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The influence of the scale of mining activity and mine site remediation on the contamination legacy of historical metal mining activity.

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ABSTRACT

Globally, thousands of kilometres of rivers are degraded due to the presence of elevated concentrations of potential harmful elements (PHEs) sourced from historical metal mining activity. In many countries, the presence of contaminated water and river sediment creates a legal requirement to address such problems. Remediation of mining-associated point sources has often been focused upon improving river water quality, however, this study evaluates the contaminant legacy present within river sediments and attempts to assess the influence of the scale of mining activity and post-mining remediation upon the magnitude of PHE contamination found within contemporary river sediments. Data collected from four exemplar catchments indicates a strong relationship between the scale of historical mining, as measured by ore output, and maximum PHE enrichment factors, calculated versus environmental quality guidelines. The use of channel slope as a proxy measure for the degree of channel-floodplain coupling, indicates that enrichment factors for PHEs in contemporary river sediments may also be highest where channel-floodplain coupling is greatest. Calculation of a metric score for mine remediation activity indicates no clear influence of the scale of remediation activity and PHE enrichment factors for river sediments. It is suggested that whilst exemplars of significant successes at improving post-remediation river water quality can be identified; river sediment quality is a much more-long-lasting environmental problem. In addition, it is suggested that improvements to river sediment quality do not occur quickly or easily as a result of remediation actions focused a specific mining point sources. Data indicate that PHEs continue to be episodically dispersed through river catchments hundreds of years after the cessation of mining activity, especially during flood flows. The high PHE loads of flood sediments in mining-affected river catchments and the predicted changes to flood frequency, especially, in many river catchments, provides further evidence of the need to enact effective mine remediation strategies and to fully consider the role of river sediments in prolonging the environmental legacy of historical mine sites.

KEYWORDS: metal mining; river sediments; remediation; contamination

1. INTRODUCTION

The mining of base and precious metal deposits results in the increased loading of potentially harmful elements (PHEs) to the Earth's surface environment (Byrne et al., 2010; Rieuwerts et al., 2009). This environmental loading occurs both during the period of active extraction (Allan, 1997) and following the cessation of mining activities (Mighanetara et al., 2009). Both scenarios are particularly relevant in environments where mining activity has been historical (Alpers et al., 2005; Hren et al., 2001); due to the historical use of less efficient extraction and processing techniques (Nash and Fey, 2007), a lack of environmental awareness and control and the lack of informed post-closure reclamation (Macklin, 1992). The latter, can result in the continued presence of point sources of PHEs to the environment, such as drainage adits (Sarmiento et al., 2009) and deposits of mine waste (Jung, 2008).

PHEs can be released into the surface drainage network in either dissolved or sediment-associated form (Bowell and Bruce, 1995; Marcus et al., 2001). However due to the processes of sorption, the dispersal of PHEs generally favours the sediment-associated form (Miller et al., 2007; Taylor and Hudson-Edwards, 2008). As a result, river sediments enriched in PHEs can be found in both within-channel (Bird et al., 2010; Martin, 2004) and overbank (Hurkamp et al., 2009; Vacca et al., 2012) deposits and will be mobilized episodically, particularly during periods of bankfull and flood flow (Dennis et al., 2003).

In Europe, increased awareness of the environmental impact of abandoned metal mines coupled with developments in environment al legislation, notably the European Union Water Framework Directive (EU WFD) (CEC, 2000), has resulted in programs of remediation works being undertaken at many historical mine sites (Palmer, 2006). Much of this remediation has been focused upon point sources (e.g. Bearcock and Perkins, 2007; Perkins et al., 2006) and attempting to reduce PHE loadings to the surface drainage network. Whilst there is no readily available data on the amount of money spent upon metal mine remediation, Palmer (2006) reports a total spend on remediation at the Minera site, North Wales, as being in excess of £2.2m. Tremblay and Hogan (2001) quantify the current and future global financial liability of remediating acid mine drainage alone to be in excess of $100 billion. For England and Wales, Jarvis and Mayes (2012) have estimated a cost of over £370 m for remediating water-related environmental problems from non-coal mines.

It is also apparent, however, that there is a spatial variability in the distribution of remediation activities with some abandoned mine sites receiving more attention than others. The legacy of historical mining activity on the geochemistry of a river catchment may therefore vary spatially due to the extent and type of remediation activity carried out. In addition, whilst there has been some coverage of specific remediation projects, there has been little attempt to evaluate the influence the degree of post-mine closure remediation has on the geochemical footprint of historical mining activity in recipient river systems. This study therefore evaluates the influence of the scale of historical mining and of post-mine closure remediation on the magnitude and spatial extent of contemporary PHE contamination in river sediments in four exemplar river catchments in North Wales, UK, an area that has a long history of base and precious metal mining and one in which there has been a varied approach to remediation.

2. STUDY AREA

2.1. Halkyn Mountain

The Halkyn Mountain area of North Wales (Figure 1), UK covers an area of approximately 2,000 acres the area, however, in the 19th Century it was the most productive mining area in Wales and the second most productive in the UK (Jones et al., 2004). The area has a diverse geology although the dominant bedrock is carboniferous limestone, the quality of which varies greatly, from high purity limestone (>97% $CaCO_3$) to that of poorer quality (Smith, 1921). Two distinct geological formations can be identified at Halkyn Mountain: in the west the carboniferous limestone faults up against the Silurian sedimentary bedrock of the Clwydian Range, and in the east it is overlain by numerous sandstone, shale and coal deposits (Davies and Roberts, 1975).

Mineralization is associated with Mississippi Valley Type deposits present within the carboniferous limestone. Vein-hosted deposits of galena, sphalerite and chalcopyrite (Jones et al., 2004). From 1790 to 1822 an estimated 120,000 tonnes of Pb was extracted from Halkyn Mountain (Ellis, 1998). Mining activity in the area ceased in 1978. Estimates of the total quantities of Pb and Zn extracted throughout the history of Halkyn Mountain vary. Recent figures estimate that between 1823 and 1978, 500,000 tonnes of Pb were extracted, and a further 100,000 tonnes of Zn were extracted between 1865 and 1978 (Ellis, 1998). Numerous small streams drain Halkyn Mountain, all of which are tributaries of the Nant-Y-Fflint River that flows northwards to the Dee Estuary (Figure 1). The area has seen some post-mining remediation, with the removal of mine buildings and some mine spoil.

2.2. Minera

The Minera mine site is situated on a band of mineralized limestone (McNeilly et al., 1984) and adjacent to the River Clywedog (Figure 1). Between 1854 and 1938 approximately 181,000 and 136,000 tons of lead and zinc, respectively were produced from the site. The Minera site has been the focus for significant remediation activity including the physical removal of spoil and the capping of remaining mine waste with a soil-forming layer (Palmer, 2006).

2.3. Parys Mountain

Parys Mountain is situated on north-eastern Anglesey (Figure 1) and played a significant role in the development of the UK metal mining industry and at one time production from the site dominated the world Cu market. Radio-carbon dating of archaeological artefacts has suggested that metal mining has been occurring at Parys Mountain since c. 3900 BP (Jenkins et al., 2000). By the 1790s production had reached 3000 tons Cu per year; mining effectively ceased in 1904 by which time an estimated 2.6×10^6 tonnes of ore had been mined yielding an estimated 0.13×10^6 tons of Cu (Jenkins et al., 2000). The Parys Mountain ore deposits are an example of VMS-type mineralization, with exhalative volcanic activity expelling sulphide-rich hydrothermal fluids, lava and ash on the sea-floor (Pearce, 1994). The mineralization is Cu-Pb-Zn with the main sulphide minerals being: pyrite (often containing As), chalcopyrite ($CuFeS_2$), galena (PbS) and sphalerite (ZnS). Mineralization at Parys Mountain occurs in an Ordivician-Silurian volcanic-sedimentary sequence overlying a Precambrian basement (Jenkins et al., 2000). Work was undertaken in 2003 to drain 270,000 m^3 of acidic, metalliferous water from the mine site (Younger and Potter, 2012), however, unlike Halkyn and Minera no work has been undertaken on the particulate waste covering Parys Mountain.

2.4. Parc Mine

Parc Mine is situated in the Llanwrst Mining Field (Figure 1) and covers approximately 6.8 ha. Mining at Parc Mine focused upon the extraction of Pb and Zn with mining intermittently until c. 1930 followed by a brief period of mining 1952-1942 (Shu and Bradshaw, 1995). Lead and zinc are predominantly present as the sulphide minerals galena and sphalerite, respectively with a gangue of calcite, quartz and shale (Johnson and Eaton, 1980). Mineralization occurs in narrow veins formed during the mid-Devonian (386-359 Ma) with some remobilization and reformation of mineral deposits approximately 336-307 Ma (Haggerty and Bottrell, 1997). The mineral veins formed within the Ordovician-aged host rocks, which consist of volcanogenic-sedimentary rocks of the Crafnant formation comprising siltstone, mudstone, shale, calcareous sandstone and tuffs (Haggerty and Bottrell, 1997). In 1977-1978 mine tailings at the site were remediated, which included reprofiling, capping and seeding the tailings (Shu and Bradshaw, 1995), however, the lower Parc Adit continues to drain mine-water into the Nant Gwydyr.

3. MATERIAL AND METHODS

Samples of stream bed sediment were collected using a plastic trowel from streams draining Halkyn Mountain (n=50), Minera (n=19), Parys Mountain (n=10) and Parc Mine (n = 5). Ten 10 spot-samples were collected over a c. 5 m^2 area to create a composite sample. Stream sediment samples were air-dried, disaggregated using a pestle and mortar and sieved through a stainless steel mesh to isolate the <2000 µm fraction. The choice of the <2000 µm provides consistency with previous studies in the UK (e.g.Bradley and Cox, 1986; Dennis et al., 2003; Hudson-Edwards et al., 1998).

Stream sediment samples were digested in 70% HNO_3 (4:1 liquid:solid ratio) for 1 hour at 100°C prior to the determination of Cu, Pb and Zn concentrations by Atomic Absorption Spectrometry. Copper data is not available for Halkyn Mountain samples. Analytical quality control was monitored through the analysis of repeat samples (10 % of total sample number) and the GSD-12 certified reference material. Digestion with concentrated HNO_3 does not provide a 'total' metal determination, however, recoveries 'total' certified values found very acceptable recoveries of 85 % (Cu), 86 % (Pb) and 93 % (Zn). Analytical precision was determined using blind repeats (10% of total sample number) and found to be 7.2 % (Cu), 3.4 % (Pb) and 4.5 % (Zn).

4. RESULTS AND DISCUSSION

4.1. PHE concentrations in mine waste

The PHE content of mine wastes at the mine sites featured in this study (Table 1) demonstrate substantial enrichments above average crustal values (Wedepohl, 1995), with higher Cu concentrations at Parys Mountain and Pb and Zn at Halkyn Mountain and Minera reflecting the nature of mineralization. If left unremediated, such as at Parys Mountain, these wastes have the potential to act as significant sources of PHEs to the surface drainage network through leaching and physical mobilization. The lower pH of waste at Parys Mountain reflects the lower base cation content of the bedrock coupled with substantial pyrite content of the mine waste (Jenkins et al., 2000).

4.2. PHE concentrations in river sediment

PHE concentrations are plotted in Figure 2 alongside Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) guidelines for freshwater river sediments (MacDonald et al., 2000). Within the four study rivers, concentrations of PHEs were found to range 32 – 7460 mg kg^{-1} (Cu), 90 mg kg^{-1} – 6960 mg kg^{-1} (Pb), 80 mg kg^{-1} to 5890 mg kg^{-1} (Zn). Highest Cu concentrations were, unsurprisingly in the Afon Goch (1550 – 7460 mg kg^{-1}), whilst peak concentrations of Pb (6960 mg kg^{-1}) and Zn (9690 mg kg^{-1}) were highest in the Nant y Fflint and Nant Gwydyr, respectively (Figure 2). Whilst, primarily draining a Cu ore-body, maximum Pb (2800 mg kg^{-1}) and Zn (4200 mg kg^{-1}) in the Afon Goch, are of a similar magnitude to those in streams draining primarily Pb/Zn mineralization.

The magnitude of enrichment of PHE concentrations can be quantified through the calculation of enrichment factors (EFs) (Reimann and de Caritat, 2005). Whilst not without some limitations (Reimann and De Caritat, 2000), EFs (equation 1) provide a valuable, simple measure of the magnitude of enrichment. Here, EFs were determined versus PEC and TEC guideline values (MacDonald et al., 2000), thus providing an indication of the risk posed to ecosystem health by PHEs present within the river sediments.

$$PHE\ EF = \frac{C}{G} \qquad \text{(Equation 1)}$$

Where EF is the enrichment factor, C is the concentration and G is the guidelines value (TEC or PEC).

EFs for Cu are greatest in the Afon Goch with concentrations exhibiting enrichment up to 50 times the upper PEC, and up to 236 times the lower TEC (Figure 3). In the Afon Clywedog, all Cu concentrations are not enriched versus the PEC, however Pb concentrations are of primary concern, given their presence at concentrations of up to 48 times to Pb PEC. EFs for for Pb in the Nant y Fflint are similar to the Clywedog in terms of maximum values (EF of 54 compared to PEC), however, the average EF in the Nant y Fflint (10) is lower than that of the Clywedog (26) or the Nant Gwydyr (18). Zinc EFs versus the PEC are highest in the Nant Gwydyr, with the lowest average EF occurring in the Nant y Fflint.

What is apparent from concentration and EF data is that active stream sediments in all four study rivers are elevated many times above guideline concentrations. PHE EF and concentration data indicate that samples taken at the lower end of the study reaches still contain PHE concentrations in excess of environmental quality guidelines (Figure 2) and that the presence of enriched river sediments is not isolated to the immediate vicinity of the mine sites. This is despite the cessation of active mining ceasing at least 35 years ago, in the case of the Nant y Fflint, and over 100 years ago in the case of the Afon Goch. These data confirm the acknowledged environmental legacy that abandoned metal mines have, particularly for fluvial environments (Hudson-Edwards, 2003). Indeed in the UK alone, it has been estimated that over 2800 km over river length are impacted by non-coal mining (Johnston et al., 2008). Furthermore, the longer-lasting legacy of PHE pollution stemming from abandoned metal mines is often most evident within river sediments (Hudson-Edwards et al., 2008; Hudson-Edwards and Taylor, 2003; Macklin et al., 2006).

It is possible to model the downstream decay in sediment-PHE concentrations as a function of channel distance with respect to linear, power and exponential functions (c.f. Lewin and Macklin, 1987). This provides a straight-forward evaluation of the nature of spatial changes in PHE concentrations with distance away from the mine sites. Results suggest that there is no dominant relationship type (Table 2). For example, whilst Pb concentrations in the Afon Goch show strong power relations (r^2=0.87), relationships for Cu and Zn in the same river are much weaker. Similarly, in the Afon Clywedog, downstream patterns in Pb concentrations best-fit an exponential pattern, showing relatively rapid decrease immediately downstream of the Minera mine site, however, Cu and Zn in the same river show much weaker spatial trends (Table 2).

The variability in downstream decay curves between different rivers and PHEs is likely to reflect the spatially variable nature of the controls upon PHE concentrations. These will include: differences in the source of PHEs and spatially variable patterns of within-channel and floodplain attenuation of sediment-associated PHEs, plus the influence of PHE supply from the erosion and remobilization of sedimentary units. The nature of downstream decay curves will also reflect patterns of dispersal and within-channel attenuation influenced by channel morphology and which are variable between different grain-sizes, with finer fractions such as silts and clays dispersed more readily. Finer fractions, such as silts and clays, are often viewed as most chemically active and may contain higher PHE concentrations compared to coarser fractions (Dennis et al., 2003). However, the silt and clay fraction may only account for a small proportion of the sediment load (Jain and Ali, 2000) or a proportion that is spatially highly variable, thus contributing to spatially variable downstream decay patterns.

There may also be additional influences from the relative sizes of the dissolved and sediment-associated PHE loads, which will reflect the influence of remediation activities and the influence of sediment-water interactions within recipient streams. A dominant relationship often observed within mining-affected rivers is the incorporation of the dissolved PHE load into the sediment-associated load through sorption processes (Brydie and Polya, 2003). Data available for the Nant Gwydyr (Figure 4) indicate that concentrations and associated fluxes of dissolved Zn within the stream, sourced from point sources at Parc Mine, vary with river discharge. This highlights the temporally variable nature of PHE fluxes from point sources, but also that substantial dissolved PHE loads may be present and available for scavenging by particulate material within the river channel.

4.3. Influence of mine 'size' and the magnitude of contemporary contamination

Interestingly, Figure 5 suggests a reasonably strong relationship in the four catchments studied, between ore output, indicative of the scale of mining activity, and maximum EFs found in contemporary river sediments. This analysis acknowledges potential errors in data for historical mine output, however, the general trends present, do suggest that the scale of mining activity is a simple predictor of the magnitude of contemporary contamination, despite the intervening influences of site-specific remediation activities. These data also further highlight the long-lasting impacts on impacts of historical mining activity that in some instances ceased over 100 years ago. This is an issue has been previously identified for, relatively more static floodplain sediments (Dennis et al., 2009), however, this data highlights the continued presence of contaminated sediments within the more active channel sediments.

Addition of data that is available for other catchments (Figure 5), reduces the strength of the regression relationship in comparison to the data from this study, however, the same general relationship remains in a number of catchments. However, the additional data also indicates that there are anomalies. For example data for Gunnerside Beck and Shaw Beck (Dennis, 2005) indicates hugely enriched sediments (maximum EF of 357) related to mining activity in that particular catchment that yielded a relatively modest amount of ore (Figure 5), certainly compared to others presented in this study. It could be argued that this is perhaps further confirmation of the need to recognise site-specific conditions relating to metal loading processes when establishing the contamination legacy of historical metal mines. This will incorporate factors such as the nature and strength of the 'coupling' between the mine site and the recipient surface drainage network. In addition, sites such as Gunnerside and Shaw Beck may reflect the importance of the influence of strong channel-floodplain coupling in some catchments. In such instances, highly polluted floodplains, representing an importance legacy-store of PHEs, are able to continue to deliver sediment-associated PHEs to the channel, potentially masking any reductions in supply from mine-site specific sources, and providing an overall high degree of PHE supply and resultantly high EFs in catchments with relatively small amounts of ore production.

Channel gradient can be used as a proxy measure of the degree of potential channel-floodplain coupling; with greater coupling via erosion in catchments with steeper channel gradients (Michaelides and Wainwright, 2004). To investigate this relationship, maximum enrichment factors are plotted versus average channel gradient in Figure 6. The data indicate that the most polluted river sediments are present within rivers channels that fall generally in the mid-range of those observed (0.027-0.051 m m^{-1}). In catchments with shallower slopes the degree of potential PHE delivery from floodplain stores will be lower than in steeper catchment (Figure 6). However, in the very steepest catchments, floodplain formation may be more limited, and therefore the potential for continued supply from these legacy stores may be less, as indicated by data in Figure 6. Overall, this highlights the important geomorphogical control upon the magnitude of contamination present within historically-mined river catchments.

4.3. Influence of remediation approaches

In an attempt to provide a first-order evaluation of the influence of the scale of mine remediation activity on the magnitude of PHE enrichment in river sediments, mean and range enrichment factors are plotted versus a metric score for remediation activity (Figure 7). The approach of calculating a metric score was used given, firstly the lack of easily accessible data on capital expenditure on such projects and secondly, in an attempt to reflect the potential influence of mine size, remediation scheme age and the variety of the remediation approaches available. The metric score for remediation activity was calculated as follows:

$$M_R = (\sum R \times A)/1000 \qquad \text{(Equation 2)}$$

Where M_R is a unitless remediation metric score, *R* are the remediation activity scores (Table 3) and *A* is the age of the remediation project in years (Table 3). Remediation activity scores were scaled to relative to each other based upon cost information provided by US EPA (1997). Information upon remediation activities undertaken at the four mine sites was sourced from Palmer (2006) and Younger and Potter (2012). The total value of *R* for a given site reflects the sum of the activity scores for remediation actions taken at that site (Table 3), with each activity score multiplied by the relevant amount of waste or water treated at that site.

Whilst acknowledging that the analysis is on a limited number of locations, the analysis suggests that there is no clear relationship between the amount of remediation undertaken and the magnitude of PHE enrichment in river sediments. This indicates, that severely enriched stream sediments remain within river systems despite significant remediation efforts and raises the question as to the success of these schemes. However, it must also be acknowledged that remediation schemes, such as at Parys Mountain and Minera, may have focused upon addressing issues associated with mine water and recipient river water quality. It is arguable, however, that there has been preponderance of focus upon the remediation of mine water quality in comparison to river sediments.

A large volume of work has been published on different approaches to remediating metal (and non-metal) mine drainage (see reviews by Johnson and Hallberg, 2005; Taylor et al., 2005). Data in Table 4 indicates that mine water treatments systems can achieve metal removal efficiencies of up to 99% and therefore substantially reduce metal loads to recipient streams. Reducing metal loads in mine drainage can lead to marked improvements in river water quality. For example Palmer (2006) reports a reduction of peak Zn concentrations in the Afon Cerist, mid Wales, from 5800 µg l^{-1} to 840 µg l^{-1} following the remediation of the Y Fan mine site. Lindeström (2003) reports reductions of Cu and Zn concentrations of 72% and 51%, respectively in river water following remediation at the Falun Mine, Sweden. The benefits of remediating mine drainage are apparent, however, data presented by this study demonstrate the long-lasting legacy of historic metal mining activity that remains present within river sediments stored within the channel zone in mining-affected catchments, despite significant attempts at mine site remediation. Importantly, this first-order evaluation suggests that large-scale remediation action is no guarantee of an improvement in river sediment quality.

4.4. Future importance of river sediments

Environmental legislation represents an important driver for remediation activities. In a European context, the EU WFD requires responsible authorities to ensure aquatic environments are of good ecological, chemical and physical/morphological quality. Remediating historical mine sites has been undertaken in this context (e.g. Jarvis et al., 2015) and improvements in water quality for PHEs have been achieved, in part through schemes such as those exemplified previously. However, arguably improvements in ecological health, the key focus of the EU WFD have lagged behind. This is indicative of the need to ensure that remediation of mining-related pollution problems focuses on both sediments and waters. Furthermore, it is also apparent that predicted changes in river regime over the coming decades could provide an additional important driver in the need to enact effective mine remediation activities. The latest intergovernmental Panel on Climate Change (IPCC) Assessment Report (IPCC, 2013) suggests that many European river catchments present within the mid-latitude land masses, will experience more intense and frequent extreme rainfall events. Such extreme weather events and associated flow events have the potential to increase the flux of metals from abandoned mine sites; both with respect to solute metals (Canovas et al., 2008) but also through the physical mobilization of metal-rich mine waste (Mighanetara et al., 2009). Indeed exemplar events of enhanced erosion of mine waste deposits during storm events have been reported by Shu and Bradshaw (1995) at Parc Mine. This risk is in addition to the potential for pollution events associated with the failure of mine tailings dams (e.g. Bird et al., 2008; Byrne et al., 2015). Figure 8 presents a collection of exemplar data, collated from the literature, regarding Pb concentrations in flood sediments within mining-affected river catchments. The sediments were deposited on floodplain surfaces during flood events and the data indicate that this material can contain highly enriched metal levels that will likely reflect enhanced metal loading during flood events (Dennis et al., 2003), which will include enhanced erosion of unremediated mine waste (Merrington and Alloway, 1994). Additional contributions may also be expected from the re-working of contaminated river sediments within the catchment (Foulds et al., 2014).

5. CONCLUSIONS

Data for PHE concentrations collected from historically-mined river catchments highlight the presence of highly elevated concentrations in river sediments. At their highest, they are hundreds of times above guideline concentrations and are present within river catchments in which mining ceased 10s to over 100 years ago. Analysis from catchments sampled in this study indicates that mine size is a strong first-order predictor of the magnitude of contemporary contamination, however, the site specific nature of historic mine sites means that severe contamination can be a legacy of relatively small mines. Comparison of PHE enrichment factors with a metric score for remediation ‘effort’ suggests that there is no clear relationship between remediation activity and subsequent magnitude of PHE enrichment in river channel sediments. Comparison to successes achieved with improving river water quality, data suggest that river channel sediments remain severely contaminated even after significant remediation activities.

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FIGURE CAPTIONS

Figure 1. Map showing the location of the four study catchments sampled in this study.

Figure 2. Concentrations of PHEs within river sediments plotted versus US EPA Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC) guidelines (MacDonald et al., 2000).

Figure 3. Minium, mean and maximum EFs for each catchment calculated versus the US EPA Threshold Effect Concentration (solid symbols) and Probable Effect Concentration (open circles).

Figure 4. Relationship between river discharge and Zn concentration and flux in the Nant Gwydyr (Bird, unpublished data). Concentrations in water filtered through 0.45 µm filter membranes and analysed by ICP-MS. Samples collected at location Ordnance Survey SH788 608 between June 2012 and January 2013.

Figure 5. The relationship between ore output and maximum PHE enrichment factor for river sediments in mining affected catchments. The regression line is the relation in rivers sampled by this study. Additional data sources are as follows: River Ystwyth (Foulds et al., 2014); Nant Silo (Wolfenden and Lewin, 1978); Gunnerside Beck (Dennis, 2005); River Tamar (Rawlins et al., 2003); Glengonnar Water (Rowan et al., 1995), Afon Twymyn (Byrne et al., 2010), River Nent, River West Allen, Rea Brook (Lewin and Macklin, 1987); Glenridding Beck (Kember, unpublished).

Figure 6. The relationship between average river channel gradient and maximum PHE enrichment factor for river sediments in mining affected catchments. Data sources for river catchments not sampled by this study is as in Figure 6.

Figure 7. Relationship between remdiation metric scores and minimum, mean and maximum EFs for river sediments within each study catchment.

Figure 8. Range and mean (black circles) Pb concentrations reported in sediments deposited following flood flows. Data from: [1]Foulds et al. (2014); [2]Dennis (2005); [3]Walling and Owens (2003); [4]Walling et al. (2003); [5]Leenaers et al. (1988); [6]Bird (unpublished data); [7]Strzebońska et al. (2015).

Table 1. Ore production (tonnes), PHE content (mg kg^{-1}) of mine waste and remediation activities at Halkyn Mountain, Minera and Parys Mountain. The Upper Continental Crust Average is also given.

	Ore production	pH	Cu	Pb	Zn	Remediation actions
Halkyn Mountain[1]	500,000 (Pb) 100,000 (Zn)	5-8	174	22882	65187	Removal of spoil.
Minera[1]	181,000 (Pb) 136,000 (Zn)	5-8	625	14000	34000	Removal of spoil, reprofiling and capping of spoil[1].
Parys Mountain[2]	130,000 (Cu)	3-6[1]	13900[1]	820-15700	11-1220	Pumping of mine water[5].
Parc Mine[3]	11680 (Pb) 4700 (Zn)	-	19-123	647-5860	720-9396	Removal of spoil, reprofiling, capping & seeding of tailings[6].
Upper Continental Crustal average[4]		-	14.3	17	52	

[1]Palmer (2006)
[2]Bird (unpublished)
[3]Johnson and Eaton (1980)
[4]Wedepohl (1995)
[5]Younger and Potter (2012)
[6]Shu and Bradshaw (1995)

Table 2. Regression relationships between PHE concentrations and river channel distance.

	Cu	Pb	Zn
Nant y Fflint			
Linear	-	0.03	0.07
Power	-	0.31	0.44
Exponential	-	0.18	0.24
Afon Clywedog			
Linear	0.28	0.50	0.20
Power	0.27	0.58	0.01
Exponential	0.31	0.71	0.01
Nant Gwydyr			
Linear	0.59	0.20	0.09
Power	0.47	0.17	0.12
Exponential	0.61	0.26	0.13
Afon Goch			
Linear	0.00	0.59	0.02
Power	0.08	0.87	0.25
Exponential	0.04	0.69	0.02

Table 3. Remediation activity values (unitless), remediation scheme age (A) and remediation activity scores (R) used to calculate a remediation metric scores (M_R) for each mine site

		***R* scores (activity value multiplied by amount of material remediated)**				
Activity	**Activity value**		**Parys Mountain**	**Minera**	**Halkyn Mountain**	**Parc**
Pumping mine water	0.05[1]		8640			
In-situ waste reprofiling	0.6[2]					8800
Soil capping plus organic amendment	10[3,4]					476500
Waste removal/relocation	1.7[2,3]			538900	1326000	
Soil capping plus synthetic membrane	45[4]			1553085		
		ΣR	8640	2091985	1326000	489700
		Age (A)	13	28	40	38

[1]per m^3 water

[2]per ton waste

[3]Given the difficulty in determining amounts of mine waste produced, this score is multiplied by the amount of ore produced, given that this data is more readily available and the amount of waste produced will be generally proportional to the amount of ore produced.

[4]per m^2 waste

Table 4. Percentage reductions in metal concentration in mine drainage due to treatment activities in some exemplar studies.

Mine	Cu	Pb	Zn	Reference
Bwlch, UK		97.3	98.5	Perkins et al. (2006)
Wheal Jane, UK	73[1], 95[2], 42[3]		66[1], 73[2], 47[3]	Whitehead et al. (2005)
Summitville, USA	90		57	Kepler and McCleary (1994)
Copper Basin, USA	91.3		69.2	US EPA (2006)
Rio Tinto, USA	99.9		99.9+	Tsukamoto (2006.)
Force Crag, UK			97	Jarvis et al. (2015)

[1]lime-dosed treatment

[2]Anoxic limestone drain treatment

[3]Lime free treatment

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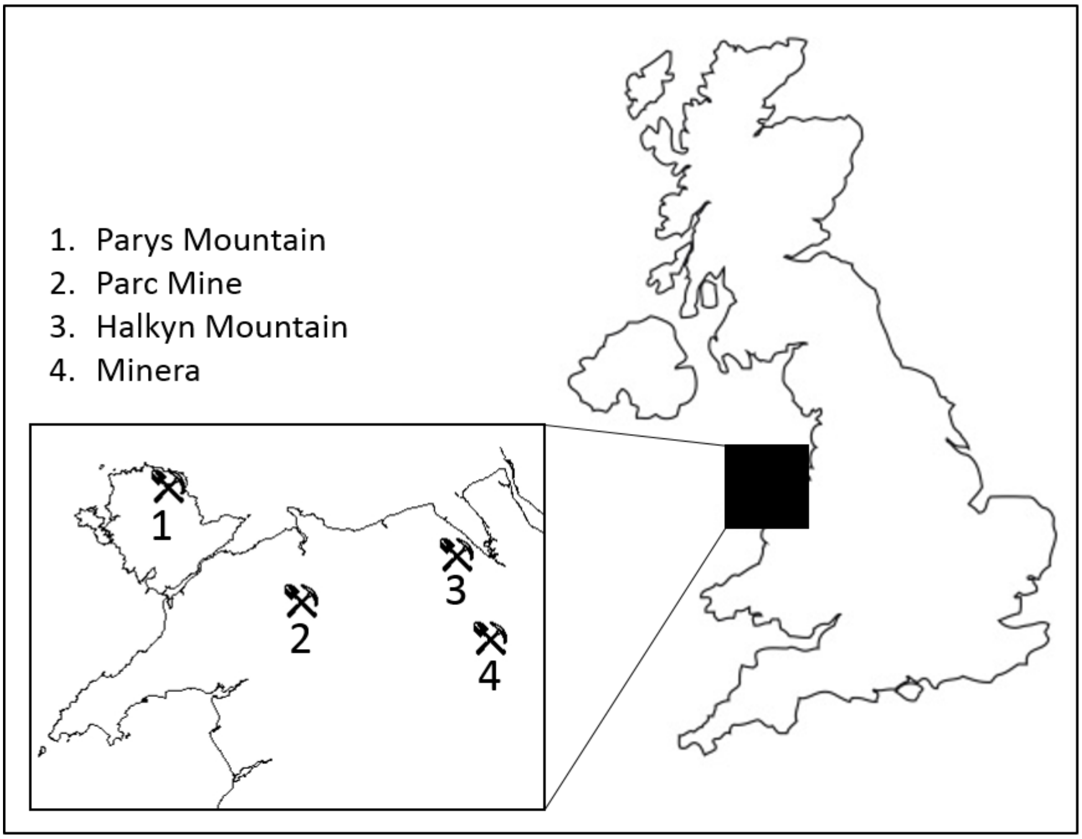

Figure 1

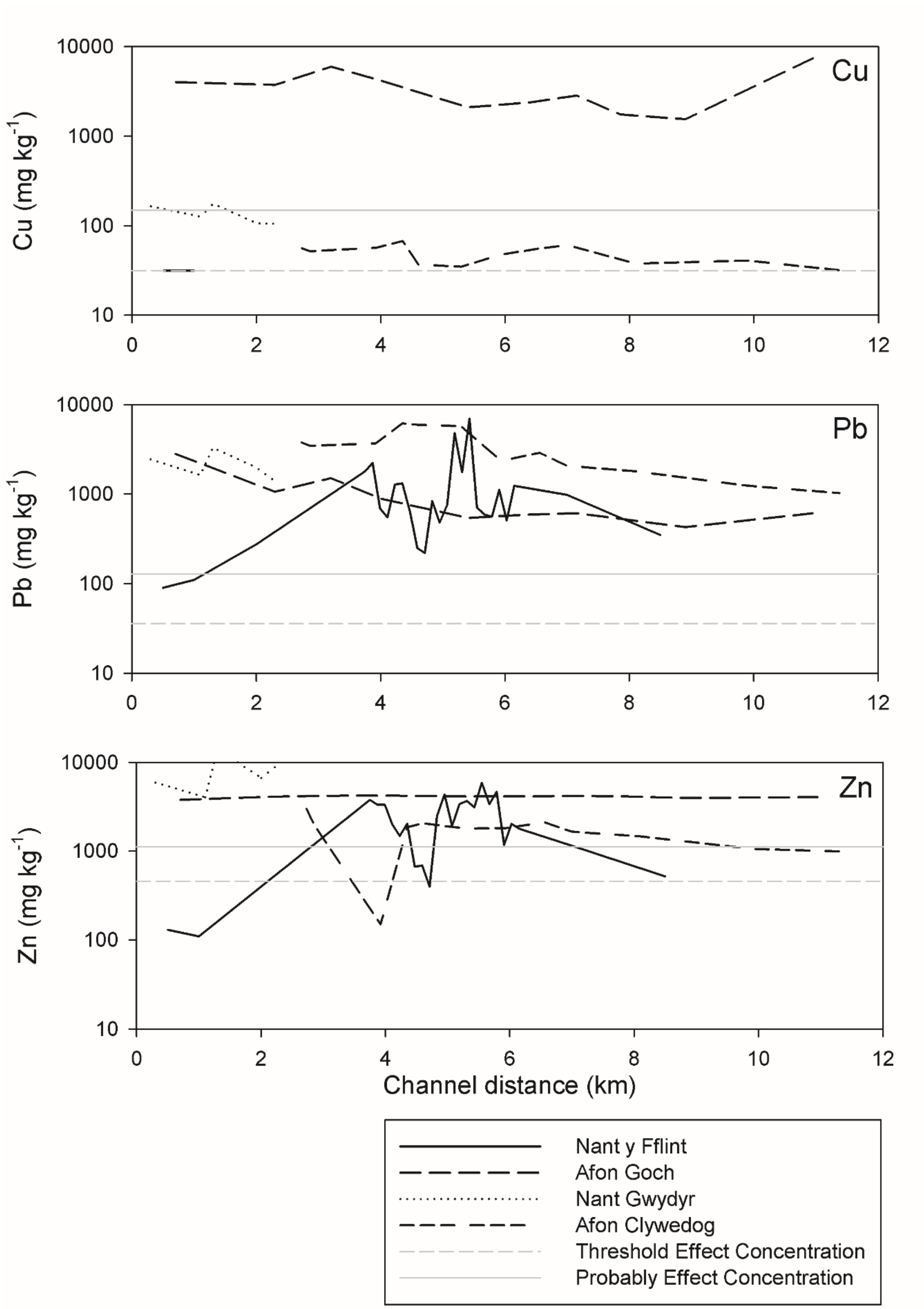
Cu
Cu (mg kg^{-1})
10000
1000
100
10
0
2
4
6
8
10
12
Pb
Pb (mg kg^{-1})
Zn
Zn (mg kg^{-1})
Channel distance (km)
Nant y Fflint
Afon Goch
Nant Gwydyr
Afon Clywedog
Threshold Effect Concentration
Probably Effect Concentration

Figure 2

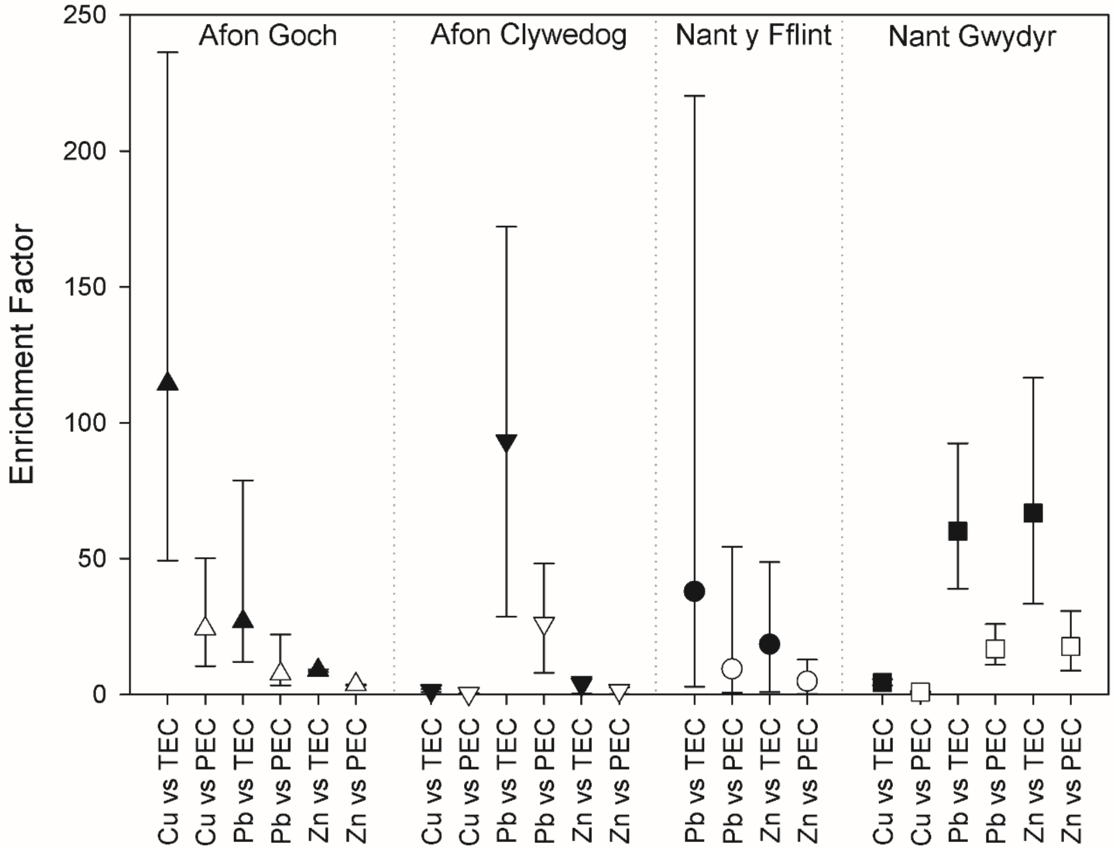
Afon Goch
Afon Clywedog
Nant y Fflint
Nant Gwydyr
Enrichment Factor
250
200
150
100
50
0
Cu vs TEC
Cu vs PEC
Pb vs TEC
Pb vs PEC
Zn vs TEC
Zn vs PEC

Figure 3

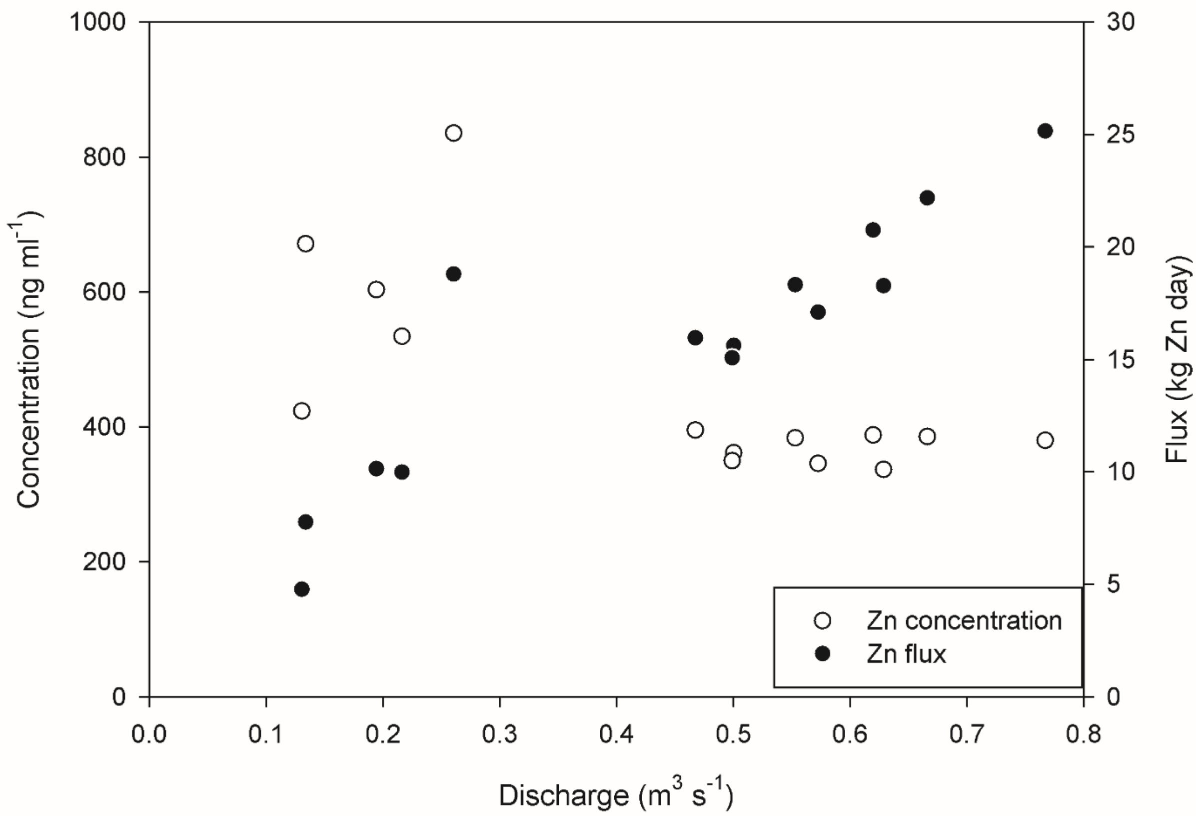

Figure 4

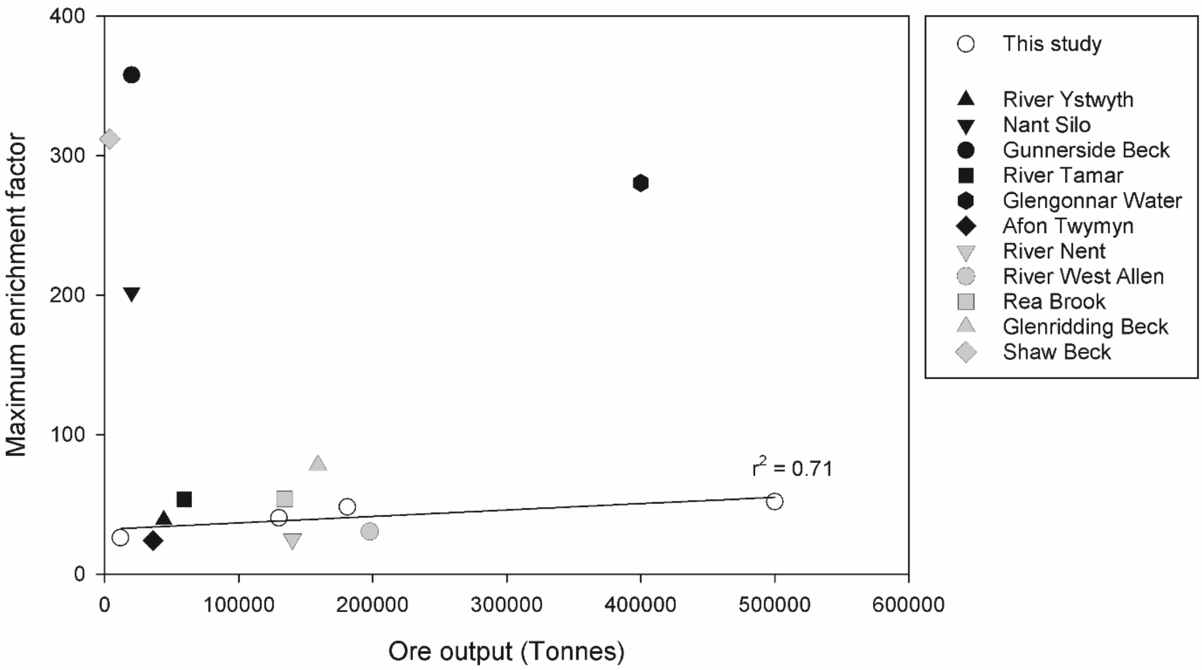

Figure 5

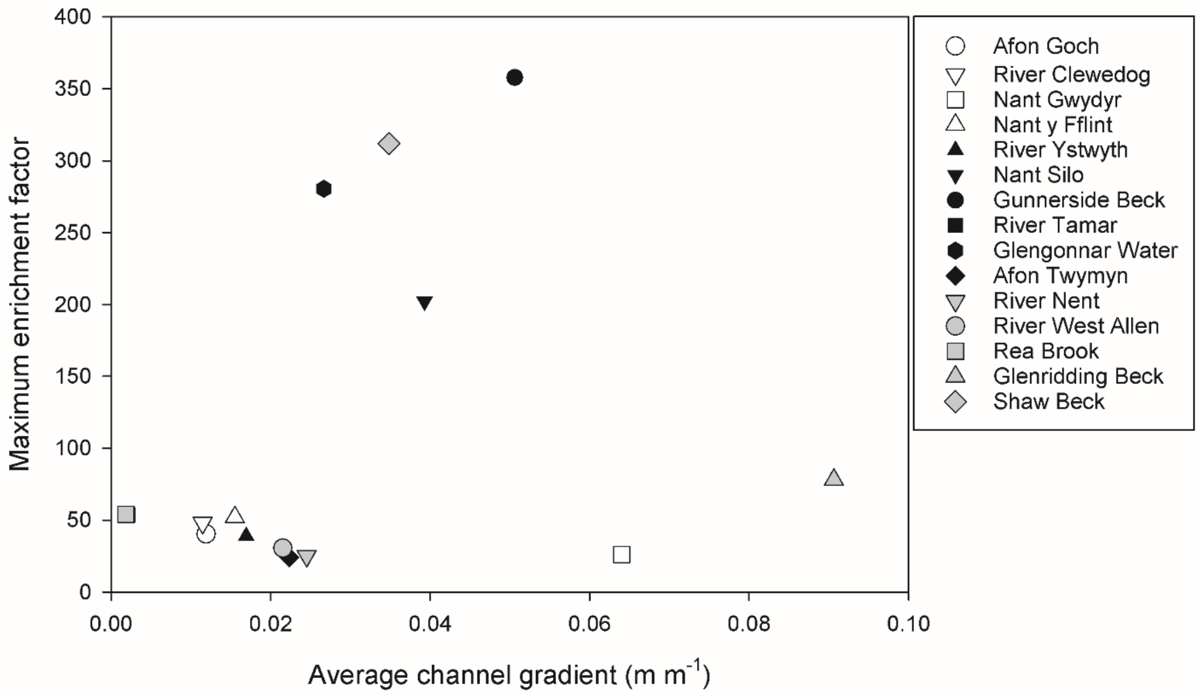

Figure 6

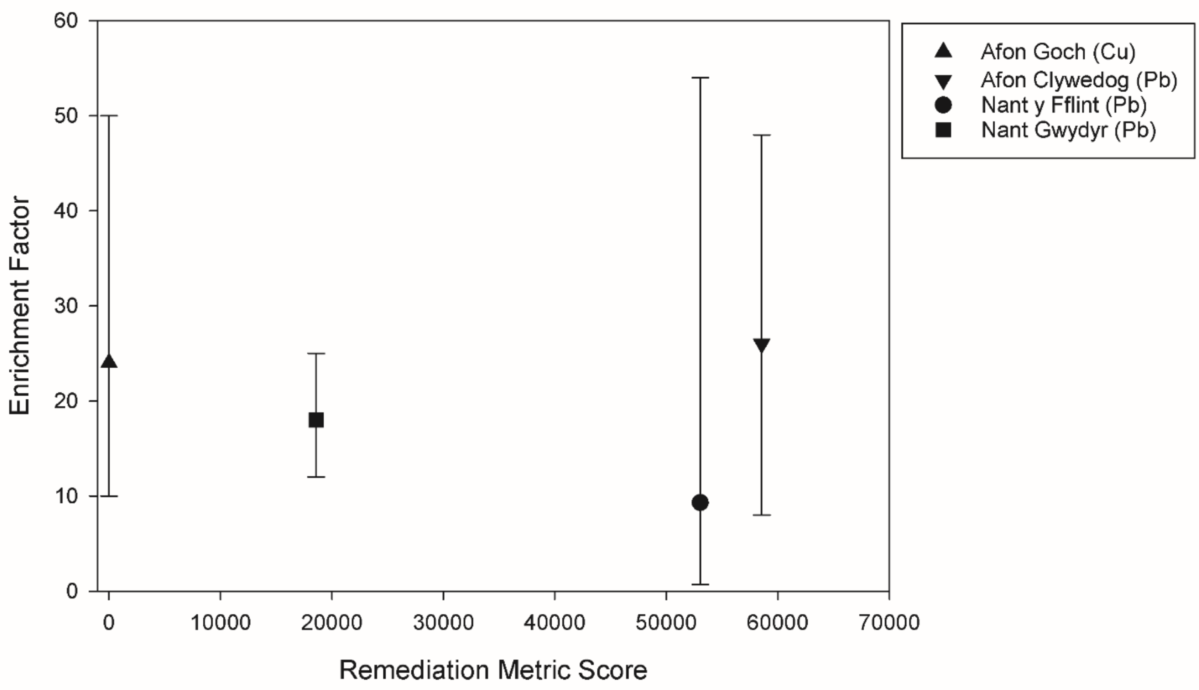

Figure 7

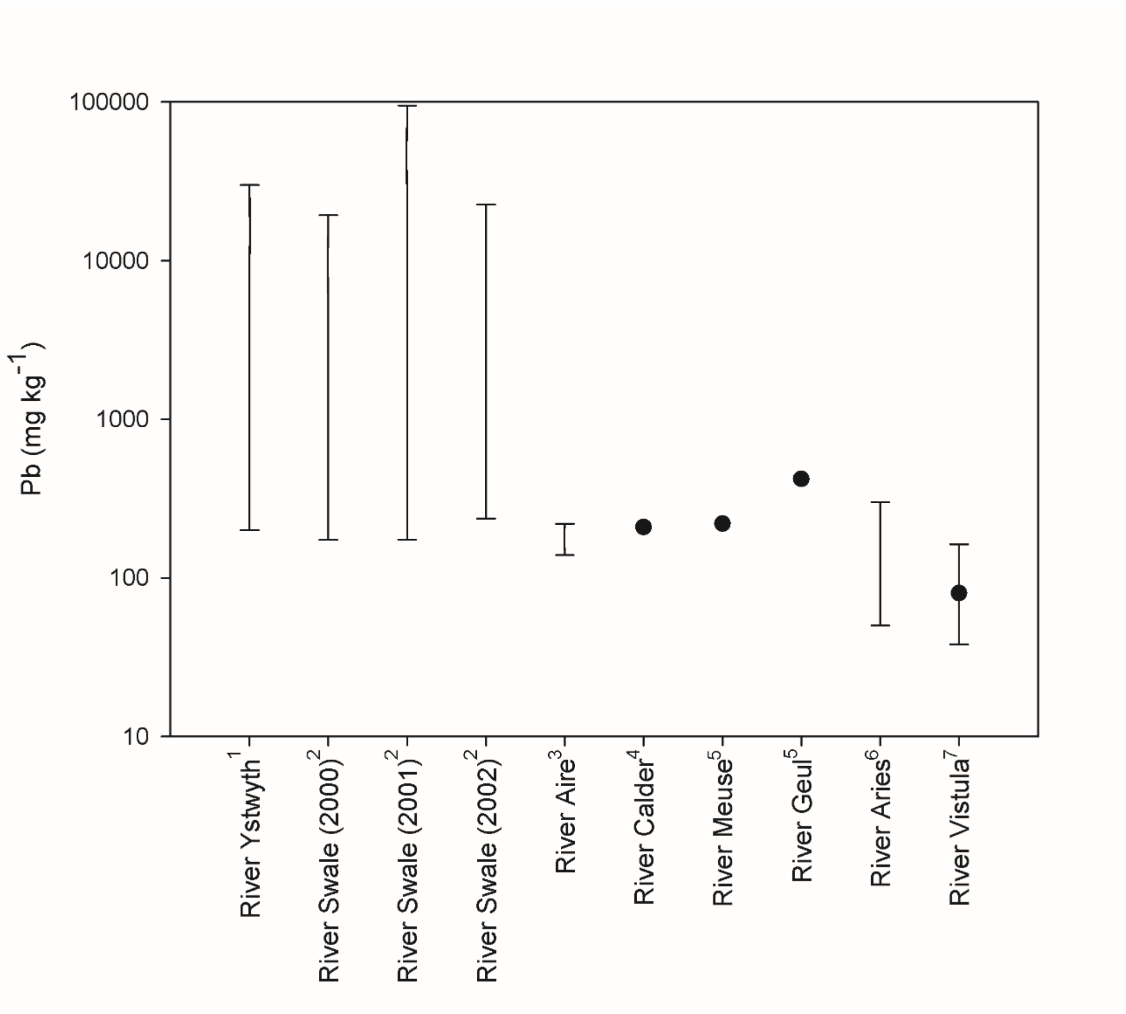
100000
10000
1000
100
10
Pb (mg kg-1)
River Ystwyth1
River Swale (2000)2
River Swale (2001)2
River Swale (2002)2
River Aire3
River Calder4
River Meuse5
River Geul5
River Aries6
River Vistula7

Figure 8