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Stormflow hydrochemistry of a river draining an abandoned metal mine: the Afon Twymyn, central Wales

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Abstract

Contaminated drainage from metal mines is a serious water quality problem facing nations that exploit metal mineral resources. Measurements of river hydrochemistry during baseflow are common at mine sites, whilst detailed hydrochemical information regarding stormflow is limited and often confined to a single event. This study investigates the seasonal evolution of stormflow hydrochemistry at an abandoned metal mine in central Wales, UK, and the possible sources and mechanisms of metal release. Significant flushing of metals was observed during stormflow events, resulting in concentrations that severely exceeded water quality guidelines. The relationship between metal concentrations and river discharge suggests dissolution of efflorescent metal sulphates on the surface of the mine spoil as the principal source of the contamination. High fluxes of Pb during stormflows are linked to extended periods of dry weather prior to storm events that produced water table drawdown and encouraged oxidation of Pb sulphide in the mine spoil. However, some Pb flushing also occurred following wet antecedent conditions. It is suggested that Fe oxide reduction in mine spoil and translatory flows involving metal-rich pore waters results in flushing during wetter periods. Detailed measurements of stormflow hydrochemistry at mine sites are essential for accurate forecasting of long-term trends in metals flux to understand metal sources and mechanisms of release, to assess potential risks to water quality and instream ecology, and to gauge the potential effectiveness of remediation. In order to protect riverine and riparian ecosystems, it is suggested that routine monitoring of stormflows becomes part of catchment management in mining-impacted regions.

Keywords: *metal mine; acid mine drainage; stormflow; hydrochemistry; water quality; toxic metals*

1. Introduction

Contaminated drainage from abandoned metal mines can cause significant degradation of the wider environment, particularly affecting freshwater and riparian ecosystems (Gray 1998; Smolders et al. 2003; Olias et al. 2004; Batty et al. 2010). Contaminated mine drainage can persist for centuries after the closure of a mine, contaminating soils and water in the immediate vicinity as well as sites further downstream (Macklin et al. 2003; Walling et al. 2003; Miller et al. 2004; Dennis et al. 2009; Gozzard et al. 2011). The source of contaminated drainage from mine sites is, typically, weathered metal sulphides (primarily pyrite) deep inside the mine or on the surface of mine spoil and tailings. Once exposed to the atmosphere, metal sulphides undergo a series of biogeochemical reactions that contaminate drainage (Younger et al. 2002). Metal mine pollution is a product of a range of factors including local mineralogy, lithology, contaminant source area and biogeochemical reactions (Johnson 2003). Typically, metal mine drainage will have high concentrations of dissolved toxic metals, sulphates and acidity (Younger et al. 2002). However, not all mine discharges are acidic and the character of water draining active and abandoned mines will be strongly influenced by meteorological and hydrological factors, including rainfall character, seasonally differentiated antecedent soil conditions, dominant water pathways and their hydrochemical character, and river discharge (Byrne et al. 2011).

A number of researchers have investigated seasonal variation in the quality of rivers draining mine sites (Grimshaw et al. 1976; Bird 1987; Keith et al. 2001; Sullivan and Drever 2001; Nagorski et al. 2002; Braungardt et al. 2003; Olias et al. 2004; Desbarats and Dirom 2005; Hammarstrom et al. 2005; Mighanetara et al. 2009; Nordstrom 2009). Many of these studies have reported maximum dissolved metal concentrations during periods of low flow during the summer months – a function of reduced dilution and, in some instances, increased metal oxidation as a result of water table drawdown and increased bacterial activity. High dissolved metal concentrations during autumn have been related to an increase in precipitation coinciding with reducing levels of evapotranspiration. Most studies measure metal concentrations and yields on a monthly or weekly basis at best. However, from the perspectives of mine site remediation and attempts to understand the relations between contaminants and the wider ecosystem, it is important to include higher resolution temporal sampling of river water chemistry that includes all flow conditions. If variations in toxic metals and other chemical parameters are substantial during stormflows at abandoned metal mines, then the absence of such data when making management and remediation decisions could result in the failure of water and sediment quality and ecosystem improvement schemes. For example, the absence of stormflow hydrochemical data compromises the ability to accurately predict long-term water quality trends, ecological impacts, pollution risks and the potential effectiveness of remediation technologies (Lambing et al. 2004). Therefore, there is a need to monitor stormflows in detail in order to adequately quantify contaminant dynamics and to allow resource managers to prioritise areas for remediation. However, detailed measurements of element transfers at mine sites during transient stormflows are limited (Grimshaw et al. 1976; Sanden et al. 1997;

Wirt et al. 1999; Keith et al. 2001; Lambing et al. 2004; Gammons et al. 2005; Lin et al. 2007; Canovas et al. 2008) and typically consider individual stormflow events or several events within a single season. The majority of studies have not considered the seasonal evolution of stormflow hydrochemistry.

This paper examines trace metal hydrochemistry (principally Pb, Zn, Cu, Cd, Fe and Mn) associated with stormflow events at an abandoned metal mine in central Wales, UK. The specific objectives of the paper are to: (a) investigate seasonal variability in metal hydrochemistry of the Afon Twymyn during rain-fed flood flows; (b) identify possible metal sources and mechanisms controlling variability in their contributions to stream hydrochemistry; and (c) highlight the importance of high-frequency stormflow hydrochemical data to contaminant and ecosystem health investigations, as well as remediation efforts at abandoned mine sites.

2. Methods

2.1 Field site

Dylife mine is located in the central Wales mining district, approximately 25 km north-east of Aberystwyth, at an elevation of 375 m above sea level (asl) **(Figure 1)**. The mine site is drained by the Afon Twymyn, which, at its confluence with the Afon Dyfi, has a catchment area of 35 km^2 and a range of elevation between 98 and 530 m asl. Active mining ceased at Dylife in the 1920s. However, it had been worked for Pb, Zn, Cu and Ag since the Bronze Age, with the principal period of ore extraction occurring in the mid to late 19th century AD. The Twymyn catchment is ranked amongst the most highly metal mine-impacted catchments in England and Wales (Mayes et al., 2009). The catchment lies on Upper Silurian argillaceous sediments, mainly comprised of shales, siltstones and mudstones (British Geological Survey 2007). Igneous activity during the Caledonian and Hercynian mountain-building periods gave rise to mineralisation. Rising hydrothermal solutions precipitated barite, fluorospar and sulphides of Zn, Pb, Cu and Fe (Evans 1975). Calcite and dolomite are rare, as are secondary minerals (Jones 1922). The mineralised faults trend east-north-east through the Ordovician and Silurian country rock (Fuge et al. 1991; **Figure 1**). Three mineral lodes are associated with Dylife mine while a number of mine shafts and adits are also present to the west of the mine site. To the east is the main spoil tip area (**Figure 1**). High precipitation (2010 mm/a; mean annual, 1979 – 2008), low temperatures (8.6 °C; mean annual, 2000 - 2008), and low permeability of the country rock have, in combination, encouraged the widespread accumulation of stagnopodzols and stagnohumic gleys (Brandt et al. 2004).

2.2 Baseflow water sampling

Baseflow hydrochemical data for the Afon Twymyn were collected on three occasions in June and October 2007 and in March 2008 during low flow periods when there had been no significant rainfall in the previous 7 days (**Table 1**). Samples for dissolved metals analysis were collected in 500 ml polypropylene bottles and refrigerated within 24 hours of collection. Measurements of stream pH were taken at the time of sampling using a Hanna portable pH meter (HI98108).

2.3 Stormflow water sampling

Permanent water sampling and monitoring stations were installed upstream of and at Dylife mine in October 2007 in order to investigate trace metal fluxes and river hydrochemistry during rain-fed stormflow events (**Figure 1**). The non-mine-impacted monitoring station was situated on the Nant Yr Lar tributary, just upstream of Rhyd Y Porthmyn reservoir, with a catchment area of 0.3 km^2. Brown (2006) reports that some spoil material was used in the construction of the reservoir but that there is no evidence of mineral prospecting upstream of this point; i.e., in the contributing area upstream from the non-mine-impacted monitoring station. The mine site monitoring station was located on the Afon Twymyn, directly downstream of the main spoil tip area at Dylife, with a catchment area of 3.6 km^2. Each station was instrumented with a YSI Hydrodata multi-parameter submerged sonde to record water column pH, temperature and conductivity at 15-minute intervals. The dissolved trace metal content of river water during stormflows was established in samples collected using a Teledyne ISCO 6712 automatic pump water sampler with SDI-12 data logger. Stormflow sampling programmes were triggered by a rise in water-stage (5 cm) and samples were taken over periods from 12 to 36 hours at intervals ranging from 15 to 120 minutes. Sample intervals were more frequent on the rising limb and peak of the hydrograph when hydrochemical changes were most likely to occur (Keith et al. 2001). Sample intervals were greater on the falling limb when significant hydrochemical changes were expected to be less likely (Canovas et al. 2008).

2.4 River stage and discharge

River stage was measured at each monitoring station using a Druck 175 mb pressure transducer. These were programmed to sample water depth every minute and log an average of this value at 15-minute intervals using a Grant Squirrel 2020 data logger. In order to establish a stage-discharge relation for each site, area-velocity estimates of discharge were established using a Valeport Model 801 electromagnetic current meter on 16 separate occasions incorporating a wide range of flows. Water discharge was then calculated for each stormflow event. Coefficients of determination for the upstream and downstream stage-discharge relationships were $r^2 = 0.816$ and $r^2 = 0.782$, respectively. The maximum flows sampled by current meter for the upstream (0.075 m^3/s) and downstream (0.471 m^3/s) stage-discharge relationships represented 61% and 52%, respectively, of the maximum flows estimated for storm-generated flood events for which hydrochemical data are available and reported here.

2.5 Precipitation

Precipitation data at 15-minute intervals were provided by the Environment Agency tipping bucket rain gauge at Dolydd, approximately 3.8 km south-south-east of Dylife at an altitude of 297 m asl.

2.6 Laboratory methods

All sample bottles used for metal analysis were immersed in 2% (v/v) nitric acid for 24 hours and rinsed with distilled water before use. On return to the laboratory, each water sample was filtered through 0.45 μm cellulose nitrate membrane filters (Whatman) and then preserved with 2% (v/v) nitric acid. Dissolved metal concentrations (Pb, Zn, Cu, Cd, Fe and Mn) were determined using a Thermo Jarrell Ash ICP-AES. Detection limits (μg/l) of the ICP were Pb: 10, Zn: 10, Cu: 30, Cd: 20, Fe: 60 and Mn: 20. Standards, replicates and blanks were used throughout the analyses. High precision of the ICP control standards is reported (±10%). The analytical accuracy of repeat control samples was ±4.2% for Pb, ±3% for Zn, ±1.5% for Cu, ±3.2% for Cd, ±3.2% for Fe and ±2.2% for Mn.

2.7 Statistical methods

Statistical dependencies between stormflow chemical and hydrological data were assessed by calculating Spearman's rank correlation coefficients. A cross-correlation function (CCF) was calculated between pairs of variables in two time-series for each stormflow event, where one time-series is increasingly lagged relative to the other. All statistical calculations were performed in the program PASW Statistics 18.

3. Results

3.1 Analysis of stormflow chemographs

3.1.1 Non-mine-impacted station

Two stormflow events were recorded at the non-mine-impacted station, one in August and one in November 2008 (**Table 2**). Due to instrumental failures, neither coincided with the events monitored at the mine station and this means that a direct comparison of mine-impacted and non-mine-impacted catchment responses to identical pre-storm and storm conditions is not possible. Nevertheless, the two non-mine-impacted station events fall in the same summer and autumn seasons and have been used to illustrate the response patterns of dissolved metal fluxes that can be expected from this terrain unaffected by historic mining activity.

During *Event 1* (09/08/08), an extended period of rainfall produced an initial, small but hydrochemically significant stream rise and fall, followed by a sluggish rise to peak storm discharge (**Figure 2**). *Event 2* (09/11/08) was characterised by two separate periods of rainfall (**Figure 2**). The first produced an initial, small rise in stage which was sustained for approximately five hours. The second produced a rapid rise to peak discharge. Both events resulted in significant chemograph changes during the first four hours of sampling. In *Event 1*, Zn, Pb, Cu, Cd, Fe and Mn exhibited similar trends, metal concentrations peaking in association with the initial, small rise and fall and preceding maximum discharge. Concentrations of all four chalcophile elements were high (510 µg/l Zn, 180 µg/l Pb, 60 µg/l Cu, 20 µg/l Cd). After four hours, metal concentrations had returned to values similar to those typical of baseflow (**Table 1**). Elevated concentrations of Pb (230 µg/l), Cu (30 µg/l) and Fe (80 µg/l) were also observed in the initial phase of runoff in *Event 2*. Cross-correlation analysis of the hydrochemical dataset from *Event 2* suggests an inverse (CCF = - 0.71; $p < 0.05$) and lagged (lag = - 4h) relationship between Zn and discharge. Copper (CCF = - 0.51; $p < 0.05$) and Pb (CCF = - 0.44; $p < 0.05$) exhibit similar relationship with discharge; however, no lag (lag = 0h) was evident between these metals and discharge. These data suggest different sources for these metals during this storm event.

3.1.2 Mine station

Six stormflow events were recorded at the mine station during the study period (**Table 2**). *Event 4* (06/07/08) was characterised by a rapid rise to a single-peaked hydrograph (**Figure 3**). Maximum Pb concentrations far exceeded mean baseflow levels (170 µg/l Pb) (**Table 2**). Clockwise hysteresis was observed in the relations between three of the metal concentrations and flow, with maximum metal concentrations (5000 µg/l Pb, 1790 µg/l Zn and 70 µg/l Mn) being recorded before peak discharge followed by rapid attenuation to levels typical of baseflow. Anti-clockwise hysteresis was evident for both Fe and Cu, their peak concentrations occurring after peak discharge, followed, in both cases, by a gradual decline to baseflow values. Hysteresis patterns for Pb, Zn and Fe during *Event 4* are illustrated in **Figure 4**. Cross-correlation of the hydrochemical data from *Event 4* illustrates differential behaviour of the metal chemographs. Both Zn (CCF = - 0.80; $p < 0.05$) and Pb (CCF = - 0.88; $p < 0.05$) demonstrated a lagged (lag = - 1h), inverse response to river discharge (clockwise hysteresis). The behaviour of Fe (CCF = 0.68; $p < 0.05$) and Cu (CCF = 0.71; $p < 0.05$) was different; these metals demonstrated a delayed (lag Fe = + 2h; lag Cu = + 5h), positive response to river discharge suggesting different sources for these metals during this storm event.

The different forms of hysteresis and the variation in the concentration of different metals during *Event 4* reflects a number of factors, including: stormflow hydrograph characteristics; antecedent soil moisture levels; the concentration of different minerals in the mine spoil (e.g., galena is more abundant than sphalerite or chalcopyrite); the different solution chemistry of each mineral; and different flowpaths (particularly in the mine spoil) operating at different times. The immediacy of the initial metal peaks for Pb, Zn and Mn and the lack of significant fluctuations thereafter might suggest that spoil surface and/or river-bed materials were the contamination sources during this stormflow event. Point source contributions from mine workings (e.g., adits and shafts) do not seem to have been important. Indeed, observations during stormflow periods identified only one mine opening (a collapsed stope) to discharge into the river and sampling of mine water emanating from this portal revealed relatively low toxic metal concentrations and circum-neutral pH (Byrne 2010; unpublished results). The incidence of the peaks in Cu and Fe concentration after peak discharge might represent a delayed throughflow (i.e., interflow) component of runoff from the mine spoil and a source rich in chalcopyrite. Another possibility is that Fe and Cu are associated with suspended sediment disturbed from the river bed at high flows, though, were this the case, the greatest turbulence and hence, suspended sediment and metal levels might be expected at peak discharge. Another consideration for the Fe behaviour is the arrival of Fe-rich waters from upland peat sources (Gozzard et al 2011). Rising Fe levels after peak discharge coincided with decreasing levels of some of the other trace metals. This produces a strong negative covariation of Pb and Fe ($r = -0.910$, $p < 0.01$) and Zn and Fe ($r = -0.965$, $p < 0.01$) on the falling limb of the hydrograph in *Event 4*, perhaps indicating that adsorption and/or co-precipitation with Fe hydroxides acted as an attenuation mechanism during this particular stormflow.

Event 5 (13/08/08) was similarly characterised by significant metal flushing before peak discharge (6150 µg/l Pb, 920 µg/l Zn, 220 µg/l Cu, 760 µg/l Fe, 210 µg/l Mn) (**Figure 3**). The event included the maximum Pb concentration recorded during the study period, exceeding that of *Event* 4. However, Zn concentrations were not as high as in *Event 4*. This may be related to the smaller magnitude of the event. The similarity of peaks in Pb between these events might be a function of its high availability in the mine spoil. Although Zn is more soluble, lower concentrations are likely to reflect its temporarily reduced availability in oxidised form as a function of the flushing associated with the previous, larger storm event.

Event 6 (03/09/08; **Figure 3**) produced the largest discharge peak (0.465 m^3/s) of the sampling period. Despite this, metal concentrations during flushing (maximum 1280 µg/l Pb, 690 µg/l Zn, 30 µg/l Cu) were considerably lower than in *Event 4*, probably reflecting the exhaustion of available oxidised material by successive summer and early autumn storms. A drop in stream pH coincided with peak Pb and Zn values, reflecting inputs of acidity that are likely to have their provenance in the sulphide oxidation products accumulated in the mine spoil and/or in the river bed or its margins. Carbonic acid from decomposing plant and animal matter in the peaty soils will also have been a factor (Neal 1997). In addition, a fall in pH might be related to precipitation of ferric iron hydroxides. Iron hydroxide precipitate (‘ochre’) is not common in the bed and banks of the Afon Twymyn; however, there are extensive deposits on the surface of the mine spoil and many small temporary channels have been observed to carry ochre during storm periods.

3.2 Trace metal fluxes during baseflow and stormflow conditions

In this section, we calculate baseflow and stormflow metal loads by combining elemental concentrations with river discharge measurements (**Table 3**). Baseflow metal load calculations are based on twelve separate measurements on different days in March, June, October and December 2008. Whilst we acknowledge the limited number of measurements used to calculate baseflow metal loads, we have attempted to cover the range of baseflows throughout the year and assert that variability in metal loads is likely to be greatest during stormflows for which we have captured high-resolution temporal data. Storm events at the non-mine-impacted monitoring station resulted in higher metals flux than at baseflow. However, storm events greater than or equal to monitored baseflow periods occurred infrequently over the study period (January to December 2008) (**Table 3**). During baseflow at the mine-impacted station, high Zn loads of between 8 and 16 kg/day (depending on season) were recorded – high loads were associated with low flows in June 2008 (Byrne 2010; unpublished results). Zinc loads during stormflows were within the baseflow range, suggesting that, here, storm events are not more significant than baseflows for export of Zn from the mine site. However, during stormflows, total Pb loads of over 16 kg/day were estimated, which compare with baseflow yields of 2 – 4 kg/day (Byrne 2010; unpublished results).

3.3 The importance of antecedent soil moisture

The importance of antecedent conditions for Pb mobilisation is evident because similar sized flow events (*Event 4* and *Event 6*) exhibited large difference in metal yields (**Table 3**). The estimation of antecedent moisture conditions in a catchment remains difficult due to the scarcity of soil moisture data, in comparison with that for rainfall and stream flow (Ali and Roy 2010). In the absence of measured soil moisture for the Afon Twymyn catchment, total storm metal loads were correlated with three different indices used as surrogates of antecedent soil moisture. The antecedent precipitation index (API) provides a measure of the state of wetness of a catchment (Shaw et al 2011) and is used widely in the absence of soil moisture data (Longobardi et al. 2003). It is calculated on a daily basis and assumes soil moisture declines exponentially when there is no rainfall. It also assumes that, the further back in time, the less important is rainfall in determining catchment wetness. Thus:

$$API_t = K*API_{t-1}$$

where API_t is the index *t* days after rainfall and K is a recession constant. If there is subsequent rainfall, then this is added to the index. Two other indices of catchment wetness were utilised: pre-event discharge; and the number of hours with rainfall in the 10 days prior to the stormflow event. Covariation of stormflow total metal yields and pre-event discharge is weak and not significant (**Table 4**). Similar weak covariation was recorded between total metal yields and the number of hours with rainfall during the preceding 10 days, with the exception of Cu, which shows a strong and significant negative association. API_5 and API_{10} (5 and 10 days prior to storm events) performed better, with strong and significant negative correlation with Pb, suggesting that the level of flushing of Pb during stormflow events is strongly linked to catchment wetness. Non-significant negative correlations for Zn may be due to its smaller range of concentrations during stormflows. The poor 'performance' of the other two indices might be due to the fact that there is no account taken of variation in the intensity of rainfall and baseflow generally declines through the summer months. The effect of dry antecedent soil moisture conditions is to increase metal oxidation and availability on the surface of the mine spoil and, in the absence of significant amounts of preferential macro-pore flow, to increase rainfall retention. Increased soil moisture retention will minimise both throughflow (interflow) and deeper seated flows that might otherwise, in wetter months, be expected to cause both lateral sub-surface flows from contaminated soil or spoil and groundwater efflux from the abandoned mine portals.

4. Discussion

4.1 Seasonal variability in stormflow hydrochemistry

Several authors have noted flushing of metals during stormflow events at abandoned metal mines (e.g., Grimshaw et al. 1976; Canovas et al. 2008). However, as far as is known, the present study is unique in investigating hydrochemical variation in multiple events during the course of the year (from April to November) and in identifying seasonal variability in metal flushing and the shape of the metals' chemographs. There was a distinct trend of increasing metal concentrations and stormflow event yields during the summer months followed by a gradual decline towards autumn and winter. The variable explaining this pattern is most likely to be antecedent soil moisture conditions in the catchment and in the mine spoil prior to stormflow events. The importance of dry antecedent soil moisture conditions in the generation of larger metal concentrations and yields has also been suggested by several authors studying mining-impacted rivers (Bird 1987; Braungardt et al. 2003; Desbarats and Dirom 2005). Bird (1987) found evidence of a link for baseflows between elevated concentrations of some metals (Zn, Cd, Mn) and low antecedent soil moisture levels. Other studies which have suggested that dry antecedent soil moisture conditions lead to increased metal flushing (e.g., Olias et al. 2004) have been undertaken in semi-arid environments (e.g., south-west Spain) where there is a clear distinction between long, dry summers and subsequent large rainfalls events in autumn and winter. However, in general, there is little quantitative evidence linking increased metal yields to low catchment wetness, and this phenomenon has not been investigated in multiple stormflow episodes previously. The strong inverse relation between stormflow yields of Pb and API in this study suggests that antecedent soil moisture conditions were important in determining the level of flushing of Pb at Dylife mine.

4.2 Metal sources and mechanisms controlling the release of trace metals

Hysteresis in the relation between solute and water discharge in relatively small river catchments, such as the Afon Twymyn, is generally a function of the changing relative significance of surface and near-surface flow paths and differentiated sources of runoff (Webb et al. 1987). Diffuse pollution has been identified as an important contributor to total metal flux in rivers affected by former mining activities across England and Wales (Jarvis and Mayes 2012), accounting for over 90% of the total mass flux of metals during stormflows (approximately 50% during baseflows) (Mayes et al. (2008; Gozzard et al. 2011). Some researchers have suggested that dissolution and flushing of efflorescent metal salts which have accumulated in a shallow oxidation zone near the surface of mine spoil is a primary diffuse contamination mechanism at mine sites (e.g., Hammarstrom et al. 2005; Canovas et al. 2008; Navarro et al. 2008; Gilchrist et al. 2009; Canovas et al. 2010; Flores and Sola, 2010). Keith et al. (2001) found efflorescent salts to occur as thin crusts in intermittent stream channels and pools on the surface of mine spoil. Evaporation of these water bodies acted to concentrate metals and acidity and eventually led to the accumulation of surface crusts which could be dissolved and flushed into rivers during subsequent storms. Extended periods of dry weather will also increase oxidation and metal availability in the upper layers of mine spoil due to water table drawdown. The role of sulphur and iron-oxidising bacteria in increasing metal availability in dry and warm periods is known to be important in semi-arid and arid regions (Hallberg and Johnson 2005; Natarajan et al. 2006; Balci 2008). However, the colder climate of central Wales is likely to mean that the activity of such bacteria in the Dylife mine spoil will be low.

During storm periods at Dylife mine, the rapid movement of water to the channel via overland flow and the dissolution of oxidised material at the surface of the mine spoil were important mechanisms leading to high dissolved metal concentrations on the rising limb of hydrographs. In some stormflow events (*Event 4*, *Event 5* and *Event 6*), peak metal concentrations were almost synchronous with peak discharge, suggesting metals may have also been derived from the riverbed via disturbance of metal-rich interstitial waters. Research has found the sediments of the Afon Twymyn to be grossly contaminated with trace metals and that a large proportion of these metals exist in acid-soluble and oxidisable geochemical fractions (Byrne et al. 2010). Disturbance and oxidation of surface sediments at high flows has been found to release sulphide / organic-bound metals to the water column (Zoumis et al. 2001). A drop in sediment pH accompanying oxidation can also release exchangeable and carbonate-bound metals (Wilkin 2008). Much of this diffuse metal load would likely be associated with fine-grained (colloidal) particulate material (Kimball et al. 1995). Overbank flows may also remobilise ochre deposits and metal-rich sulphates formed on the alluvium during dry periods (Hudson-Edwards et al. 1999; Braungardt et al. 2003).

In addition to overland flow and the dissolution of surface salts during dry periods, it is highly likely that translatory flows (Hewlett and Hibbert 1967) played a role in generating the observed metal peaks in wetter periods. It is well known that subsurface translatory flow associated with a fluid pressure wave can result in pre-event or ‘old’ water contributing significantly to runoff during a storm event. Genereax and Hooper (1998) calculated, from a range of catchment sizes and land covers, that 70 ±20% of storm flow at peak discharge was composed of pre-event resident water. The relative contribution of translatory flow to the stormflow hydrograph is strongly linked to the saturation level of the soil (Hewlett and Hibbert 1967). If the water content of the soil is near that required for fluid flow (near or above retention capacity), then only a relatively small volume of rainfall is required to transmit a wave of fluid pressure (almost instantaneously) through a soil system (Charbeneau 1984). The predominant rainfall pattern (low intensity, high frequency) in the upper Twymyn catchment ensures that the Dylife mine spoil remains saturated at deeper levels throughout the year, resulting in the development of a reducing and anoxic environment. Trace metal attenuation could occur in the saturated waste rock as a consequence of the formation of insoluble metal sulphides. Where the mine spoil is rich in organic carbon, the same reducing process could also liberate large quantities of trace metals to the dissolved phase through reduction of ferric iron to ferrous iron and the release of co-precipitated and adsorbed trace metals. However, most mine spoil does not contain large amounts of organic carbon, except perhaps when an organic cover is introduced to reduce oxygen ingress (Ribet et al. 1995). Periodic flushing of these mobile metal reservoirs by subsurface translatory flows may result in higher metal levels than that leached from surface efflorescent salts. In this way, prolonged saturation of the mine spoil may result in metal flushing in wetter periods (e.g., *Event 5* - a number of smaller high flow events occurred in the previous week in response to similar precipitation events).

Flushing of metals at the non-mine-impacted station was expected, due to high levels of local mineralisation. However, some metal concentrations were extremely high and far in excess of those encountered under baseflow conditions. Mighall et al. (2009) noted metal contamination of peatlands in mid-Wales resulting from Cu and Pb smelting as early as the Bronze Age. Rothwell et al. (2005) found Pb to be associated with a specific sediment source in peatlands, namely that of organic sediment eroded from the acrotelm (upper peat layers). In a similar way to Pb, Cu exhibits a high affinity with organic matter which may explain the similar behaviour of these metals at the non-mine-impacted station in this study. The very high Zn concentrations (512 µg/l) observed during the initial stages of *Event 1* were almost certainly related to the greater mobility of this metal and the poor sorption of this metal to organic matter (Rothwell et al. 2007b; Mighall et al. 2009). A further important factor might have been catchment wetness prior to the stormflow event. Dry antecedent soil moisture conditions prior to *Event 1*, indicated by a low API, might have created high Zn availability in the surface peat layer as a result of oxidising conditions produced by a low water table. With the onset of rainfall, oxidised Zn in the acrotelm will have been rapidly flushed to the stream via quick return flow. The catchment topography above the non-mining-impacted monitoring station is relatively steep (>30°) and characterized by eroding gullies. Recent research has shown the importance of water table draw down at peatland gully edges for the mobilisation of As and Sb (Rothwell et al. 2010) and it is possible that Zn shares a similar fate in peatlands. The current investigation also found little effect of water table draw down on the mobility of Pb and Cu. This suggests that Zn may be being sourced primarily from gully edge sediments which have experienced oxidation, whilst less mobile elements such as Pb and Cu are sourced from organic-rich sediments at a distance from the gully edge.

4.3 Importance of monitoring stormflow hydrochemistry at mine sites

During stormflow flushing at Dylife, dissolved Pb concentrations were up to 500 times greater than background concentrations recorded at non-mine impacted sample sites in the Nant Yr Lar (**Figure 1**). Stormflow Pb loads were also far greater than those encountered under baseflow. This evidence would challenge the picture presented by standard water quality monitoring data that Zn is the primary contaminant from an ecological and water quality perspective (Parsons Brinckerhoff Ltd., 2005). Considering metal loads during stormflows, total Pb loads were up to four times greater than maximum recorded baseflow yields (Byrne 2010; unpublished results). On one occasion (*Event 4*), the high Pb load was associated with a peak storm discharge which was only exceeded 2% of the time during the study period. However, a similarly high Pb load occurred in *Event 5* which had a much lower peak storm discharge which was exceeded 20% of the time during the study period. The similar load response between storm events with different hydrological characteristics stresses the importance of conditions antecedent to the storms and not simply storm hydrological characteristics in accounting for variability in metal load between events. Lead transport by stormflows is undoubtedly significant to the annual metal load. However, because of the variable response to runoff events of similar magnitude, it is difficult to establish with confidence the overall contribution of stormflows to the annual metal load. The different behaviour observed for Pb and Zn is likely to be related to their solution chemistry. Zinc is more soluble than Pb at circum-neutral pH and a greater proportion of this metal can be leached by the slow-moving subsurface waters that contribute baseflow (Rothwell et al. 2007b). However, the greater stability of Pb means that high dissolved loads are restricted to stormflow conditions which disturb and oxidise Pb-enriched sediment and solubilise Pb salts (Rothwell et al. 2007a). These results highlight the importance of including stormflow sampling during water quality monitoring in mining-impacted sites.

Mine water drainage can emanate from multiple sources in a catchment, from mine portals or mine tailings and spoil. In the present study, it would appear that diffuse source drainage from mine spoil is the major source of contamination. This poses the greatest challenge from a remediation perspective. Point sources of contamination can be relatively easily collected and routed to treatment areas. The chemistry, flow, and contaminant yields of point discharges can be established relatively easily, allowing treatment technologies to be designed and implemented. This has been the approach at several metal and coal mine sites throughout Europe (e.g., Whitehead and Prior 2005) and North America (e.g., Hedin et al. 1994). Such systems have proved relatively efficient at treating point source discharges, where iron, sulphates and acidity are the principal contaminants, though effective removal of Zn and Cd remains problematic (Byrne et al. 2011; Jarvis et al. 2012). However, during storm events at abandoned mine sites, many small seepages draining mine spoil can combine to create a significant diffuse discharge which could bypass or inundate a treatment system. In upland central Wales, where large storm flows are frequent, this could mean significant quantities of mobilised mine waste not receiving treatment. This highlights the need to quantify, at high temporal resolution, variation in metal concentration and flux between and within hydrological events. Without these measurements, long-term predictions of the contaminant removal capacity of treatment systems will be based on underestimates, giving false expectations of the lifespan of the system. Instantaneous metal loads during runoff events might exceed system design limits, affecting efficiency. Predictions of potential improvements to the water quality and ecology of rivers draining abandoned mines will be over-estimated (Lambing et al. 2004). Agricultural floodplains downstream of mine sites will continue to be inundated with contaminated sediment. This study also identified decreases in stream water pH during the initial stages of storm runoff. Although the scale of the decline in pH was not large at Dylife, due to the predominant sedimentary lithology and lack of pyritic minerals at the mine, greater levels of acidity might be expected at mine sites with greater quantities of pyritic minerals (e.g., Canovas et al. 2008). Large-scale acid flushes might compromise the functioning of alkalinity-based treatment systems, many of which are effective over only narrow pH ranges (e.g., Nuttall and Younger 2000). Despite the importance of high temporal resolution monitoring of stormflow chemistry, budgetary constraints mean that current UK guidance is for low temporal resolution synoptic loading assessments under varying hydrological conditions intended to incorporate, however inadvertently, high flow conditions (Jarvis and Mayes 2012). At complex sites (e.g., those with multiple point sources and diffuse pathways) such as Dylife, regulators are likely to accept that high flow events are beyond most treatment technologies and that point source treatment will focus on baseflow conditions (Jarvis et al. 2012). A variety of filter strips, swales, grassed waterways and infiltration trenches, similar to those applied to tackle other types of diffuse pollution could also be utilized (Novotny 2003).

This study has shown that stormflow events are a significant transport mechanism in the annual metal yield of a mining-impacted river, even in a region where the climate might limit the availability of metals that can be flushed. Current regulatory practice suggests that stormflow events with high metal yields will remain untreated at the majority of abandoned metal mine sites in England and Wales (Jarvis and Mayes 2012). Predicted increases in stormflow frequency and magnitude as a result of climate change (Rance et al. 2012) have raised concern of increased mobilisation and deposition of toxic metals in floodplains used for arable and pastoral farming (Dennis et al. 2009; Nordstrom, 2009), raising long-term health concerns for those ingesting contaminants via crops produced on this land (Conesa et al. 2010). If we are to experience more drought and more extreme high flow events in the future, our data supports the idea of increased metal delivery to floodplains and, potentially, more short-term, extreme perturbations which may have implications for aquatic ecosystem health. The highly elevated toxic metal concentrations recorded during stormflows in this study will probably cause harm to aquatic communities and degrade biological quality (Wolz et al. 2009). This gives an emphasis to understanding the relationship between the physical remobilisation of contaminants during stormflows and the potential toxicological impacts (Wolz et al. 2009).

5. Conclusions

At mine sites, the evolution of river hydrochemistry during stormflows is poorly understood due to inherent difficulties of obtaining measurements. This poor understanding has wider implications for the assessment of contaminant mobility and dispersal, remediation design and effectiveness, ecological health of affected rivers, and potential floodplain contamination downstream. This study has presented hydrological and hydrochemical data from stormflow events during the course of a year (from April to November) at an abandoned metal mine within a small river catchment. Most stormflows substantially increased dissolved trace metal concentrations and yields and, therefore, the potential toxicity of river water at abstraction sites on the Afon Twymyn. The immediacy of the metal flush on the rising limb and peak of each hydrograph suggests the surface of spoil as the primary source of contamination and overland flow as the principal component of runoff delivering metals to the river. The metals were most likely derived from efflorescent metal sulphates on the surface of the mine spoil. A second source was likely to be the highly mobile and bioavailable metals that were desorbed from the fine sediment that forms a matrix in the river bed and its margins. However, metal-rich, translatory flows emanating from the bank and upwelling through the hyporheic zone of the channel fill may become increasingly important during wetter periods, metal release being associated with Fe(III) oxide and hydroxide reduction in anoxic mine spoil sediments. Dry antecedent soil moisture conditions appear to have been important in creating higher Pb concentrations in summer. This facilitated Pb dissolution in rainwater that was being redistributed through the soil profile, a translocation that manifested itself in the first, but not necessarily the largest, pulse of stream runoff. A distinct seasonal pattern was observed, the greatest levels of metal flushing occurring during stormflows of summer.

Future climate change predictions for the UK indicate scenarios of warmer, drier summers with stormflow events having greater magnitude. Such a scenario might result in increased biogeochemical cycling of toxic metals in mine spoils and transportation of these contaminants downstream and onto floodplains. Future research should focus on understanding the relative contribution of diffuse sources (surface efflorescent salts, reduced metals in the saturated waste rock, and mobile metal fractions in river bed sediments) to contaminant export from mine sites, the role of stormflows in dispersing contaminated sediment from mine sites now and in the future, and the geochemical and mineralogical processes controlling metal mobility and speciation in mining-impacted sediment-water systems.

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References

1. Ali, G. A., & Roy, A. G. (2010). A case study on the use of appropriate surrogates for antecedent moisture conditions (AMCs). *Hydrology and Earth System Sciences, 14*(10), 1843-1861.
2. Balci, N. C. Effects of bacterial activity on the release of trace metals from sphalerite oxidation. In N. Rapantova, & Z. Hrkal (Eds.), *Mine Water and the Environment, 2008*: Ostrava (VSB – Technical University of Ostrava)
3. Batty, L. C., Auladell, M., & Sadler, J. (2010). The impacts of metalliferous drainage on aquatic communities. In L. C. Batty, & K. B. Hallberg (Eds.), *Ecology of Industrial Pollution* (pp. 70-100). Cambridge: Cambridge University Press.
4. Bird, S. C. (1987). The effect of hydrological factors on trace metal contamination in the River Tawe, South Wales. *Environmental Pollution, 45*, 87-124.
5. Brandt, C., Robinson, M., & Finch, J. W. (2004). Anatomy of a catchment: the relation of physical attributes of the Plynlimon catchments to variations in hydrology and water status. *Hydrology and Earth System Sciences, 8*, 345-354.
6. Braungardt, C. B., Achterberg, E. P., Elbaz-Poulichet, F., & Morley, N. H. (2003). Metal geochemistry in a mine-polluted estuarine system in Spain. *Applied Geochemistry, 18*, 1757-1771.

7. British Geological Survey (2007). *British Regional Geology: Wales*. Nottingham: British Geological Survey.
8. Brown M (2006). Dylife. *The industrial and social history of a famous Welsh lead mine*. Ceredigion: Y Lolfa Cyf.
9. Byrne, P., Reid, I., & Wood, P. J. (2010). Sediment geochemistry of streams draining abandoned lead/zinc mines in central Wales: the Afon Twymyn. *Journal of Soils and Sediments, 4*, 683-697.
10. Byrne, P., Wood, P. J., & Reid, I. (2011). The impairment of river systems by metal mine contamination: A review including remediation options. *Critical Reviews in Environmental Science and Technology*, doi:10.1080/10643389.2011.574103.
11. Canovas, C. R., Hubbard, C. G., Olias, M., Nieto, J. M., Black, S., & Coleman, M. L. (2008). Hydrochemical variations and contaminant load in the Rio Tinto (Spain) during flood events. *Journal of Hydrology, 350*, 25-40.
12. Canovas, C. R., Olias, M., Nieto, J. M., & Galvan, L. (2010). Wash-out processes of evaporitic sulfate salts in the Tinto river: Hydrogeochemical evolution and environmental impact. *Applied Geochemistry, 25*(2), 288-301.
13. Charbeneau, R. J. (1984). Kinematic Models for Soil-Moisture and Solute Transport. *Water Resources Research, 20*(6), 699-706.
14. Conesa, H.M., Perez-Chacon, J.A., Arnaldos, R., Moreno-Caselles, J., Faz-Cano, A., (2010). In situ heavy metal accumulation in lettuce growing near a former mining waste disposal area: Implications for agricultural management. *Water, Air and Soil Pollution, 208*, 377-383.
15. Dennis, I.A., Coulthard, T.J., Brewer, P., & Macklin, M.G. (2009). The role of floodplains in attenuating contaminated sediment fluxes in formerly mined drainage basins. *Earth Surface Processes and Landforms, 34*, 453–466.
16. Desbarats, A. J., & Dirom, G. C. (2005). Temporal variation in discharge chemistry and portal flow from the 8-Level adit, Lynx Mine, Myra Falls Operations, Vancouver Island, British Columbia. *Environmental Geology, 47*, 445-456.
17. Evans, L. J., & Adams, W. A. (1975). Chlorite and illite in some lower Palaeozoic mudstones of mid-Wales. *Clay Minerals, 10*, 387-397.
18. Flores, A. N., & Sola, F. M. (2010). Evaluation of Metal Attenuation from Mine Tailings in SE Spain (Sierra Almagrera): A Soil-Leaching Column Study. *Mine Water and the Environment, 29*(1), 53-67.
19. Fuge, R., Laidlaw, I. M. S., Perkins, W. T., & Rogers, K. P. (1991). The influence of acidic mine and spoil drainage on water quality in the mid-Wales area. *Environmental Geochemistry and Health, 13*, 70-75.
20. Gammons, C. H., Shope, C. L., & Duaime, T. E. (2005). A 24 h investigation of the hydrogeochemistry of baseflow and stormwater in an urban area impacted by mining: Butte, Montana. *Hydrological Processes, 19*, 2737-2753.
21. Generaux, D. P., & Hooper, R. P. (1998). Oxygen and hydrogen isotopes in rainfall-runoff studies. In C. Kendall, & J. J. McDonnell (Eds.), *Isotope Tracers in Catchment Hydrology* (pp. 319-346). New York: Elsevier.

22. Gilchrist, S., Gates, A., Szabo, Z., & Lamothe, P. J. (2009). Impact of AMD on water quality in critical watershed in the Hudson River drainage basin: Phillips Mine, Hudson Highlands, New York. *Environmental Geology, 57,* 397-409.
23. Gozzard, E., Mayes, W.M., Potter, H.A.B. & Jarvis, A.P. (2011). Seasonal and spatial variation of diffuse (non-point) source zinc pollution in a historically metal mined river catchment, UK. *Environmental Pollution*, *159*, 3113-3122.
24. Gray, N. F. (1998). Acid mine drainage composition and the implications for its impact on lotic systems. *Water Research, 32*, 2122-2134.
25. Grimshaw, D. L., Lewin, J., & Fuge, R. (1976). Seasonal and short-term variations in the concentration and supply of dissolved zinc to polluted aquatic environments. *Environmental Pollution, 11*, 1-7.
26. Hallberg, K. B., & Johnson, D. B. (2005). Microbiology of a wetland ecosystem constructed to remediate mine drainage from a heavy metal mine. *Science of the Total Environment, 338*(1-2), 53-66.
27. Hammarstrom, J. M., Seal, R. R., II., Meier, A. M., & Kornfeld, J. M. (2005). Secondary sulfate minerals associated with acid drainage in the eastern US: recycling of metals and acidity in surficial environments. *Chemical Geology, 215*, 407-431.
28. Hedin, R. S., Nairn, R. W., & Kleinmann, R. L. P. (1994). Passive Treatment of Coal Mine Drainage. US Bureau of Mines.
29. Hewlett, J. D., & Hibbert, A. R. Factors affecting the response of small watersheds to precipitation in humid areas. In W. E. Sopper, & H. W. Lull (Eds.), *Proceedings of the International Symposium on Forest Hydrology, 1967* (pp. 275-290): Pergamon, New York
30. Hudson-Edwards, K. A., Schell, C., & Macklin, M. G. (1999b). Mineralogy and geochemistry of alluvium contaminated by metal mining in the Rio Tinto area, southwest Spain. *Applied Geochemistry, 14,* 1015-1030.
31. Jarvis, A.P., & Mayes, W.M. (2012). *Prioritisation of abandoned non-coal mine impacts on the environment*. Environment Agency Science Report SC030136/R12, Bristol: Environment Agency.
32. Jarvis, A.P., Gandy, C.J., & Gray, N.D. (2012). *Mitigation of pollution from abandoned metal mines Part 1: Review of passive treatment technologies for metal mine drainage remediation*. Environment Agency Science Report SC090024/R1, Bristol: Environment Agency.
33. Johnson, D. B. (2003). Chemical and microbiological characteristics of mineral spoils and drainage waters at abandoned coal and metal mines. *Water, Air, and Soil Pollution, 3,* 47-66.
34. Jones, O. T. (1922). *Lead and zinc. The mining district of north Cardiganshire and west Montgomeryshire*. London: British Geological Survey.
35. Keith, D. C., Runnells, D. D., Esposito, K. J., Chermak, J. A., Levy, D. B., Hannula, S. R., et al. (2001). Geochemical models of the impact of acidic groundwater and evaporative sulfate salts on Boulder Creek at Iron Mountain, California. *Applied Geochemistry, 16*, 947-961.
36. Kimball, B.A., Callender, E., & Axtmann, E.V. (1995). Effects of colloids on metal transport in a river receiving acid-mine drainage, Upper Arkansas River, Colorado, USA. *Applied Geochemistry, 10*, 285-306.
37. Lambing, J. H., Nimick, D. A., & Cleasby, T. E. (1999). Short-term variation of trace-element concentrations during base flow and rainfall runoff in small basins. U.S. Geological Survey.

38. Lin, C., Wu, Y., Lu, W., Chen, A., & Liu, Y. (2007). Water chemistry and ecotoxicity of an acid mine drainage-affected stream in subtropical China during a major flood event. *Journal of Hazardous Materials, 142*(1-2), 199-207.
39. Longfield, S. A., & Macklin, M. G. (1999). The influence of recent environmental change on flooding and sediment fluxes in the Yorkshire Ouse basin. *Hydrological Processes, 13*(7), 1051-1066.
40. Longobardi, A., Villani, P., Grayson, R. B., & Western, A. W. On the relationship between runoff coefficient and catchment initial conditions. In *Proceedings of MODSIM 2003867-872, 2003.*
41. Macklin, M. G., Brewer, P. A., Balteanu, D., Coulthard, T. J., Driga, B., Howard, A. J., et al. (2003). The long-term fate and environmental significance of contaminant metals released by the January and March 2000 mining tailings dam failures in Maramures County, upper Tisa Basin, Romania. *Applied Geochemistry, 18*, 241-257.
42. Mayes, W.M., Gozzard, E., Potter, H.A.B., & Jarvis, A.P. (2008). Quantifying the impacts of diffuse minewater pollution in a historically heavily coal mined catchment. *Environmental Pollution, 151*, 165-175.
43. Mayes, W.M., Johnston, D., Potter, H.A.B., & Jarvis, A.P. (2009). A national strategy for identification, prioitisation and management of pollution from abandoned non-coal mine sites in England and Wales. I. Methodology development and initial results. *Science of the Total Environment, 407*, 5435-5447.
44. Mighall, T.M., Timberlake, S., Foster, I.D.L., Krupp, E., & Singh, S. (2009). Ancient copper and lead pollution records from a raised bog complex in Central Wales, UK. *Journal of Archaeological Science, 36*, 1504-1515.
45. Mighanetara, K., Braungardt, C. B., Rieuwerts, J. S., & Azizi, F. (2009). Contaminant fluxes from point and diffuse sources from abandoned mines in the River Tamar catchment, UK. *Journal of Geochemical Exploration, 100*, 116-124.
46. Miller, J. R., Hudson-Edwards, K. A., Lechler, P. J., Preston, D., & Macklin, M. G. (2004). Heavy metal contamination of water, soil and produce within riverine communities of the Rio Pilcomayo basin, Bolivia. *Science of the Total Environment, 320*, 189-209.
47. Nagorski, S. A., Moore, J. N., & Smith, D. B. (2002). Distribution of metals in water and bed sediment in a mineral-rich watershed, Montana, USA. *Mine Water and the Environment, 21*, 121-136.
48. Natarajan, K. A., Subramanian, S., & Braun, J. J. (2006). Environmental impact of metal mining - biotechnological aspects of water pollution and remediation - an Indian experience. *Journal of Geochemical Exploration, 88*, 45-48.
49. Navarro, A., Cardellach, E., Mendoza, J. L., Corbella, M., & Domenech, L. M. (2008). Metal mobilization from base-metal smelting slag dumps in Sierra Almagrera (Almeria, Spain). *Applied Geochemistry, 23*, 895-913.
50. Neal, C. (1997). A view of water quality from the Plynlimon watershed. *Hydrology and Earth System Sciences, 1*, 743-753.
51. Nordstrom, D.K. (2009). Acid rock drainage and climate change. *Journal of Geochemical Exploration, 100*, 97-104.

52. Nuttall, C. A., & Younger, P. L. (2000). Zinc removal from hard circum-neutral mine waters using a novel closed-bed limestone reactor. *Water Research, 34,* 1262-1268.
53. Novotny V. (2003). *Diffuse Pollution and Watershed Management*. New York: Wiley & Sons.
54. Olias, M., Nieto, J. M., Sarmiento, A. M., Ceron, J. C., & Canovas, C. R. (2004). Seasonal water quality variations in a river affected by acid mine drainage: the Odiel River (South West Spain). *Science of the Total Environment, 333*, 267-281.
55. Parsons Brinckerhoff Ltd., (2005). *Remedial design of former metal mines in Wales - Dylife feasibility report*. Report prepared for Environment Agency Wales. Cardiff: Parsons Brinckerhoff Ltd.
56. Ribet, I., Ptacek, C. J., Blowes, D. W., & Jambor, J. L. (1995). The potential for metal release by reductive dissolution of weathered mine tailings. *Journal of Contaminant Hydrology, 17*, 239-273.
57. Rance, J., Wade, S.D., Hurford, A.P., Bottius, E., & Reynard, N.S. (2012) *Climate Change Risk Assessment for the Water Sector*. Defra Project Code GA0204, London: Department for the Environment, Food and Rural Affairs.
58. Rothwell, J. J., Evans, M. G., & Allott, T. E. H. (2007). Lead contamination of fluvial sediments in an eroding blanket peat catchment. *Applied Geochemistry, 22*(2), 446-459.
59. Rothwell, J. J., Evans, M. G., Daniels, S. M., & Allott, T. E. H. (2007). Baseflow and stormflow metal concentrations in streams draining contaminated peat moorlands in the Peak District National Park (UK). *Journal of Hydrology, 341*(1-2), 90-104.
60. Rothwell, J. J., Robinson, S. G., Evans, M. G., Yang, J., & Allott, T. E. H. (2005). Heavy metal release by peat erosion in the Peak District, southern Pennines, UK. *Hydrological Processes, 19*(15), 2973-2989.
61. Rothwell, J. J., Taylor, K. G., Chenery, S. R. N., Cundy, A. B., Evans, M. G., & Allottt, T. E. H. (2010). Storage and Behavior of As, Sb, Pb, and Cu in Ombrotrophic Peat Bogs under Contrasting Water Table Conditions. *Environmental Science & Technology, 44*(22), 8497-8502.
62. Sanden, P., Karlsson, S., Duker, A., Ledin, A., & Lundman, L. (1997). Variations in hydrochemistry, trace metal concentration and transport during a rain storm event in a small catchment. *Journal of Geochemical Exploration, 58*, 145-155.
63. Shaw, E. M., Beven, K. J., Chappell, N.A., Lamb, R. (2011). *Hydrology in Practice* (4th ed.). Oxford: Spon Press.
64. Smolders, A. J. P., Lock, R. A. C., Van der Velde, G., Medina Hoyos, R. I., & Roelofs, J. G. M. (2003). Effects of mining activities on heavy metal concentrations in water, sediment, and macroinvertebrates in different reaches of the Pilcomayo River, South America. *Archives of Environmental Contamination and Toxicology, 44*, 314-323.
65. Sullivan, A. B., & Drever, J. I. (2001). Spatiotemporal variability in stream chemistry in a high-elevation catchment affected by mine drainage. *Journal of Hydrology, 252*, 237-250.
66. Vivian, C. M. G., & Massie, K. S. (1977). Trace metals in waters and sediments of the River Tawe, South Wales, in relation to local sources. *Environmental Pollution, 14*, 47-61.
67. Walling, D. E., Owens, P. N., Carter, J., Leeks, G. J. L., Lewis, S., Meharg, A. A., et al. (2003). Storage of sediment-associated nutrients and contaminants in river channel and floodplain systems. *Applied Geochemistry, 18*, 195-220.

68. Webb, B. W., Davis, J. S., & Keller, H. M. (1987). Hysteresis in stream solute behaviour. In V. Gardiner (Ed.), *International Geomorphology 1986 Part I* (pp. 767-782). London: Wiley.
69. Whitehead, P. G., & Prior, H. (2005). Bioremediation of acid mine drainage: An introduction to the Wheal Jane wetlands project. *Science of the Total Environment, 338*, 15-21.
70. Wilkin, R.T. (2008). Contaminant attenuation processes at mine sites. *Mine Water and the Environment*, *27*, 251–258.
71. Wirt, L., Leib, K. J., Bove, D. J., Mast, M. A., Evans, J. B., & Meeker, G. P. (1999). Determination of chemical-constituent loads during base-flow and storm-runoff conditions near historical mines in Prospect Gulch, Upper Animas River Watershed, Southwestern Colorado. U.S. Geological Survey.
72. Wolz, J., Cofalla, C., Hudjetz, S., Roger, S., Brinkmann, M., Schmidt, B., et al. (2009). In search for the ecological and toxicological relevance of sediment re-mobilisation and transport during flood events. *Journal of Soils and Sediments*, 9, 1-5.
73. Younger, P. L., Banwart, S. A., & Hedin, R. S. (2002). *Mine Water. Hydrology, Pollution, Remediation*. Dordrecht: Kluwer Academic Publishers.
74. Zoumis, T., Schmidt, A., Grigorova, L., & Calmano, W. (2001). Contaminants in sediments: remobilisation and demobilization. *Science of the Total Environment, 226*,195–202.

Figure Captions

Fig 1 Map of the Afon Twymyn, central Wales, showing the location of the automatic water sampling stations and Dylife mine

Fig 2 Changes in dissolved metals, stream discharge, conductivity, pH and rainfall for *Event 1* (09/08/08-10/08/08) and *Event 2* (09/11/08-10/1108) at the non-mine-impacted station

Fig 3 Changes in dissolved metals, stream discharge, conductivity, pH and rainfall for Event 4 (06/07/08-07/07/08), Event 5 (13/08/08-14/08/08) and Event 6 (03/09/09-04/09/08) at the mine-impacted station

Fig 4 Clockwise (Pb, Zn) and anti-clockwise (Fe) hysteresis in the relations between metal concentration and discharge in Event 4 (06/07/08-07/07/08)

Table 1. Baseflow hydrochemistry of the Afon Twymyn measured in June 2007, October 2007 and March 2008 (Byrne, 2010; unpublished results)

Variable	Non-mine-impacted sites (*n* = 24)		Mine and downstream sites (*n* = 63)	
	Mean	Range	Mean	Range
Pb[a]	20	<10 – 50	170	<10 – 400
Zn[a]	<10	<10	520	<10 – 1660
Cu[a]	<30	<30	<30	<30
Cd[a]	<20	<20	<20	<20
Fe[a]	180	<60 – 570	65	<60 – 330
Mn[a]	60	<20 – 150	20	20 – 100
pH	6.4	6.0 – 6.7	6.9	6.5 – 7.9

[a] µg/l.

Table 2. Range of values of stormflow event characteristics and hydrochemistry at non-mine-impacted and mine gauging stations

	Pcp.[a]	Q[b]	pH	Pb[c]	Zn[c]	Cu[c]	Cd[c]	Fe[c]	Mn[c]	EC[d]
Non-mine-impacted station										
Event 1 (09/08/08)	29.2	0.008 – 0.039	6.2 – 6.6	10 – 180	<10 - 512	<30 – 60	<20	<60 – 200	<20 – 30	24 – 26
Event 2 (09/11/08)	26.2	0.017 – 0.126	6.0 – 6.2	10 – 40	20 – 230	<30	<20	<60 – 180	<20 – 60	8
Mine station										
Event 3 (12/04/08)	14.8	0.147 – 0.259	6.7 – 6.9	110 – 270	460 – 650	<30	<20	<60	<20	52 – 54
Event 4 (06/07/08)	17.4	0.120 – 0.460	6.0 – 6.4	260 – 5000	580 – 1790	<30	<20	<60 – 90	20 – 70	48 – 58
Event 5 (13/08/08)	10.8	0.141 – 0.255	6.3 – 6.3	150 – 6150	410 – 920	<30 – 220	<20	60 – 920	20 – 210	44 – 46
Event 6 (03/09/08)	32.4	0.160 – 0.465	6.0 – 6.7	170 – 1280	10 – 690	<30	<20	<60	<20 – 50	40 – 46
Event 7 (30/09/08)	50.2	0.070 – 0.163	6.4 – 6.5	140 – 840	500 – 880	<30	<20	110 – 390	30 – 80	46 – 52
Event 8 (08/11/08)	13.4	0.070 – 0.364	6.5 – 6.6	70 – 150	380 – 640	<30	<20	70 – 130	<20 – 50	34 – 38

[a] Total storm precipitation (mm).

[b] m^3/s.

[c] µg/l.

[d] Electrical conductivity (µS/cm)

Table 3. Total mass flux of metals at monitoring stations in the Afon Twymyn under baseflow and stormflow discharge conditions.

	Non-mine-impacted station			**Mine-impacted station**						
	Baseflow range [a]	Event 1 (09/08/08) [b]	Event 2 (09/11/08) [b]	Baseflow range [a]	Event 3 (12/04/08) [b]	Event 4 (06/07/08) [b]	Event 5 (13/08/08) [b]	Event 6 (03/09/08) [b]	Event 7 (30/09/08) [b]	Event 8 (08/11/08) [b]
Pb	<0.01 – 0.02	0.03	0.18	2.8 – 4.1	3.7	16.1	15.9	9	3.9	1.8
Zn	<0.01 – 0.02	0.07	0.11	8.7 – 15.9	9.7	12.3	8	13	7	6.3
Cu	<0.01	0.02	0.07	0.06 – 0.23	0.21	0.26	0.59	0.47	0.18	0.2
Cd	<0.01	<0.01	<0.01	0.07 – 0.1	0.14	0.1	0.04	0.11	0.07	0.07
Discharge [c]	0.006 – 0.021	0.039	0.126	0.082 – 0.202	0.259	0.46	0.255	0.465	0.163	0.364
Q event [d]	99 – 13	6	1	86 – 35	19	2	20	2	50	6

[a] kg/day - range based on twelve separate discharge and solute measurements in March, June, October and December 2008.

[b] kg/day – calculated storm metal yield represents 24 hr period.

[c] m^3/s.

[d] Percent time a particular flow was exceeded over the study period based on 15-minute data (January to December 2008).

Table 4 Pearson correlation coefficients between stormflow event metal yields and catchment wetness indices

Metal	API_5	API_{10}	Pre-event Q (m^3/s)	Hours with rainfall in prior 5 days	Hours with rainfall in prior 10 days
Pb	-0.910*	-0.950**	0.570	-0.611	-0.736
Zn	-0.292	-0.336	0.330	-0.243	-0.193
Cu	-0.623	-0.492	0.506	-0.349	-0.847*
Cd	0.378	0.313	0.188	-0.218	0.272

** Correlation significant at 0.01

* Correlation significant at 0.05