrations of dissolved Pb to be below detection (Montserrat, 2010).

A previous mesocosm study by Lynch et al. (2017) found high concentrations of dissolved Zn may be released from stream riverbanks over prolonged flood periods due to the reductive dissolution of Mn (hydr)oxides. Pb is generally reported as less mobile than dissolved Zn. However, results from the current study indicate that high concentrations of dissolved Pb could be released in response to longer or more frequent flood events where periodic drainage events serve to keep conditions more oxic, particularly at the surface.

This is a concern because climate projections indicate a rise in the occurrence of localized heavy rainfall events, particularly in winter (DEFRA, 2012b). Projected increases in flood events, particularly during winter months could result in a rise in river stage leading to prolonged inundation of river bank sediment and the mobilisation of dissolved Pb. Anglesite solubility may control dissolved Pb concentrations with depth, but have little control at the sediment surface where continual oxidation of galena and subsequent releases of dissolved Pb may occur. Where flood conditions subside a fall in river stage and exfiltration could result in a pulse of dissolved Pb released into river systems. Dilution calculations indicate that concentrations of dissolved Pb released are likely to exceed MAC in river water and therefore pose a significant environmental risk.

Table 7
Diluted Pb min and max average concentrations for 1st and 2nd mesocosm experiments.

Mesocosm experiment #	Pb mg L ⁻¹	Pb after dilution $\mu\text{g l}^{-1}$
1st experiment (max)	21.5	34.4
1st experiment (min)	10.8	17.28
2nd experiment (max)	10	16
2nd experiment (min)	3.8	6.08

This study is unique in linking key hydrological processes that may occur due to climate change to hydrogeochemical mechanisms controlling dissolved Pb mobilisation. The mineralogy at the Cwmystwyth site is common to many mining impacted sites and it is likely that the mechanisms identified in the current study would be widespread in the UK and worldwide. As these pollution events are transient the "exact sources" of Pb pollution would be difficult to identify in the field in the absence of continuous sampling methodologies. As a result Pb pollution events could go unnoticed. The authors suggest that further field studies are carried out that focus on understanding how stream-floodplain connectivity could drive diffuse Pb pollution at mining impacted sites particularly under variable hydrometeorological conditions.

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Conflicts of interest

The authors declare no conflict of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2018.04.368>.

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