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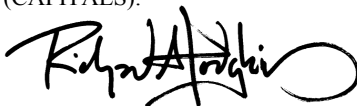
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# **Contaminant hydrogeochemistry and aquatic ecosystem health at abandoned metal mines: the Afon Twymyn, central Wales**

by

Patrick Byrne

A Doctoral Thesis

Submitted in partial fulfilment of the requirement for the award of  
Doctor of Philosophy of Loughborough University

December 2009

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## Abstract

Following the decline of the UK metal mining industry by the 1920s, over 3,000 abandoned metal mines exist in England and Wales. Contaminated drainage from this historical industry causes approximately 20% of all water quality failures in England and Wales. In this thesis, a holistic geographical approach, incorporating aspects of hydrology, hydrogeochemistry and freshwater ecology, is employed to investigate the hydrological, sedimentological and ecological impacts of the abandoned Dylife lead/zinc mine on the Afon Twymyn (central Wales). Examination of river sediment quality highlights the need for measurements of the quality of this component of the river ecosystem and, in particular, measurement of bioavailable as opposed to total metals. The majority of heavy metals in bed sediments of the Afon Twymyn exist in highly mobile geochemical phases, potentially posing serious threats to ecological integrity. Significant metal flushing occurred during flood events at Dylife mine and a distinct seasonal pattern was observed with greater levels of flushing occurring during flood events in the summer months. It is suggested that investigations of contaminant/ecosystem relations and potential remediation strategies should include high-resolution temporal sampling of river water chemistry under conditions of flood flow. Paradoxically, a range of biological indices failed to identify significant negative impacts of metal mine contaminants on macroinvertebrate communities, suggesting there is little contamination of the river ecosystem. However, Canonical Correspondence Analysis did identify significant differences in community structure between polluted and unpolluted river stretches, suggesting that standard unimetric biological indices might only be successful in identifying impacts at the most severely polluted mine sites. It is suggested that the ecological approach of the European Union Water Framework Directive to the assessment of river ecosystem status may not yield an accurate representation of contamination in rivers such as the Afon Twymyn where contamination by mining is moderate, circum-neutral and the mining operation is long abandoned.

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# 1. Introduction

## 1.0 Introduction

Contaminated drainage from abandoned metal mines and mine wastes is an issue of international concern (Gray, 1998; Smolders *et al.*, 2003; Olias *et al.*, 2004) that can result in significant ecological degradation (Sola *et al.*, 2004; Neal *et al.*, 2005; Ruiz *et al.*, 2009) and contaminate human food and water supplies (Macklin *et al.*, 2006). The varied geology of the United Kingdom (UK) has provided many valuable natural mineral resources (Environment Agency 2008a). During the mid-nineteenth century, the UK experienced a boom in the metal mining industry. However, falling metal prices and the discovery of large metalliferous deposits in South America, Australia and the Iberian Peninsula forced the closure of most UK metal mines by the 1920s. Today, a major legacy of the UK metal mining industry exists in the form of over 3,000 abandoned metal mines (Jarvis *et al.* 2008). The environmental legacy of metal mining may persist for centuries after the closure of a mine (Johnson, 2003). In England and Wales, approximately a fifth of all river water quality objective failures can be attributed to the impacts of metal mine pollution (Environment Agency, 2002).

Contaminated drainage is produced by weathering of sulphide minerals deep underground and in surface waste tips (Smolders *et al.*, 2003). Typically, mine water drainage is characterised by low pH and high concentrations of dissolved heavy metals and sulphates (Robb and Robinson, 1995). Acidic discharges are known as acid mine drainage (AMD) and cause the most severe environmental impacts due to the relationship between low pH and high dissolved metal concentrations (Younger *et al.*, 2002). Many types of mine workings can produce AMD including deep mines, backfilled surface mines and quarries, tailings dams and mine spoil (Norton, 1992). AMD can enter a watercourse as drainage from exposed mine shafts, adits or surface spoil heaps.



Mine water discharges can severely degrade river water quality (Gray, 1997). Many of the rivers of north-east England, south-west England and Wales suffer elevated levels of dissolved heavy metals and low pH due to former metal mining in their catchments (Jarvis *et al.*, 2008). One of the principal long-term impacts of metal mining on river systems in the UK is contamination of sediment in river channels and floodplains by heavy metals (Yim 1981; Hudson-Edwards *et al.* 1997; Dennis *et al.* 2009). As particulates, metals can clog the river substrate, destroying the habitat of invertebrates, and the feeding and spawning areas of fish. This effect is best illustrated by blankets of ochre or 'yellowboy' (iron hydroxide) which are deposited in streams receiving highly ferrous mine drainage (Batty *et al.*, 2005). Metals can exist in the substrate in various geochemical phases which largely control the degree to which they remain 'stored' in the substrate. As weakly complexed or adsorbed species, metals are more bioavailable to organisms and some can be readily released into solution given changes in hydrological and hydrochemical conditions (Salomons, 1987). Heavy metals can be remobilised from mine wastes and river beds by the action of flooding; and dispersed in agricultural floodplains where they can accumulate in livestock and crops (Macklin *et al.*, 2006). The prospect of increased magnitude and frequency of flooding in the UK due to climate change (Wilby *et al.*, 2006) raises serious concerns over the future safety of food generated on contaminated floodplains. The decline of metal mining in the UK has slowed down the process of metal release and water/sediment/soil contamination. However, significant volumes of contaminated drainage and sediment are still being produced at abandoned metal mines (Macklin *et al.* 2006).

Heavy metal contaminants in river systems can alter the composition and health of plant and animal communities resulting in the destabilisation of river ecosystems (Armitage *et al.*, 2007). They can alter species composition by replacing sensitive species with tolerant species while the health of surviving species can be severely impaired (Marques *et al.*, 2003). Impairment can occur through deformities, mutations and alterations to species behaviour which might affect the future success of the affected species (Martinez *et al.*, 2004).

Bioconcentration of metals in organisms can affect entire ecosystems and human health (Sola and Prat, 2006).

The main legislative driver for the improvement and protection of water resources and freshwater ecosystems in Europe is the European Union Water Framework Directive (WFD) (2000/60/EC). The WFD ushers in a new management framework with the achievement of 'good ecological status' at the core of all legislation. Currently, contamination of water bodies in the UK by abandoned metal mines poses a serious barrier to the achievement of WFD objectives. As a result, there has been a call for investigations into the physical, chemical and biological processes operating at abandoned metal mines in order to facilitate a greater understanding of these processes and also to inform decision makers responsible for remediation/management plans (Environment Agency, 2002; Environment Agency 2008a; Environment Agency 2008b; Jarvis *et al.* 2008). In the wider context of mine water management, specific knowledge gaps exist as to the impact of flood events on metal mobility and toxicity and in the relationship between mine water contaminants and aquatic ecology. Short-term flood events have the potential to flush into river systems quantities of contaminants far in excess of those observed in routine sampling studies (Gammons *et al.*, 2005). The ecological focus of the WFD has placed an emphasis on understanding the relationship between metal mine contaminants and aquatic ecology. Baseline hydrogeochemical and ecological data are essential to identify spatial and temporal patterns of contamination, sources of contamination, to evaluate impacts and potential risks to aquatic biota and to evaluate the effectiveness of remediation strategies (Environment Agency 2008b).

Metal mine drainage is a multi-factor contaminant causing a myriad of potential problems. The solution requires an interdisciplinary analytical approach. A geographical approach integrating the disciplines of hydrology, hydrogeochemistry and freshwater ecology should provide important hydrogeochemical information for remediation strategies and decision makers, and also a valuable insight into the relationship between metal mine contaminants and aquatic ecology.

## 1.1 Research questions

The overarching aims of this project are: 1) to investigate the hydrological, sedimentological and ecological impacts of historic metal mining and 2) establish whether there is a contemporary environmental legacy of historical metal mining in the UK. Six specific research questions are outlined below, with additional objectives being outlined in individual chapters.

1. How chemically mobile are heavy metals of the bed sediments of metal mining-impacted rivers, and do they pose a threat to instream ecology? (Chapter 6)
2. How can analysis of bioavailable metals rather than total metals improve our understanding and management of sediment contamination? (Chapter 6)
3. How does river hydrochemistry vary during short-term flood events at abandoned metal mines? (Chapter 7)
4. What are the primary contaminant sources and mechanisms controlling metal concentrations and loads during flood events? (Chapter 7)
5. How do metal mine contaminants influence the benthic macroinvertebrate community of mining-impacted rivers? (Chapter 8)
6. How useful are biological indices for identifying the impacts of metal mine contamination? (Chapter 8)

## 1.2 Thesis structure

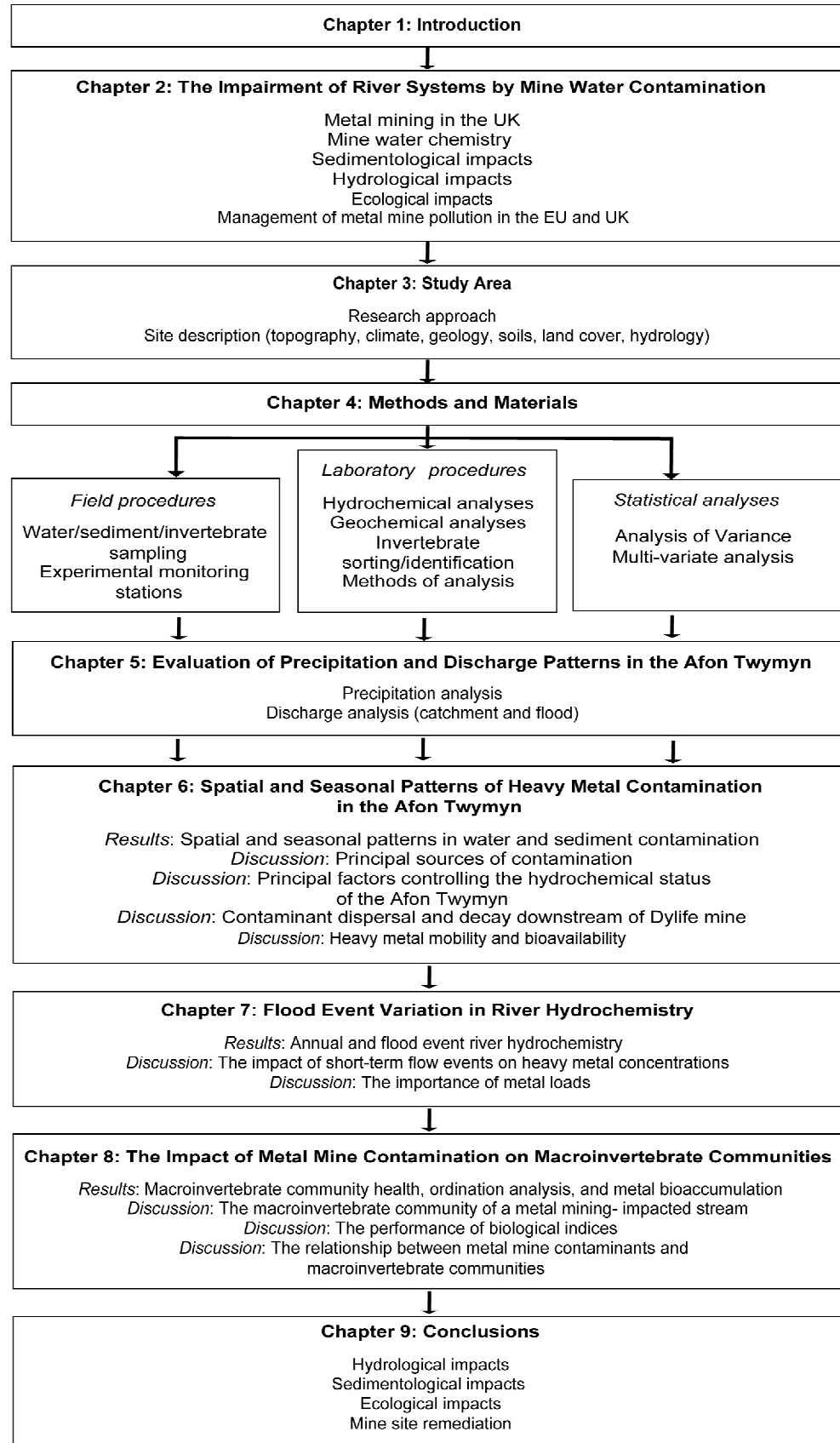
The structure of the thesis is presented in **Figure 1.1**. Chapter 1 introduces the environmental issue of abandoned metal mines and briefly outlines some of the major problems associated with metal mine drainage. This chapter also outlines the research framework and parallels the layout and development of the thesis. Chapter 2 reviews and assesses the scientific literature surrounding mine water contamination in greater detail. The generation and character of minewater pollution has been well studied; however, the impact of this drainage on aquatic ecosystems can vary widely depending on many hydrogeochemical and meteorological factors. Processes of contaminant transport and deposition,

transformation, attenuation and release in rivers are discussed in detail with reference to studies of active and abandoned metal mines. Evidence of the toxic effects of these contaminants is addressed through a review of the literature that examines their chronic and acute impacts on macroinvertebrates determined from laboratory and field-based research. Lead, zinc, copper and cadmium are focussed on as these are among the most commonly mined and discharged metals. In addition, current EU and UK legislation and management practices for freshwaters are discussed, as is the current UK strategy for management of abandoned metal mines. Chapter 3 introduces the study site which the project uses to address the research questions. The study site is described in terms of its topography, climate, geology, soils, land cover and hydrology. Chapter 4 presents the standard field and laboratory techniques used in this study and other hydrogeochemical and ecological investigations. Where possible, the techniques used follow standard protocols allowing comparisons to be made with existing published findings. Chapter 5 presents and analyses meteorological and hydrological data for the Afon Twymyn catchment and sets the present study period in the context of medium to long-term patterns.

Chapters 6, 7, and 8 form the core results of the research and address the key research questions outlined in section 1.1. Contaminant sources, river hydrochemistry, sediment geochemistry and contaminant dispersal are examined in Chapter 6. Essential for the remediation of mine sites and affected watercourses is the identification of contaminant sources, characterisation of discharges, and an understanding of the interaction between discharges and hydrological and sedimentological systems. A particular concern in metal mining-impacted rivers is the geochemical mobility of heavy metals in sediments and the dispersal of mine waste downstream of mine sites. Traditionally, assessments of sediment contamination have focussed on the concentration of total metals rather than bioavailable metals which may yield information more pertinent to ecological health. Chapter 7 presents hydrological and hydrochemical data from two experimental monitoring stations set up to investigate river hydrochemistry during flood events. Significant hydrochemical variability is known to occur in rivers during flood events. At mine sites, the evolution of river hydrochemistry during flood events is generally poorly understood due to inherent difficulties in

measuring such events. This lack of understanding has wider implications for assessments of contaminant mobility and dispersal, remediation design and effectiveness and, possibly, ecological health. Chapter 8 explores the relationship between metal mine contaminants and the macroinvertebrate community of the study river through the use of biological indices, multi-variate analysis and metal bioaccumulation studies. The ecological focus of the WFD necessitates a comprehensive understanding of mine water impacts on riverine ecosystems. Benthic macroinvertebrates are used widely as bioindicators of river ecosystem health, however, their usefulness in assessing the health of metal mining-impacted rivers is questionable. The performance of macroinvertebrates as bioindicators of metal mine contamination is assessed with reference to the study site and other published findings.

The significant findings and conclusions of the thesis are outlined in Chapter 9, as are the wider implications for the management of river systems affected by metal mine drainage. The overall health of the study river is assessed with reference to the hydrological, sedimentological and ecological findings. The significance of flood event contaminant transport and heavy metal mobility in sediments are discussed; and the usefulness of macroinvertebrates as biomonitors of mine water contamination is evaluated. Finally, potential remediation and management options for the study site are discussed.



**Figure 1.1: A schematic representation of the thesis structure**

### **1.3 Chapter summary**

Water quality and riverine ecology have been undoubtedly affected by the spate of metal mine closures which occurred during the early part of the 20<sup>th</sup> century. The vast quantities of reactive material in most deep mines and surface mine wastes suggest that polluted discharge will be generated for decades, even centuries, to come. The failings of the environmental policies of the past, as in the preferential management of coal mine pollution, combined today with increased awareness of water quality and ecological issues and the requirements of EU and UK law, have pushed metal mine pollution to the forefront of concern for environmental managers. As a result, there is currently a concerted effort among researchers to investigate the physical, chemical and biological impacts of metal mine pollution.

## **2. The Impairment of River Systems by Metal Mine Contamination**

### **2.0 Introduction**

Since the 1960s, concerns over the impacts of metal mining on riverine systems have gained increasing significance (Macklin *et al.*, 2006). These concerns have been reflected in the growing body of literature on the subject. However, due to the wide range of environmental impacts at mine sites and the often site-specific nature of many of the investigations, the literature is scattered through many, often, unrelated journals. Metal mine pollution affects all components of the river environment. Therefore, a holistic understanding of metal mine impacts on river environments requires an interdisciplinary analytical approach. With this in mind, this literature review draws on work undertaken in a range of disciplines, including hydrology, hydrochemistry, geochemistry and freshwater ecology. Evidence is presented through a review of both laboratory and field-based research. The discussion is concerned with abandoned metal mines, primarily because the biogeochemical processes occurring at coal mines have been extensively studied and are well understood (Environment Agency, 2008a).

### **2.1 The rise and fall of metal mining in the UK**

The environmental problems caused by metal mining are not restricted to regions of the world where active mineral exploitation is occurring. In the UK, mineral exploration has occurred since the early Bronze Age (Environment Agency, 2008a). Early methods of ore extraction involved the digging of open trenches and shallow shafts. The Industrial Revolution led to the development of more sophisticated mining techniques which allowed deeper and more fruitful mining below the water table. Pumps and adits were used to drain mines and explosives and mechanised drilling increased the amount of ore which could be processed while at the same time reducing the labour needed to extract it (Environment Agency, 2002). Ore extraction reached its peak in the UK in the nineteenth century when, for a time, the UK was the largest lead, tin and copper producer in



the world (Lewin and Macklin, 1987) (**Figure 2.1; Table 2.1**). The major lead and zinc producing regions included the North Pennines, Halkyn-Minera, Derbyshire and Central Wales. The period between 1845 and 1938 saw the peak in Welsh zinc and lead production when the principality accounted for 25% and 43% of the total UK output respectively (Environment Agency, 2002). Zinc, lead and silver were mined in north Ceredigion, near Aberystwyth. In Meirionnydd, copper and gold were extracted and there are extensive copper workings at Parys Mountain, Anglesey.

A sudden downturn of metal prices in the 1920's, combined later with the discovery of large deposits of lead and copper in the Iberian Peninsula, South America and Australia, led to the gradual decline of metal mining in the UK in the 20<sup>th</sup> century. Most metal mines in the UK are now abandoned and the mining landscape now consists of spoil heaps of waste rock, adits and shafts, and derelict structures. The total number of abandoned metal mines in the UK is estimated to be over 3,000, with almost half of these (1,311) located in Wales (Jarvis *et al.*, 2007). After diffuse agricultural pollution, metal mine drainage poses the most serious threat to water quality objectives in England and Wales (Environment Agency, 2006). Approximately 7% of river length and 14% of groundwater volume in England and Wales (2% and 6% respectively in Scotland) are affected by metal mine drainage (Gandy *et al.*, 2007). As a result there is a significant risk of these waters failing to achieve 'good' chemical and ecological status as required by the European Union Water Framework Directive (WFD).



**Figure 2.1:** Former metal mining areas of England and Wales (from Lewin and Macklin, 1987)

**Table 2.1:** Metal output from British ore fields in 1000's tonnes (from Schnellmann and Scott, 1970)

Ore field	Lead	Zinc	Copper
North Pennines	4000	267	
Lake District	226	34	
Derbyshire	678	91	60
West Shropshire	237	21	
<b>Central Wales</b>	<b>479</b>	<b>151</b>	
Llanrwst-Harlech	47	33	
Mynydd Parys			130
Halkyn-Minera	1870	290	
Mendip	200		
Devon-Cornwall	322	89	
South-West Scotland	317	14	
Isle of Man	268	256	

## 2.2 Mine water chemistry

Investigation of mine water chemistry (as opposed to the chemistry of rivers receiving mine water) is beyond the scope of this thesis. However, appreciation of mine water character and processes of formation is necessary to understand its potential impact on riverine systems.

Sulphidic minerals such as galena (lead sulphide - PbS), sphalerite (zinc sulphide – ZnS) and pyrite (iron sulphide – FeS<sub>2</sub>) are amongst the most commonly mined metal ores. These minerals are chemically stable in dry, anoxic and high pressure environments deep underground. However, these solid phases become chemically unstable when they are exposed to the atmosphere (oxygen and water) during and after mining (Johnson, 2003). A series of complex biogeochemical reactions occur in the sulphide weathering process leading to the generation of a toxic leachate and the release of contaminants into hydrological pathways (Banks *et al.*, 1997). The biogeochemical weathering of pyrite has been studied extensively (Atkins and Pooley, 1982; Rawat and Singh, 1982; Johnson, 2003) and is used here as an example of the sulphide weathering process. Pyrite

exposed to oxygen and water oxidises to produce dissolved ferrous iron, sulphate and sulphuric acid. The acidic conditions can lead to the dissolution of heavy metals. With a sufficient supply of oxygen, ferrous iron may be further oxidised and precipitate as ferric iron. At low pH (2 – 5) and low dissolved oxygen levels, acidophilic bacteria can continue to oxidise ferrous iron to ferric iron releasing more acidity and lowering the pH further which, in turn, increases the solubility of iron (and other metals) and decreases the rate of ferric iron precipitation (Younger *et al.*, 2002). Dissolved ferric iron can keep the cycle of acid production and metal dissolution running by oxidising further pyrite in anoxic conditions. However, the pyrite weathering rate is finite and its longevity will depend on the amount of sulphide and carbonate minerals present, grain size distribution, the exposed mineral surface area, the concentration of reactants such as dissolved oxygen, and microbial activity (Younger *et al.*, 2002; Natarajan *et al.*, 2006; Environment Agency, 2008a; Wilkin, 2008). The process of pyrite weathering is described in more detail in **Appendix 2.1**.

#### 2.2.1 Factors affecting the aquatic environment

The leachate generated during the sulphide weathering process is complex and, if the process is a net-acid producing reaction, the leachate is referred to as acid mine drainage (AMD) or acid rock drainage (ARD). AMD is most commonly characterised by high levels of dissolved heavy metals and sulphates, low pH and metal precipitates (Robb and Robinson, 1995; Braungardt *et al.*, 2003). These contaminants can be generated in underground mine workings and emerge at the surface as direct point discharges from adits and shafts. Similar reactions occur in spoil heaps and tailings with many small individual discharges potentially adding up to create a significant diffuse discharge (Environment Agency, 2008a). Information on the type and concentration of contaminants found at metal mining-affected watercourses in various parts of the world can be found in **Table 2.2**.

#### *Acidity*

Sulphide weathering at mine sites can generate sulphuric acid which can lower the pH of receiving streams. Acidity is present as proton acidity and mineral

acidity produced by oxidation and hydrolysis of metal sulphides, respectively (Johnson, 2003). The effect of low pH is to dissolve carbonates and silicates limiting the ability of the stream to buffer inputs of acid from the mine (Kelly, 1988). The ability of a stream to recover from acidic inputs will depend on the availability and type of sulphide and carbonate/silicate minerals. Therefore, local lithology is an important control on stream chemistry in metal mining regions.

Stream pH is known to be a major control on metal solubility and transport (Younger *et al.*, 2002). In general, metal hydroxides display an increasing tendency to dissolve as pH decreases. The critical pH values are about 4.3 for iron, 6.3 for lead, 7.2 for copper, 8.4 for zinc, and 9.7 for cadmium (Kelly, 1988). Below these pH values most of the metal will remain in solution. Moderate to extremely acidic waters can be found at abandoned metal mines and values can vary considerably depending on where the sample is obtained. For example, in regions with large deposits of carbonate minerals, the pH of rivers and tailings drainage can exceed pH 8.0 (Cidu and Mereu, 2007). However, in regions of low carbonate lithology, the pH of rivers and mine waters can be substantially lower (Nordstrom *et al.*, 2000; Alderton *et al.*, 2005). Much of central and north Wales is underlain by Lower Palaeozoic shales and mudstones with low concentrations of base materials (Evans and Adams, 1975). As a result, many of the headwater streams of the region have low acid-buffering capability. The Afon Ystwyth which drains Cwm Ystwyth mine in central Wales suffers pH levels as low as 4.1, resulting in high levels of dissolved heavy metals (Fuge *et al.*, 1991).

### *Dissolved heavy metals*

In natural waters, trace amounts of metals and other dissolved solids are present and vary in concentration according to geology, soils, erosion and transport processes (Webb and Walling 1974; Foster and Charlesworth, 1996). However, the acidity generated by sulphide weathering can lead to the leaching of heavy metals from the surrounding rock strata and dissolved heavy metal concentrations in rivers far in excess of background levels (Merefield, 1995). The widespread occurrence of galena (lead) veins in central Wales has resulted in many rivers having elevated lead, zinc, copper and cadmium concentrations. These metals

are amongst the most dangerous and commonly discharged metal mine contaminants (Novotny, 1995).

### *Precipitate*

Aqueous metal concentrations can be lowered downstream of inputs by precipitation of iron hydroxide and sulphate phases, and co-precipitation or sorption of heavy metals onto these phases (Environment Agency, 2008b). Iron hydroxide 'ochre' and other metal hydroxides can smother river beds and destroy important breeding and feeding habitats of macroinvertebrate and fish populations (Batty, 2005; Mayes *et al.*, 2008).

**Table 2.2:** A comparison of dissolved metal (mg/l), sulphate (mg/l) and pH concentrations from metal mining-affected watercourses

Location	Sample type	Zn	Pb	Mn	Cd	Fe	Cu	SO <sub>4</sub> <sup>2-</sup>	pH	Author(s)
Black Foot River, USA	Channel	535		245	2.6	37	<4	88.8	7.3	Nagorski et al. (2002)
Elqui River, Chile	Channel	2.2					12.7		4.7	Oyarzun et al. (2003)
Rio Tinto, Spain	Channel	420	2.4				240	16000	1.4	Hudson-Edwards et al. (1999b)
Fluminese mining district, Spain	Mine waters	40	0.05	18	0.1	12		640	6.3	Cidu et al. (2007)
Funtana Raminosa region, Sardinia	Tailings drainage	342	<0.01	0.09	0.9	0.25	0.04	330	7.6	Cidu and Mereu (2007)
Tinto Santa Rosa Mine, Spain	Mine drainage	85	0.08	31-45	0.15	996	23	4026	2.6	Asta et al. (2007)
Squaw Creek, USA	Channel	156		4.4		1600	190	5100	2.4	Filipek et al. (1987)
Viseu/Tisa/Lapus/Somes Rivers, Romania	Channel	20	0.5		0.2		1		3.5	Macklin et al. (2003)
Gezala Creek, Spain	Tailings pond	19	0.05	2.4		0.3	0.03			Marques et al. (2001)
River Zletovo, Macedonia	Adit drainage	22	0.06	26	0.14	98	0.5		3.4	Alderton et al. (2005)
River Buchim, Macedonia	Channel	1.5	0.18	46	<0.01	0.3	139		5.1	Alderton et al. (2005)
Richmond Mine, Iron Mountain, USA	Mine waters	24	<0.01		0.2	141	4.8	760	-3.6	Nordstrom et al. (2000)

Location	Sample type	Zn	Pb	Mn	Cd	Fe	Cu	SO <sub>4</sub> <sup>2-</sup>	pH	Author(s)
Tintillo River, Spain	Mine drainage	0.02		42	0.6	430	9.1	7.5	2.8	<i>Sanchez Espana et al. (2006)</i>
Lynx Mine, BC, Canada	Mine discharge	130				200		900	2.5	<i>Desbarats and Dirom (2005)</i>
Rio Tinto, Spain	River	2590	4	775		18	856	27	2.2	<i>Braungardt et al. (2003)</i>
River Carnon, UK	River	23000	22	1800	22	49000	1300	789	3.3	<i>Neal et al. (2005)</i>
Mt. Morgan, Australia	Open pit	22	1.5	71		253	45	13600	2.7	<i>Edraki et al. (2005)</i>
River Dee, Australia	River	10	0.6	46		74	45	5950	2.7	<i>Edraki et al. (2005)</i>
North Wales	Mine pool					2261		6590	2.4	<i>McGinness and Johnson (1993)</i>
Davis Mine Brook, USA	River	5				2.9	0.5	293	2.9	<i>Adams et al. (2007)</i>
Levant mine, Cornwall	Mine water	41		76		>2500	665	11220	2.1	<i>Bowell and Bruce (1995)</i>
Cwm Rheidol mine, Wales	Adit	72	0.035		0.112		0.068	846	2.8	<i>Fuge et al. (1991)</i>
Cwmystwyth mine, Wales	Spoil run-off	4.6	3.3		0.009		0.008		4.1	<i>Fuge et al. (1991)</i>
Phillips Mine, New York	River	0.174	<0.001	364		42400	3130	368000	2.3	<i>Gilchrist et al. (2009)</i>
Boulder Creek, California	River	469	32	122	5	2820	246	97400	3.3	<i>Keith et al. (2001)</i>



## 2.3 Metal mining impacts on sedimentological systems

During the lifetime of a metal mine, ore extraction and processing can introduce vast quantities of solid waste into the river environment. Even after mine abandonment, erosion of material from mine spoil and tailings can continue to introduce contaminated solid wastes into river channels and floodplains (Martin and Maybeck, 1979). Recognition of the importance of sediment-associated transport of heavy metal contaminants has prompted a growing body of research in the last few decades that (i) characterise the geochemistry of channel and floodplain sediments impacted by mining wastes and (e.g. Luoping *et al.*, 2009), (ii) document the physical and chemical dispersion patterns of heavy metals in contaminated sediment (e.g. Macklin *et al.*, 2006).

### 2.3.1 Sediment geochemistry

Gross contamination of sediments is reported in most metal mining regions of the world (**Table 2.3**), with metal concentrations in sediments usually being several orders of magnitude greater than that in the water column (Aleksander-Kwaterczak and Helios-Rybicka, 2009). Metal concentrations are usually greatest in fine sediments and, in particular, in clays and silts (<63  $\mu\text{m}$ ) (Lewin and Macklin, 1987; Stone and Droppo, 1996; Forstner, 2004). This is due to the increase in surface area per unit mass with a decrease in particle size, and the exchange of ions between negatively charged silt and clay-sized fractions (clay minerals, iron hydroxides, manganese oxides, and organic matter) and positively charged metal ions. In many regions, the impact of metal mining on sediment geochemistry has been to increase the proportion of heavy metals in the more mobile (and bioavailable) geochemical phases (Morillo *et al.*, 2002; Galan *et al.*, 2003) (**Table 2.4**). There can be considerable variability in the geochemical partitioning of metals in sediments not only from distinct river catchments but also from separate areas within single large catchments. In many cases important variables determining the geochemical partitioning of heavy metals are the type and concentration factors of the metals mined, sediment characteristics and water chemistry.

**Table 2.3:** Metal concentrations (mg/kg) in channel and floodplain sediments from metal mining-affected rivers

Location	Size fraction	Geochemical phase	Pb	Zn	Cu	Cd	Author(s)
<b>Channel sediments</b>							
River Allen (England)	< 170 µm	Total	2,330	1,410	-	-	Goodyear et al. (1996)
River Swale (England)	< 63 µm	Total	10,000	14,000	-	7,500	Dennis et al. (2003)
River Aire (England)	< 63 µm	Total	237	580	198	-	Walling et al. (2003)
River Calder (England)	< 63 µm	Total	343	907	235	-	Walling et al. (2003)
River Tees (England)	< 2000 µm	Total	6,880	1,920	77	5.95	Hudson-Edwards et al. (1997)
Red River (England)	< 2000 µm	Total	120	630	1,320	-	Yim (1981)
River Tawe (Wales)	< 2000 µm	Total	6,993	35,796	2,000	335	Vivian and Massie (1977)
River Tinto (Spain)	< 2000 µm	Total	1,650	6,730	2,650	23	Galan et al. (2003)
River Odiel (Spain)	< 2000 µm	Total	1,320	240	2,090	5	Galan et al. (2003)
River Mala Panew (Poland)	< 20 µm	Total	3,309	11,153	483	559	Aleksander-Kwaterczak and Helios-Rybicka (2009)
River Cedar (USA)		Total	315	2,050	101	3.8	Ouyang et al. (2002)
River Elqui (Chile)	< 60 µm	-	-	404	1,022	-	Oyarzun et al. (2003)
River Kangjiaxi (China)	-	Total	1645	178	34	3.27	Licheng and Guiju (1996)
River Wear (England)	< 150 µm	Total	15,000	1,500	340	-	Lord and Morgan (2003)
Copper Mine Brook (USA)	< 1000 µm	Total	30	15	398	-	Gilchrist et al. (2009)

Location	Size fraction	Geochemical phase	Pb	Zn	Cu	Cd	Author(s)
West Squaw Creek (USA)	< 177 µm	Total	-	5,940	3,180	-	<i>Filipek et al. (1987)</i>
Black Foot River (USA)	< 63 µm	Total	1,300	5,700	1,400	32	<i>Nagorski et al. (2002)</i>
Gezala Creek (Spain)	< 177 µm	Total	37,630	22,100	1,691	41	<i>Marques et al. (2001)</i>
River Somes (Romania)	< 2000 µm	Total	6,800	19,600	8,400	110	<i>Macklin et al. (2003)</i>
River Towy (Wales)	< 2000 µm	Total	5,732	3,722	259	83	<i>Wolfenden and Lewin (1978)</i>
River Twymyn (Wales)	< 2000 µm	Total	5,523	6,955	2,557	44	<i>Wolfenden and Lewin (1978)</i>
River Avoca (Ireland)	< 1000 µm	Total	-	1,520	674	-	<i>Herr and Gray (1996)</i>
Dale Beck (England)	< 2000 µm	Total	13,693	442	206	-	<i>Geer (2004)</i>
River Derwent (England)	< 1000 µm	Total	3,120*	2,760	-	13.8	<i>Burrows and Whitton (1983)</i>
<b>Overbank floodplain sediments</b>							
River Swale (England)	< 63 µm	Total	5,507	3,066	-	18	<i>Macklin et al. (1994)</i>
River Tyne (England)	< 2000 µm	Total	2,340	2,340	42.5	8	<i>Macklin et al. (1992)</i>
River Derwent (England)	< 2000 µm	Total	1,696	1,179	64	12.5	<i>Bradley and Cox (1990)</i>
River Ystywth (Wales)	< 2000 µm	Total	1,543	4,646	-	-	<i>Lewin et al. (1983)</i>
River Rheidol (Wales)	< 2000 µm	Total	630	2,098	85	3.5	<i>Davies and Lewin (1974)</i>
River Severn (England)	< 2000 µm	Total	936	204	67	6.4	<i>Taylor (1996)</i>
River Rheidol (Wales)	< 210 µm	Total	1,717	383	120	-	<i>Wolfenden and Lewin (1977)</i>

**Table 2.4:** Examples of the chemical speciation of Pb (%) in various sediments

Region	River Odiel, Spain	River Tinto, Spain	Kangjiaxi River, China	Gold Coast Broadwater, Australia	River Yamuna, India
Study	Morillo et al. (2002)	Galan et al. (2003)	Licheng and Gujiu (1996)	Burton et al. (2005)	Jain (2004)
<i>Extracted phase</i>					
Exchangeable	-	-	0.5	ND	30
Carbonate	5	2	16	17	5
Easily reducible	25	93	65	68	15
Organic and Sulphide	20		15	3	7
Residual	50	5	3.5	12	43

ND = not detectable

### 2.3.2 Physical dispersion/attenuation processes

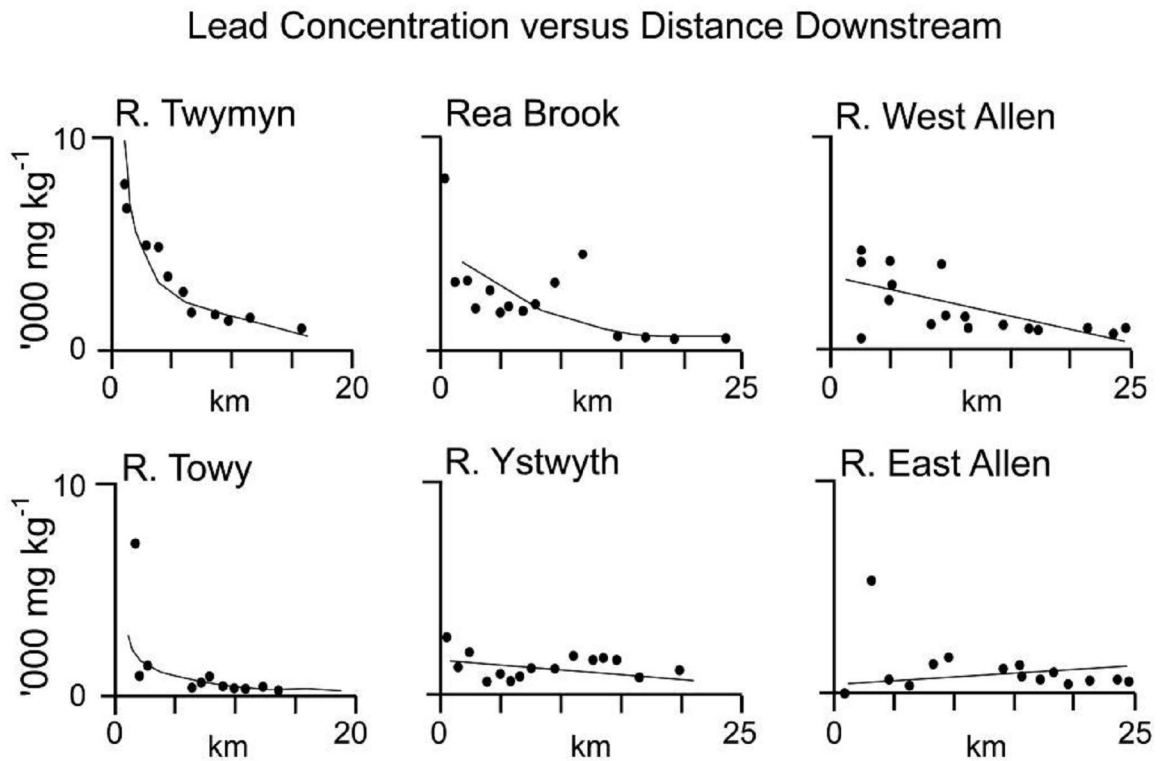
The influx of large volumes of contaminated sediment into river systems can disturb natural physical and chemical processes of sediment transport and deposition. Most researchers agree that river systems are morphologically adjusted to transport the water and sediment delivered to them from upstream areas, and is termed geomorphological equilibrium (Miller, 1997). Lewis and Macklin (1987) suggested that fluvial geomorphic disturbances due to mining could be divided into processes of *passive dispersal* and *active transformation*, two end members of a continuum through which waste introduced into a river system may be redistributed from a mine site. In *passive dispersal*, geomorphological equilibrium remains intact and only slight changes in processes occur. Variation can occur in depositional environments. Generally, slow moving waters and deep pools are preferential sites for the contaminant-enriched finer material to collect (Miller, 1997). Transport of coarse-grained material may be limited to high flow conditions. However, fine material may be transported under all flow conditions. In-channel sediment contamination generally decreases downstream from a single contaminant source at a predictable rate (Lewin *et al.*,

1977; Lewin and Macklin, 1987; Marcus, 1987), for example, due to dilution with uncontaminated sediment, hydraulic sorting of sediment based on size and density of ore particles (e.g. galena is more dense than sphalerite), hydrogeochemical reactions and biological uptake (**Figure 2.2**). The majority of studies investigating metal dispersal from mine sites have measured the concentration of total metals in the sediment (e.g. Lord and Morgan, 2003). However, if the dispersal of metals is being investigated in the context of aquatic health or floodplain contamination, then measurements of bioavailable metal fractions may be more appropriate.

Under *active transformation*, dramatic increases in the input of mining debris into the fluvial system results in a threshold crossing event and the collapse of geomorphological equilibrium (Lewin and Macklin, 1987). Significant changes in the type, rate and magnitude of erosional and depositional processes can occur. Channel aggradation can immediately follow mining activity with channel degradation occurring after the closure of the mine (Gilbert, 1917). In wide valley floors, rivers with narrow meandering channels can be altered to a wide, braided pattern (Warburton *et al.*, 2002). Other depositional features can include filled meanders, point bars and substantial overbank floodplain deposits (Miller, 1997; Macklin *et al.*, 2006).

Processes of passive dispersal and active transformation can enrich floodplain soils with heavy metals (**Table 2.3**). Heavy metals are extremely persistent in the environment and can remain in floodplains for decades to millennia (Miller, 1997). In recent years, an increasing number of studies have highlighted the contamination of floodplains in historically mined catchments in the UK and worldwide (Bradley, 1984; Miller, 1997; Hudson-Edwards *et al.*, 1997; Walling *et al.*, 2003; Dennis *et al.*, 2009). Brewer *et al.* (2005) estimate that over 55% of the agriculturally important River Swale floodplain in northern England is significantly contaminated by heavy metals. Dennis *et al.* (2009) further estimate that approximately 28% of the lead produced in the Swale catchment still remains in channel and floodplain sediments and that, at present removal rates, it may take over 5,000 years for all of the metal-rich sediment to be removed from the

catchment. Such investigations suggest that human health may be adversely affected by ingestion of contaminated vegetables, fruit and livestock.



**Figure 2.2:** Relationship between sediment-bound lead concentrations and distance downstream in some UK rivers (from Lewin and Macklin, 1987)

### 2.3.3 Chemical dispersion/attenuation processes

Chemical transportation processes become increasingly important after the closure and abandonment of metal mines (Lewin and Macklin, 1987; Bradley, 1995). Heavy metals can be attenuated downstream of a mining input through pH buffering, acid neutralisation, and precipitation and adsorption reactions (Ford *et al.*, 1997; Lee *et al.*, 2002; Ren and Packman, 2004).

As pH increases, aqueous metal species display an increasing tendency to precipitate as hydroxide, oxyhydroxide and hydroxysulphate minerals (Salomons, 1987). The effects of increasing pH below mine discharges can be seen in some rivers by changes in precipitate mineralogy with distance downstream, with iron

hydroxides occurring close to mine discharges and aluminium oxides occurring further downstream (Munk *et al.*, 2002). A major control on metal precipitation is the amount of carbonate minerals present in the surrounding rock. Carbonate minerals such as calcite, dolomite and siderite weather quickly and can buffer pH and act as adsorption sites for dissolved metals. Non-carbonate minerals weather slowly, therefore, rivers where non-carbonate minerals predominate can be extremely slow to react to changes in pH (Wilkin, 2008). Precipitated metal oxides and hydroxides can act as sorbents for other heavy metals (Enid-Martinez and McBride, 1998; Asta *et al.*, 2007). Sorption, like precipitation, is heavily dependent on pH concentrations (Salomons, 1987), however, several other water quality parameters can influence adsorption processes, including salinity (Salomons, 1980; Achterberg *et al.*, 2003), organic matter content (Dojlido and Taboryska, 1991; Zhou and Banks, 1992), iron/aluminium/manganese concentrations (Lee *et al.*, 2002) and calcium/magnesium concentrations (Hart, 1982). Increases in the concentrations of any of these variables will increase the amount of sorption sites available for heavy metals.

Under invariant environmental conditions, sediment geochemical phases are stable, chemical attenuation of metals will proceed at a regular rate, and, thus, metals remain immobile in bed sediments (Morillo *et al.*, 2002). However, sediments are not a permanent sink for metals. Metals can be released into the water column should suitable conditions for dissolution occur. Several studies have noted the mobilisation of reduced sediment-bound metals to the water column under oxidising conditions, for example during floods and dredging activities (Calmano *et al.*, 1993; Petersen *et al.*, 1997; Kuwabara *et al.*, 2000; Knott *et al.*, 2009). Bioturbation (Zoumis *et al.*, 2001) and changes in pH (Hermann and Neumann-Mahlkau, 1985), dissolved organic carbon (Butler, 2009), ionic concentration (Dojlido and Taboryska, 1991), and/or the concentration of complexing agents (Fergusson, 1990; Morillo *et al.*, 2002) have also been found to release stored metals from sediments.

Once released to the water column, metals can move through aquatic environments causing poor water quality in stretches of river/coast that were

previously unaffected by mine drainage. Released metals can also interact with, and accumulate in, higher organisms that spend the majority of their time in the water column, e.g. fishes and semi-aquatic mammals (Farag *et al.*, 1998). The threat posed by large deposits of heavy metal contaminated sediments has been highlighted by reference to them as 'chemical time bombs' (Stigliani, 1991).

## **2.4 Metal mining impacts on hydrological systems**

The generation of mine water pollution is a product of many factors including local mineralogy, lithology, contaminant source area and biogeochemical reactions. However, the character of mine water pollution in surface waters will be strongly influenced by meteorological and hydrological factors, including rainfall characteristics, season, antecedent conditions, dominant transport pathways and their hydrochemical characteristics, and river discharge.

Traditionally, river discharge has been seen as the master variable driving river hydrochemistry (Bradley and Lewin, 1982). In general, ion concentrations in rivers are believed to be greatest in low flows and lowest in high flows, when uncontaminated runoff dilutes solute concentrations (Webb and Walling, 1983). Since the 1970s, many researchers have cited the effects of seasonal variability in stream discharge on heavy metal concentrations (Grimshaw *et al.*, 1976; Keith *et al.*, 2001; Sullivan and Drever, 2001; Nagorski *et al.*, 2002; Desbarats and Dirom, 2004; Hammarstrom *et al.*, 2005). Most of these measurements were taken on a weekly or monthly basis. Hysteretic behaviour in annual metal concentrations is apparent in some rivers, primarily reflecting the flushing of oxidised sulphides accumulated over dry summer months. Olias *et al.* (2004), in a study of the Rivers Odiel and Tinto in Spain, found the maximum sulphate and heavy metal concentrations occurred during the first rains of the hydrological year in autumn. In a similar study of the region, Braungardt *et al.* (2003) observed maximum dissolved metal concentrations during autumn and early winter and lower concentrations in late winter, spring and summer. Desbarats and Dirom (2004) monitored effluent draining from an adit at an abandoned mine in British Columbia. Conductivity and dissolved metal concentrations were observed to peak with the first rains of October and November. In regions of the world where



dry summers are atypical, maximum heavy metal concentrations usually occur during the summer months, principally due to the effects of reduced dilution. Bird (1987) found heavy metal concentrations were highest in spring/early summer in the River Tawe, Wales. Mighanetara *et al.* (2009) observed the highest metal concentrations in the River Tamar, England, to occur between July and September.

It is understood that a major part of element transfer in rivers takes place during short-term flood events (Sanden *et al.*, 1997). Therefore, flood events are key to understanding metal transport processes. However, the literature on heavy metals flux and hydrochemical variability during flood events in former metal mining regions is relatively limited (Grimshaw *et al.*, 1976; Sanden *et al.*, 1997; Lambing *et al.*, 1999; Wirt *et al.*, 1999; Keith *et al.*, 2001; Gammons *et al.*, 2005; Canovas *et al.*, 2008). Many studies have observed hysteretic behaviour in the relationship between metal concentrations and discharge, whereby metal concentrations increase on the rising limb of the hydrograph and decrease on the falling limb, associated with flushing and exhaustion/dilution events (Webb *et al.*, 1987). In many cases, the source of metals in the initial flush was metal sulphates accumulated on the surface of mine waste (Keith *et al.*, 2001) and/or contaminated groundwater efflux from mine portals (Canovas *et al.*, 2008). Metal attenuation on the falling limb has been attributed to rain-water dilution and the fact that available contaminant has been scavenged in the first flush (Canovas *et al.*, 2008). Most of these studies have investigated single storm events with no attempt made to examine the evolution of storm event hydrochemistry through the seasons.

Variations in the timing and shape of chemographs during high flow events has been attributed to varying climatic, geologic, hydrochemical and anthropogenic conditions (Gammons *et al.*, 2005); to the origin and storage of contaminants in different locations within a catchment (Webb and Walling, 1983); and to the aggregation in the main river channel of contrasting responses from different tributaries (Walling and Webb, 1980). Important hydrodynamic factors can include antecedent soil moisture conditions (controlling to a large degree the availability of

contaminants in a catchment), travel time of water and responses of areas with different hydrological properties (Klein, 1981; Grimshaw *et al.*, 1976; Bird, 1987; Chapman *et al.*, 1993; Sanden *et al.*, 1997; Canovas *et al.*, 2008).

In the future, predicted increases in the frequency and magnitude of major floods in the UK associated with climate change (Wilby *et al.*, 2006) may result in increased mobilisation and deposition of heavy metals in floodplains (Macklin *et al.*, 2006; Environment Agency, 2008b; Forstner and Salomons, 2008). The autumn 2000 floods in northern England caused large scale remobilisation of contaminated sediments in the headwaters and floodplains of the River Swale, and deposition across large areas of farming land (Dennis *et al.*, 2003). The large total surface area of contaminated sediment introduced into rivers during flood events can also result in desorption of heavy metals to the more toxic aqueous phase (Dawson and Macklin, 1998). Understanding metal concentrations and fluxes during flood events, and the evolution of river hydrochemistry throughout the seasons, is important to assess the risk of contaminant mobilisation from mine sites to agricultural areas, and for the development of mine water treatment systems.

#### 2.4.1 Mine spoil hydrology

No discussion of the hydrological impacts of metal mining would be complete without reference to the hydrology of mine wastes. 70% of all material mined worldwide ends up as spoil (Younger *et al.*, 2002). As a result, significant volumes of waste material are deposited at mine sites and this material can alter natural surface and sub-surface flow pathways. Spoil heaps often have 'perched aquifers' above the underlying bedrock, resulting in unique flow paths. These additional hydrological pathways can influence the timing, magnitude and chemical form of contaminants delivered to river systems. Changes in flow paths and direction can occur slowly through the seasons and more rapidly during rainfall events as different flow paths become active as the water table fluctuates (Qiang *et al.*, 2006). The development of a water table in mine spoil depends on the predominant lithology of the spoil. For example, sandstone forms high permeability spoils whereas mudstone (e.g. central Wales) produces low

permeability spoils (Davies, 1983). If no water table develops, surface runoff will be the predominant flow path (Younger *et al.*, 2002). Leaching of trace metals from mine spoil occurs via microbial, physical and chemical weathering processes. Important parameters influencing the leaching of metals include water residence time, rainfall characteristics, climate, age of spoil material and spoil pH (Brown *et al.*, 1984; Qiang *et al.*, 2006; Cidu and Mereu, 2007).

## **2.5 Metal mining impacts on aquatic ecology – macroinvertebrate communities**

Freshwater macroinvertebrates fulfil an important role in the stream ecosystem. Macroinvertebrates are important food sources for aquatic and terrestrial predators, and are important decomposers in the recycling of organic matter and energy (Gerhardt, 1993). The ability of macroinvertebrates to tolerate and incorporate in their tissue the effects of pollution has led to their widespread use as indicators of river ecosystem health (Beasley and Kneale, 2002). Metal mine contamination can have a number of impacts on macroinvertebrate communities ranging from changes in community composition to mutations and deformities in individuals (**Table 2.5**). Studies have investigated community and individual species response to contaminants in rivers, microcosms and laboratory bioassays. Exposure can occur in the water column through interaction with dissolved metals or metals bound to suspended sediment. Exposure in bed sediment can occur through contact with sediment-bound metals or metals in solution in pore water (Beasley, 2001).

### **2.5.1 Changes in invertebrate community composition**

Studies investigating impacts on community composition have identified a variety of changes occurring as a result of metal mine contamination. Winner *et al.* (1980) observed the most contaminated stretches of two rivers in Ohio, USA, to be inhabited primarily by Chironomidae (Diptera – true fly larvae), while pollution sensitive taxa such as Trichoptera (caddisfly) and Ephemeroptera (mayfly) were largely restricted to less contaminated stretches. Armitage (1980) found species composition in the metal contaminated River Nent, England, to be dominated by Diptera and Plecoptera (stonefly), while Trichoptera and Ephemeroptera were not

abundant. Decreases in the number of macroinvertebrate taxa and number of individuals appear to be common occurrences in metal mining-impacted rivers (Willis, 1985; Gray, 1998). A variety of biotic and diversity indices have been employed to discern the impacts of metal mine contaminants on macroinvertebrate communities. However, the success of these indices has been mixed. Decreases in diversity are common in many of the more severely impacted rivers (Smolders *et al.*, 2003; Van Damme *et al.*, 2008), however, other studies have noted the inadequacy of diversity indices in general to discern the impacts of metal pollution (Chadwick and Canton, 1984; Willis, 1985; Chadwick *et al.*, 1986). It would appear that the multi-factor nature of many metal mine discharges (i.e. acidity, dissolved metals, sulphates and metal precipitates) makes it difficult to diagnose problems clearly.

#### 2.5.2 Changes in behaviour and biological functions

Changes in macroinvertebrate behaviour due to mine drainage have also been investigated. Petersen and Petersen (1983) observed anomalies in the capture nets of Hydropsychidae (Trichoptera) in rivers affected by heavy metal pollution. Brinkman and Johnston (2008) found *Rhithrogena hageni* (Ephemeroptera), exhibited decreased moulting rates after exposure to high levels of copper, cadmium and zinc. Woodcock and Huryn (2007) observed macroinvertebrate secondary production and stored organic matter to decrease in response to a gradient of metal pollution in a stream in Maine, USA. Leland *et al.* (1989) observed an increase in the drift rates of *Baetis* sp. (Ephemeroptera) in a natural stream dosed with copper. Roper *et al.* (1995) found that juvenile *Macomona lilliana* (Bivalve) showed avoidance of copper and zinc-spiked sediments through reduced burial rates and increased crawling and drifting away from the contaminated sediment. In an experimental stream, Clements *et al.* (1989) found high copper doses increased predation pressure, so much so, that the number of caddisfly, mayfly and chironomids dramatically fell. Differences in sensitivity among macroinvertebrate taxa have been attributed to trophic status. Leland *et al.* (1989) found herbivores and detritivores were more sensitive to contamination than predators, possibly indicating the primary route of toxicity was through ingestion rather than from solution.

Organism locomotion and ventilation has been noted to increase in acid mine drainage and metal contaminated solutions prepared in laboratories (Janssens De Bisthoven *et al.*, 2004; Gerhardt *et al.*, 2005; Janssens De Bisthoven *et al.*, 2006; Gerhardt, 2007). Increased locomotion is possibly related to the organism attempting to drift and avoid the toxic environment. Increased ventilation is related to changes in the organism's respiratory system, as it attempts to process and rid the body of toxic metals. Heavy metal contamination can also induce deformities and mutations in macroinvertebrate species. Vermeulen *et al.* (2000) observed increased mentum and pecten deformation and decreased moulting success with increasing lead exposure in *Chironomus riparius* larvae (Chironomidae). Martinez *et al.* (2004) found both zinc and lead to act as teratogens in *Chironomus tentans* (Chironomidae) (inducing deformities as a result of chronic exposure during the lifetime of the organism). Lead further acted as a mutagen (inducing deformities in offspring due to DNA damage in parents from chronic exposure). Certain macroinvertebrate species may possess or develop natural tolerances to certain metal pollutants. Gower and Darlington (1990) found *Plectrocnemia conspersa* (Trichoptera), common in streams in south-west England affected by metal mine drainage, to be quite tolerant of copper pollution. Bahrndorff *et al.* (2006), in microcosm experiments, showed adaptation to metal polluted sediments by *Chironomus februaryi* (Chironomidae). Spehar *et al.* (1978) observed Amphipods exposed to low lead levels over long time periods (> 96 hrs) had greater LC50's (lethal concentration for 50% of the population) than those exposed to higher levels over shorter time periods, suggesting that chronic low level metal pollution may have a similar or more severe impact on macroinvertebrates than acute high level metal pollution.

Metals can be bioaccumulated by organisms and plants, and concentrated or magnified in the food chain (Farag *et al.*, 1998; Smolders *et al.*, 2003; Yi *et al.*, 2008). Metal accumulation can vary between species depending on a number of factors including cuticle type, the presence or absence of external plate gills, physiology, and the processes which control metal distribution in the cell (Sola and Prat, 2006). Typically, the highest heavy metal concentrations are found in top predators (e.g. birds of prey) rather than organisms in closest contact with the

pollutant (e.g. macroinvertebrates) (Reeve, 1994). However, in areas where metals accumulate to a great degree (e.g. sediments), metal concentrations may be greater in the organisms most closely associated with the pollution (Enk and Mathis, 1977). Metal uptake or intake takes place at a cell membrane, e.g. the gill or gut, depending on whether the metal came from the water or food. The potential for bioaccumulation depends largely on metal concentrations in the water, water hardness, amount of organic matter present and the ionic stage of the metal (Jop, 1991). Other factors may include organism feeding mechanism, degree of organism sediment contact and organism size and larval stage (Dressing *et al.*, 1982; Jop, 1991; Farag *et al.*, 1998).

### 2.5.3 Influence of water quality parameters

Changes in some water quality parameters can affect the chemistry and, therefore, the toxicity of metals. The effects of water hardness and alkalinity on metal toxicity have been studied extensively (Stiff, 1971; Brkovic-Popovic and Popovic, 1977; Gauss *et al.*, 1985; Lauren and McDonald, 1986; Gower *et al.*, 1994; Yim *et al.*, 2006). These studies generally found metal toxicity to increase with low values of alkalinity and hardness. Dissolved organic material (i.e. humic and fulvic acids) can act in a similar manner to carbonate minerals to decrease the toxicity of metals (Gower *et al.*, 1994). Kashian *et al.* (2004; 2007) and Winch *et al.* (2002) reported on the potential for high UV-B radiation levels at high altitudes to destroy dissolved organic carbon (DOC) and reduce its ability to mitigate heavy metal toxicity in macroinvertebrates and algae. Garcia-Garcia and Nandini (2006) found high turbidity levels generally decreased lead toxicity in two pelagic (*Diaphanosoma birgei* and *Moina micrura*) and one littoral (*Alona rectangula*) Cladocera. DeNicola and Stapleton (2002) found that dissolved heavy metals in the water column had a greater impact on invertebrate communities than substrata coated with metal precipitate.

The chemical form of a metal has been shown to influence metal bioaccumulation. Dodge and Theis (1979) showed copper uptake by Chironomidae to be significantly inhibited by copper complexation with glycine. Similarly, Podolski (1979) found cadmium accumulation in *Daphnia magna* to be strongly dependant

on the type of complexing agent present. However, Dressing *et al.* (1982) found little difference in metal accumulation in *Hydropsyche* sp. between free cadmium and cadmium complexed with nitrilotriacetic acid (NTA), and suggested that differences in other studies may have been a function of species and metal type.

Clearly, metal mine contaminants can exert a wide variety of impacts on macroinvertebrate communities and one can infer, due to the key role of macroinvertebrates in river ecosystem function, that a poor macroinvertebrate community reflects the broader status of aquatic ecosystem health. Indeed, this is the current philosophy of EU and UK water-related legislation. However, many of the studies described above have investigated the impact of mine water contaminants in non-natural situations. For example, laboratory studies and microcosms will never be able to replicate a 'real' river ecosystem and the complex physical, chemical and biological interactions occurring therein. In addition, surveys of macroinvertebrate communities in actual mining-impacted rivers have yielded mixed results.

**Table 2.5:** Impacts of metal mine drainage on macroinvertebrate communities

Location	Taxa	Impact	Author(s)
<b>Community composition</b>			
River Nent (England)	Community	Decrease in number of individuals and number of taxa; community dominated by Diptera and Plecoptera	Armitage (1980)
Two Ohio streams (USA)	Community	Heavily contaminated sites dominated by Chironomidae	Winner <i>et al.</i> (1980)
Microcosm	Community	Influenced total abundance, taxa richness and predation intensity	Kiffney (1996)
River Avoca (Ireland)	Community	Decrease in number of taxa and total abundance	Gray (1998)
Port Kembla (Australia)	Community	Resuspension of contaminated sediments affects recruitment of macroinvertebrates	Knott <i>et al.</i> (2009)
Clinch River (USA)	Community	Reduced species richness, reduced abundance, shift from sensitive to tolerant taxa	Clements <i>et al.</i> (1992)
Monday Creek (USA)	Community	Isolation of good quality headwater streams by AMD-polluted reaches reduces biotic index scores, species numbers and numbers of individuals	Stoertz <i>et al.</i> (2002)
High Andes (Bolivia)	Community	Decrease in community diversity	Van Damme <i>et al.</i> (2008)
River Crafnant (Wales)	Community	Decrease in number of individuals and number of taxa	Willis (1985)
Estanda stream (Spain)	Community	Decrease in species richness, density and increase in dominance	Marques <i>et al.</i> (2003)



Location	Taxa	Impact	Author(s)
Pilcomayo River (South America)	Community	Reduced diversity	Smolders et al. (2003)
Mesocosm	Community	Reduced taxa richness and number of EPT taxa	Hickey and Golding (2002)
Dalarna (Sweden)	Community	Reduced taxa richness, number of mayflies and stoneflies, and number of EPT taxa	Malmqvist and Hoffsten (1999)
Upland streams (Wales and England)	Community	Reduced diversity, richness, total abundance; increased evenness	Hirst et al. (2002)
<b><i>Behaviour and biological processes</i></b>			
Central and southern Sweden	Hydropsychidae	Anomalies in capture nets	Petersen and Petersen (1983)
Goosefare Brook (USA)	Community	Decrease in secondary production and stored organic matter	Woodcock and Huryn (2007)
Bioassay	<i>Macomona liliana</i> (Bivalve)	Decrease in burial rates	Roper et al. (1995)
Microcosm	Community	Increase in predation pressure	Clements et al. (1989)
	<i>Gammurus pulex</i> (Gammaridae)	Decrease in reproduction rates	Maltby and Naylor (1990)
Bioassay	<i>Chironomus</i> sp. (Chironomidae)	Decreased locomotion	Janssens De Bisthoven et al. (2004)
Bioassay	<i>Choroterpes picteti</i> (Leptophlebiidae)	Increased locomotion and ventilation	Gerhardt et al. (2005)
Bioassay	<i>Atyaephyra desmaresti</i> (Natantia)	Increased locomotion and ventilation	Janssens De Bisthoven et al. (2006)

Location	Taxa	Impact	Author(s)
Bioassay	<i>Lumbriculus</i> <i>variegates</i> (Oligochaeta)	Increased locomotion, decreased ventilation	Gerhardt (2007)
Bioassay	<i>Chironomous riparius</i> (Chironomidae)	Increased deformity, decreased moulting success	Vermeulen <i>et al.</i> (2002)
Bioassay	<i>Chironomous tentans</i> (Chironomidae)	Organism and offspring deformities	Martinez <i>et al.</i> (2004)
Microcosm	<i>Plectrocnemia</i> <i>conspersa</i> (Trichoptera)	Tolerance of copper	Gower and Darlington (1990)
Microcosm	<i>Chironomous</i> <i>februarius</i> (Chironomidae)	Tolerance of metal-polluted sediments	Bahrndorff <i>et al.</i> (2006)
Bioassay	Community	Chronic toxicity less severe than acute toxicity	Spehar <i>et al.</i> (1978)
Microcosm	Community	Chronic toxicity less severe than acute toxicity	Winner <i>et al.</i> (1980)
Guadamar River (Spain)	<i>Hydropsyche</i> sp. (Hydropsychidae)	Metal bioaccumulation	Sola and Prat (2006)
Pilcomayo River (South America)	Chironomidae	Metal bioaccumulation Metal bioaccumulation	Smolders <i>et al.</i> (2003) Yi <i>et al.</i> (2008)
Coeur d'Alene River (USA)	Community	Metal bioaccumulation dependent of feeding group	Farag <i>et al.</i> (1998)
Bioassay	<i>Rithrogena hageni</i> (Heptageniidae)	Decreased moulting rate	Brinkman and Johnston (2008)

Location	Taxa	Impact	Author(s)
Bioassay	Chironomidae	Age and body weight affect metal bioaccumulation	Krantzberg (1989)
Bioassay	Lumbriculus variegates (Oligochaeta)	Contaminated water causes higher locomotion than contaminated sediment	Gerhardt (2007)
Convict Creek (dosed stream) (USA)	Community	Differences in sensitivity related to trophic status	Leland <i>et al.</i> (1989)
East Prong Creek (USA)	Community	Differences in sensitivity related to trophic status	Schultheis <i>et al.</i> (1997)
Bioassay	<i>Callinassa kraussi</i> (Crustacea)	Negative impacts on brood and larval development	Jackson <i>et al.</i> (2005)
Bioassay	<i>Biomphalaria glabrata</i> (Gastropoda)	Increased enzyme inhibition	Aisemberg <i>et al.</i> (2005)
<b>Water quality parameters</b>			
Bioassay	<i>Chironomus tentans</i> (Chironomidae)	Increased water hardness and alkalinity reduces metal toxicity	Gauss <i>et al.</i> (1985)
Bioassay		Water hardness mitigates metal toxicity	Berglund and Goran (1984)
Bioassay		Water hardness mitigates metal toxicity	Lauren and McDonald (1986)
Bioassay		Water hardness mitigates metal toxicity	Gower <i>et al.</i> (1994)
Bioassay	<i>Daphnia magna</i> (Daphniidae)	Increased water hardness reduces metal toxicity	Yim <i>et al.</i> (2006)
Microcosm	Community	Increased dissolved organic material mitigates metal toxicity	Gower <i>et al.</i> (1994)

Location	Taxa	Impact	Author(s)
Microcosm	Community	High UV-B radiation reduces ability of DOM to mitigate metal toxicity	Kashian <i>et al.</i> (2007)
Microcosm	Community	High UV-B radiation reduces ability of DOM to mitigate metal toxicity	Winch <i>et al.</i> (2002)
Bioassay	Cladocera	Increased turbidity reduces metal toxicity	Garcia-Garcia and Nandini (2006)
Slippery Rock Creek (USA)	Community	Dissolved metals greater impact than metal precipitate	DeNicola and Stapleton (2002)
Lane Bloto (Poland)	Ephemeroptera	Metal bioaccumulation dependent on water hardness, metal concentration, DOM, metal species	Jop (1991)
Bioassay	Chironomidae	Copper bioaccumulation influenced by complexation with glycine	Dodge and Theis (1979)
Bioassay	<i>Daphnia magna</i> (Daphniidae)	Cadmium bioaccumulation dependent on type of complexing agents present	Podolski (1979)
Bioassay	<i>Diplostomum spathaceum</i> (Diplostomatidae)	Antagonistic effect of cadmium and zinc	Morley <i>et al.</i> (2002)
Microcosm	Community	Synergistic effect of cadmium and zinc	Clements (2004)
Lusatia lignite field (Germany)	Community	Acid-resistant macroinvertebrate species found in waters with pH $\leq 3$	Goncalves Rodrigues and Scharf (2001)

## 2.6 European Union legislation

The present research is being carried out in the context of the European Union Water Framework Directive (WFD) (2000/60/EC). Published in 2000, it is the largest and most important piece of European water-related legislation to date (Crane, 2003). The WFD establishes a new planning system based on river catchments and attempts to integrate previously disjointed legislation governing how we assess, protect, improve and manage our rivers, lakes, estuaries, coastal waters, wetlands, groundwater and their associated ecological resources (Chave, 2001; Environment Agency, 2008a). The WFD implements two principal changes. The first change switches from a philosophy of protecting water resources for particular uses (e.g. drinking water) to focussing on the ecological status of water bodies (Macklin *et al.*, 2006). The ultimate aim of the WFD is for each Member State to achieve 'good' ecological status for all water resources by 2015. Five ecological status categories will be used to assess the quality of water bodies – high, good, moderate, poor and bad. 'High status' is defined as the biological, chemical and morphological conditions associated with no or very low human pressure. Developing such a classification system requires a well-developed understanding of the interaction between aquatic biota and habitat variables, such as water and sediment quality. The second major change concerns how we manage our water resources and introduces the river basin management planning system. River Basin Management Plans (RBMPs) are prepared and reviewed every six years. The main elements of RBMPs include:

- Characterisation and assessment of impacts on water bodies.
- Environmental monitoring and classification.
- Setting environmental objectives.
- Design and implementation of measures needed to achieve objectives.

Two important European Directives which will be incorporated into the WFD in 2013 are the Dangerous Substances Directive (76/464/EEC), which aims to protect the aquatic environment from the most dangerous polluting substances, and the Freshwater Fish Directive (2006/44/EC), which aims to maintain freshwaters which are suitable for fish life. The Dangerous Substance Directive

identifies two categories of pollutants known as List I (most dangerous) and List II (less dangerous but can result in chronic toxicity) substances (Gray, 2003). Its main aim is to limit and control discharges of these pollutants to inland surface, coastal and territorial waters. Cadmium, mercury and dangerous organic pollutants are included on List I. Copper, lead and zinc are included on List II. Environmental Quality Standards (EQS) for lead, zinc, copper and cadmium are given in **Table 2.6**. The Freshwater Fish Directive lists 14 physico-chemical parameters necessary to maintain water quality suitable for supporting and improving fish life. The main parameters of concern are listed in **Table 2.7**. Member States have the freedom to specify rivers or lakes as either salmonid (salmon and trout) or coarse/cyprinid waters (carp, tench barbel, rudd, roach).

**Table 2.6:** *Environmental Quality Standards for lead, zinc, copper and cadmium in the Dangerous Substances Directive (Environment Agency, 2008c)*

Substance	Water Hardness Category (mg/l CaCO <sub>3</sub> )	
	0-10	>10 – 50
<i>Dangerous Substances Directive</i>		
Lead <sup>4</sup>	4	10
Zinc <sup>2</sup>	30	200
Copper <sup>3</sup>	5	22
Cadmium <sup>1</sup>	-	5

1 Total (annual average)

2 Total (95 percentile), salmonid standard

3 Dissolved (95 percentile), cyprinid and salmonid standard

4 Dissolved (annual average), salmonid standard

This general approach of the European Union to river assessment has two main limitations when it comes to evaluating aquatic systems in river catchments affected by metal mine drainage. The first limitation stems from the nature of heavy metal pollutants. Assessment of metal toxicity is confounded by natural background concentrations, the existence of a number of chemical species, the concentrations of certain physico-chemical parameters, and the fact that some metals (e.g. Zn, Cu) are essential trace elements for organisms (Comber *et al.*,

2008). These facts mean that metal toxicity to organisms can vary considerably between regions and measurement of metal concentrations alone may not be enough to accurately quantify the ecological health of mining-impacted rivers. The second limitation concerns pollution of river sediments by heavy metals. Currently, there are no agreed European guidelines pertaining to pollution of river sediments. This is mainly due to a preferential focus on water column contaminants in the past (Macklin *et al.*, 2006) and also a lack of knowledge surrounding sediment-bound contaminants (Environment Agency, 2008b). Some European countries (e.g. The Netherlands) apply their own sediment guidelines, however, these guidelines only evaluate total metal concentrations and not the more dangerous and ecotoxic, non-residual metals. Given that most mining-impacted rivers will have highly contaminated sediments and the likely impact of these polluted sediments on aquatic ecology, the absence of sediment guidelines represents a serious flaw in EU water legislation and an obstacle to the achievement of the aims of the WFD.

**Table 2.7:** Main parameters for assessment of water quality suitable for fish life in the Freshwater Fish Directive (Environment Agency, 2004)

Parameter	Salmonid		Coarse	
	Guideline	Mandatory	Guideline	Mandatory
Dissolved oxygen (mg/l)	>9	>9	>8	>7
pH		6 - 9		6 – 9
Suspended solids (mg/l)	<25		<25	
BOD (mg/l)	<3		<6	
Nitrites (mg/l)	<0.01		<0.03	
Total ammonia (mg/l)	<0.04	<1	<0.2	<1
Total residual chlorine (mg/l)		<0.005		<0.005
Total zinc (mg/l)*		<0.03		<0.3
Dissolved copper (mg/l)*		0.005		0.005

\*Water hardness of <10 mg/l CaCO<sup>3</sup>

## 2.7 River water quality auditing in the UK

As a member of the European Union, the UK government is required to comply with EU legislation. As such, the WFD was incorporated into UK law in 2003. The Dangerous Substances Directive and Freshwater Fish Directive are enforced in the UK by the Environment Agency of England and Wales (EA) through the Water Resources Act 1991. Currently, auditing of river water quality in the UK is carried out by the EA.

The principal method of assessing river water quality in the UK is by General Quality Assessment (GQA) of a river reach. From the GQA, a range of use-related River Quality Objectives (RQOs) can be set for that reach. The GQA system aims to define the chemical, biological, nutrient and aesthetic status of a river reach (Environment Agency, 2004). However, to date, only the chemical, biological, and nutrient components are established. Furthermore, only three chemical determinants are routinely monitored: biochemical oxygen demand (BOD), dissolved oxygen (DO) and ammonia. These three determinants grade the chemical quality of rivers from A (very good) to F (bad) (**Table 2.8**).

A similar gradation of biological quality is employed, based instead on a qualitative assessment of macroinvertebrate community health. Macroinvertebrates are useful indicators of overall stream ecosystem for several reasons (Chadd and Extence, 2004).

- Their diversity and abundance makes them easy to collect.
- Well-known taxonomy.
- Their relatively long life span (several months to a year) enables them to integrate the effects of pollution.
- They live sedentary lives and are thus representative of local conditions.
- They are differentially sensitive to pollutants and are capable of a graded response to a broad range of stresses.
- Their importance in river function.



Overall river biological health is classified by an Environmental Quality Index (EQI). Two macroinvertebrate scores are necessary to calculate the EQI. The Biological Monitoring Working Party (BMWP) gives a score for different families of macroinvertebrates depending on their sensitivity to pollution. The Average Score Per Taxon (ASPT) is independent of sample size and is the BMWP score divided by the number of scoring families present. The EQI is calculated by dividing the observed ASPT and number of taxa by corresponding values calculated by the River InVertebrate Classification Scheme (RIVPACS) model. RIVPACS attempts to predict values that should be found in a healthy river ecosystem. An EQI of 1 indicates that the ASPT or number of taxa observed was the same as that predicted by RIVPACS and, therefore, the site is not ecologically damaged. Each EQI is assigned a biological grade (**Table 2.9**).

One of the principal criticisms of the BMWP scoring system is that it was developed for rivers subject to organic pollution and, therefore, may not perform well in river systems impacted by other contaminants, including heavy metals (Washington, 1984). As a result, the nationwide use of the BMWP score to derive EQIs may result in many rivers and streams in metalliferous regions being incorrectly graded for biological quality. A second major flaw in the current EA river auditing strategy is the absence of monitoring of sediment quality, although this could be said to be due to lack of guidance from the EU.

**Table 2.8:** Grades of river water quality for chemical GQA (from Beasley, 2001)

<b>Chemical Grade</b>	<b>Likely Uses and Characteristics*</b>
A - Very good	All abstractions
	Very good salmonid fisheries
	Cyprinid fisheries
	Natural ecosystems
B - Good	All Abstractions
	Salmonid fisheries
	Cyprinid fisheries
	Ecosystems at or close to natural
C - Fairly good	Potable supply after advanced treatment
	Other abstractions
	Good cyprinid fisheries
	Natural ecosystems, or those corresponding to good cyprinid fisheries
D - Fair	Potable supply after advanced treatment
	Other abstractions
	Fair cyprinid fisheries
	Impacted ecosystems
E - Poor	Low grade abstraction for industry
	Fish absent or sporadically present, vulnerable to pollution**
	Impoverished ecosystems**
	Very polluted rivers which may cause nuisance
F - Bad	Severely restricted ecosystems

\*Provided other standards are met

\*\*Where the grade is caused by discharges or organic pollution

**Table 2.9:** Grades of river water quality for biology GQA (Environment Agency, 2004)

Grade	Outline description
A. Very good	Biology similar to (or better than) that expected from an average and unpolluted river of this size, type and location: high diversity of taxa, usually, with several species in each: rare to find dominance of any one taxon.
B. Good	Biology falls a little short of that expected for an unpolluted river: small reduction in the number of taxa that are sensitive to pollution: moderate increase in the number of individuals in the taxa that tolerate pollution.
C. Fairly good	Biology worse than expected for an unpolluted river: many taxa absent, or a number of individuals reduced: marked rise in numbers in taxa that tolerate pollution.
D. Fair	Sensitive taxa scarce and contain only small number of individuals: a range of pollution tolerant taxa present, some with high numbers of individuals.
E. Poor	Biology restricted to pollution tolerant species with some taxa dominant in terms of the numbers of individuals: sensitive taxa are rare or absent.
F. Bad	Biology limited to a small number of very tolerant taxa such as worms, midge larvae, leeches, water loghouse, present in very high numbers: in worst case, there may be no life present.

## **2.8 Management of metal mine contamination of river systems in the UK**

Section 2.1 discussed the rise and fall of the metal mining industry in the UK and the impact of pollution from abandoned metal mines on UK rivers. Over the last century, the environmental impact of the metal mining industry has largely been hidden, apart from some high profile incidents (e.g. Wheal Jane Mine, Cornwall) (Whitehead *et al.*, 2005). This situation is perhaps due to a preferential focus in the last few decades on the coal mining industry; partly because most metal mines have long been abandoned, have less visible impacts (ochre is more common in coal mine discharges) and were mostly owned by private companies (Johnston *et al.*, 2007). After the closure of over half of the state coal mines in Britain by the Department of Trade and Industry in 1992, and in recognition of the

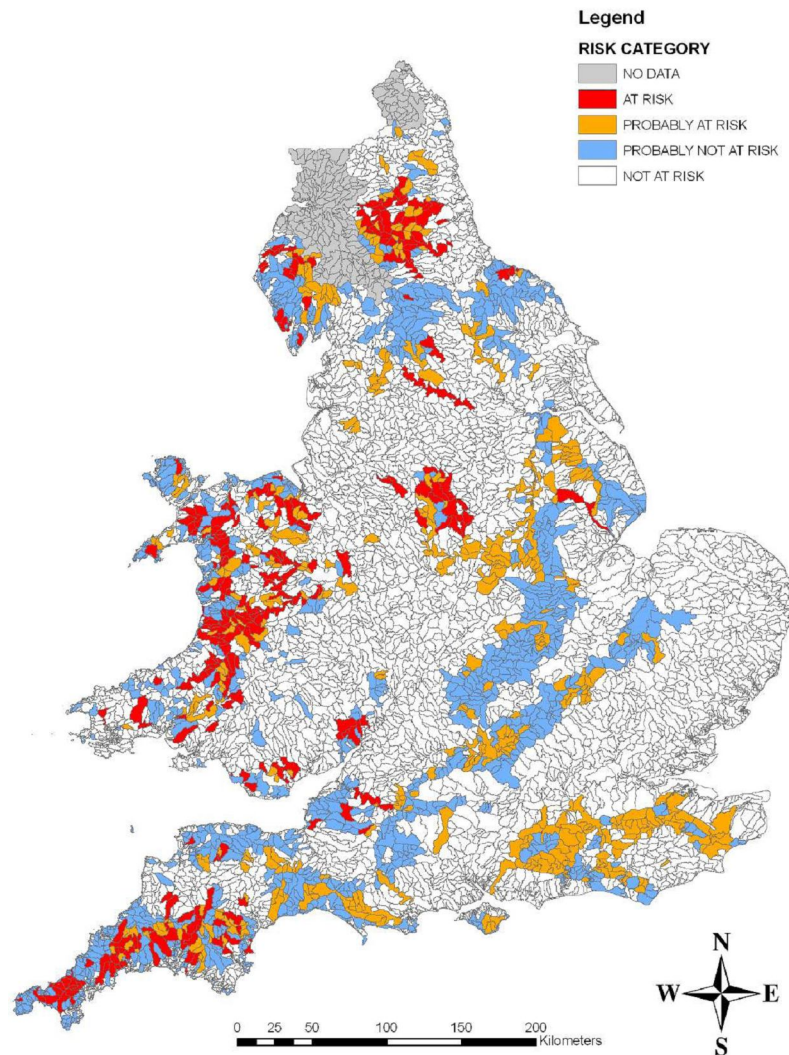
potential for serious pollution from these abandoned mines, the Coal Authority was set up in 1995 to manage the environmental impacts of abandoned coal mines and gather information on the physical, chemical and biological processes occurring at these sites. The results allowed the ranking of polluted discharges in order of severity and the development of suitable remediation strategies (e.g. wetlands). As a result, there are now 52 mine water treatment plants in the UK. However, only two of these treat metal mine drainage (Johnston *et al.*, 2007). This is primarily because of a lack of information and understanding of metal mine pollution in the UK, which stems from the lack of an organisation like the Coal Authority to guide and drive research into metal mine pollution (Environment Agency, 2008a).

In preparation for the WFD, the EA published its Metal Mine Strategy for Wales (Environment Agency, 2002) which was a preliminary assessment of the environmental effects of metal mine drainage in Wales. The project identified 1,311 abandoned metal mines in Wales and compiled a list of the top 50 most polluting discharges. However, this priority list did not fully consider the environmental impact of these mines. Following on from this, in 2007, the Department of Environment, Food and Rural Affairs (DEFRA) commissioned a two-year research project aimed at identifying and prioritising abandoned non-coal mines in England and Wales for remediation. This was intended to be a more in-depth study aimed at developing a methodology to prioritise sites for remediation. The assessment is based mainly on known mine discharges, geological strata and existing water quality and biological data (Jarvis *et al.*, 2007). Initial results have allowed the number and percentage of water bodies in River Basin Districts (RBD) across England and Wales at risk of failing to meet WFD requirements as a result of mine water pollution to be calculated (**Table 2.10**). These data are also illustrated in **Figure 2.3**. Nationally, 8.6% of all water bodies are at risk or probably at risk of pollution from metal mine drainage. The figure for western Wales is 9.8% making it one of the most impacted RBDs in England and Wales.

**Table 2.10:** Number of water bodies in England and Wales River Basin Districts at risk or probably at risk of failing to meet WFD requirements (modified from Jarvis *et al.*, 2008).

River Basin District	At risk	Probably at risk	Probably not at risk	Not at risk	Total	% At risk and Probably at risk
Anglian	1	30	146	929	1106	2.8
Dee	7	10	10	84	111	15.3
Humber	15	56	111	761	943	7.5
North West	15	28	63	469	575	7.5
Northumbria	23	43	41	302	409	16.1
Severn	37	38	82	639	796	9.4
South East	0	47	61	403	511	9.2
South West	59	73	419	887	1438	9.2
Thames	0	65	81	509	655	9.9
<b>Western Wales</b>	<b>70</b>	<b>36</b>	<b>190</b>	<b>783</b>	<b>1079</b>	<b>9.8</b>
<b>Total</b>	<b>227</b>	<b>426</b>	<b>1204</b>	<b>5766</b>	<b>7623</b>	<b>8.6</b>

The ultimate aim of the current DEFRA project is to develop a programme of measures which will allow the UK to meet WFD requirements. The initial prioritisation was completed in late 2007 and identified 3% of water bodies in England and Wales at risk of serious pollution with the mines responsible given priority for remediation planning. A further 5.6% of water bodies were assessed as probably at risk and given priority for further monitoring (Jarvis *et al.*, 2008). The next stage of the project is to investigate each RBD in greater detail.



**Figure 2.3:** River catchments in England and Wales sensitive to mining-related contamination (from Environment Agency, 2008a)

## 2.9 Chapter summary

Almost a century after the closure of most UK metal mines, there exists today a significant environmental legacy in the form of widespread contamination of aquatic ecosystems. Significant quantities of contaminated sediment are being eroded and transported into aquatic systems from abandoned metal mines. The potential mobility and bioavailability of sediment-associated heavy metals poses serious concerns over ecological health and the safety of human food supplies. However, sediment systems have, so far, not received much attention in European legislation and there has been a lack of guidance from Europe

regarding sediment quality. Where sediment guidelines do exist, they focus solely on total metal concentrations rather than bioavailable metals. The hydrochemistry of rivers draining metal mines has received much attention from researchers in the past. Most of these studies have investigated variation in river hydrochemistry under steady flow conditions. A greater percentage of studies have examined seasonal variability. However, relatively few studies have sought to quantify the impact of short-term flood events on river hydrochemistry and the contribution of these events to metal concentrations and fluxes. Appreciation of the impacts of flood events on river hydrochemistry is essential in order to fully understand contaminant mobility and to develop remediation strategies. Benthic macroinvertebrates are used as a key indicator of overall aquatic ecosystem health. However, the response of macroinvertebrates to metal mine contamination is extremely variable. Many studies have investigated organism response to metal pollution in very simplified ecosystems. Those studies which have investigated macroinvertebrate communities of 'real' rivers impacted by metal mine drainage, have shown indices of macroinvertebrate health to differ markedly in their assessment of community health. The European Union WFD seeks to harmonise existing water-related legislation and protect and improve water resources by applying an ecosystem-centred management approach. However, the WFD approach to the assessment and improvement of aquatic ecosystems may have significant limitations in regions affected by metal mining.

## 3. Study Area

### 3.0 Introduction

In 2002, the Environment Agency published its Metal Mine Strategy for Wales which identified the 50 most polluting metal mines in Wales (Environment Agency, 2002). A number of abandoned mine sites were identified from this list as candidate study sites for the present research. Amongst the most important site selection criteria were:

- 1) Expected level of mine impact on the aquatic system.
- 2) Presence or absence of other polluting industries in the river catchment.
- 3) Ease of access to the river channel and mine environment.
- 4) Presence of suitable control channels within the river catchment.

1) Dylife mine was listed as the 5<sup>th</sup> most polluting metal mine in Wales in the Metal Mine Strategy for Wales (Environment Agency, 2002) and water quality impacts in the Afon Twymyn are known to extend for at least 20 km downstream of the mine (Johnston, 2004).

2) River catchments were sought where the impact of metal mining could be considered without interference from other contaminants, e.g. organic pollution from agriculture, which would confound the problem.

3) Many abandoned metal mines in the UK are located in mountainous regions with little or no road access links, steep and uneven terrain, and dense forest, all of which make for a dangerous working environment. Therefore, sites were sought which could be accessed easily by road and where the working hazards were judged to be acceptable.

4) Most metal mines are located in the headwaters of rivers having no 'clean' upstream channels. One of the primary aims of this thesis is to investigate the impact of metal mining on the aquatic system with reference to the conditions



which might be expected without mining impact. Therefore, sites were sought where unimpacted channel reaches could be found in the river catchment to act as control channels.

A number of sites were excluded as they were not easily accessible and/or had other polluting industries in the river catchment. However, the majority of sites were excluded on the grounds of having no control channels. Following a pilot study field investigation and consultation with the Environment Agency, Dylife mine in central Wales was selected for study. The Afon Twymyn which drains Dylife mine has a historical legacy of poor water quality. The river has been known to be polluted by mine drainage since the 19<sup>th</sup> century and has attracted the interest of researchers since the 1930s (James, 1935). Dylife is an excellent site from an experimental point of view, as it possesses both impacted and unimpacted areas within the same catchment. Upstream of the mine there are no negative impacts apart from some small-scale pastoral farming. Downstream of the mine there are no potential polluting industries in the catchment.

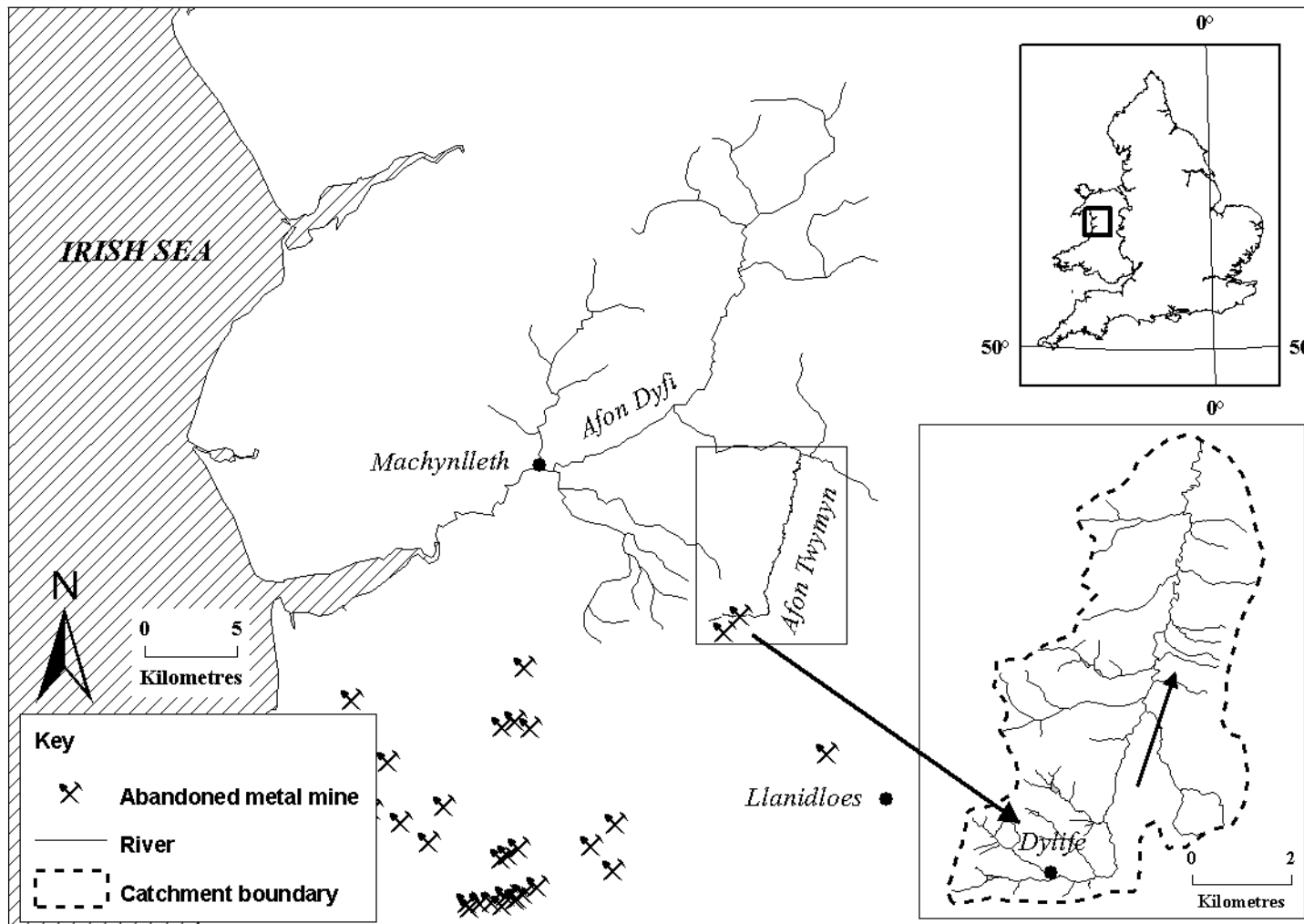
### **3.1 Site description**

The Afon Twymyn is a tributary of the Afon Dyfi which flows into the Irish Sea near Machynlleth (**Figure 3.1**). The Afon Twymyn merges with the Afon Dyfi near the town of Glantwymyn. This study considers the upper Twymyn catchment (35 km<sup>2</sup>) from its confluence with the Afon Laen at Llanbrynmair to its source above Dylife (**Figure 3.2**). Dylife mine (SN 859 940) is located in the headwaters of the Afon Twymyn, approximately 28 kilometres north-east of Aberystwyth.

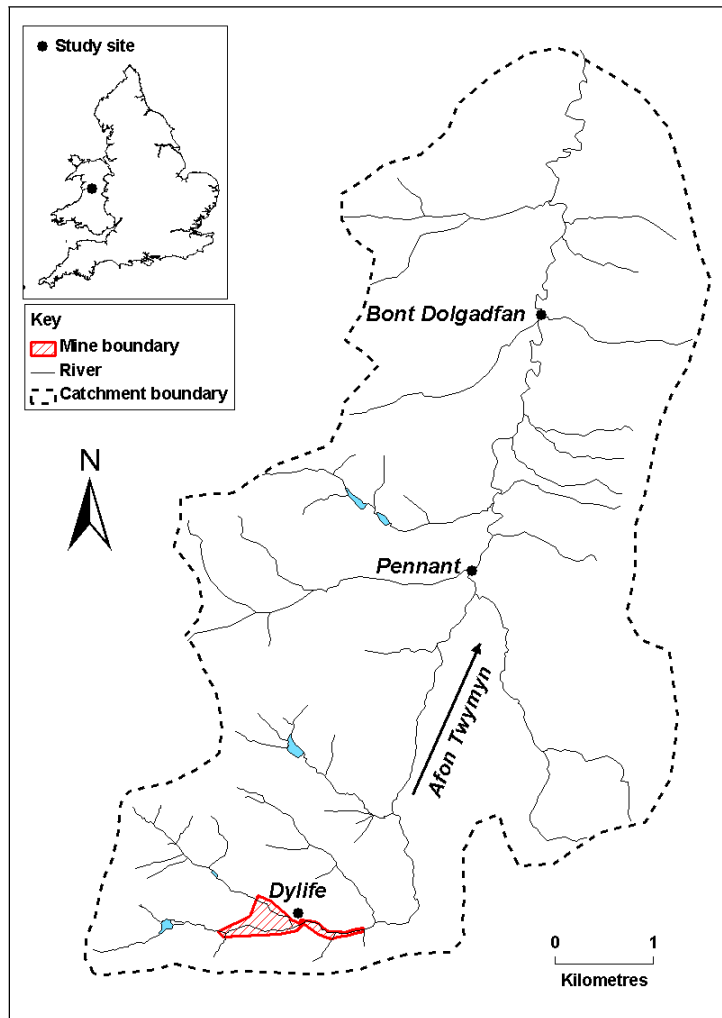
#### **3.1.1 Topography**

Dylife mine lies at the centre of an elevated plateau between Machynlleth and Llanidloes known as the central Wales mining district. Most of this land is over 300 mAOD with the highest ground reaching over 500 mAOD. The smooth profile of the mountains is dissected in places by deep and broad valleys (Rudeforth *et al.*, 1984). There is considerable range of elevation (98 – 530 mAOD) in the Afon Twymyn catchment (**Figure 3.3**). The catchment above Dylife mine is composed of two steep-sided (>30°) river valleys. These valleys descend approximately

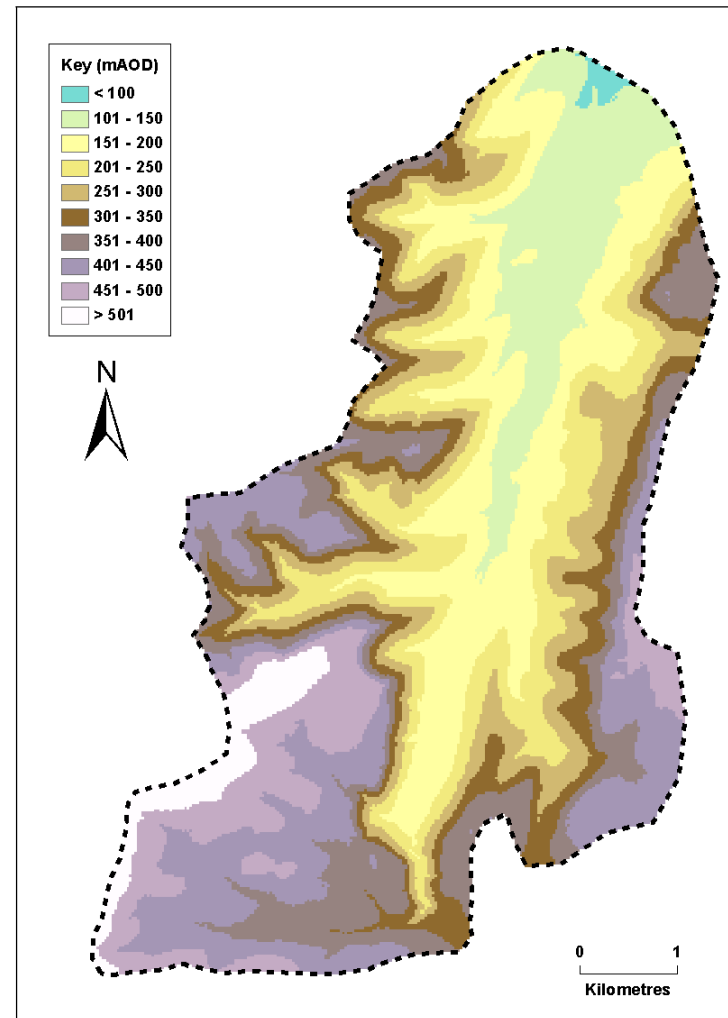
150m over 2.5 kilometres to converge at Dylife. The abandoned deep mine (375 mAOD) forms a excavation approximately 1,500 m long and 150 m wide in places. The mine site elevation varies between 390 mAOD at the south-west boundary and 350 mAOD at its eastern boundary. The construction of the mine essentially truncated the river valley increasing the valley slope and lowering the level of the river. Beyond the mine to the east, the valley begins to narrow into a gorge and eventually a steep 50m drop to the valley floor below (200 – 250 mAOD). Thereafter, the valley gradually widens to a floodplain up to 600 m wide in places. Beyond the floodplain, the valley sides rise steeply to between 300 and 450 mAOD. The lowest point in the catchment is at the confluence with the Afon Laen, near Llanbrynmair.



**Figure 3.1:** Map of central Wales mining district showing location of Dylife mine and the Afon Twymyn catchment



**Figure 3.2:** Afon Twymyn catchment and Dylife mine

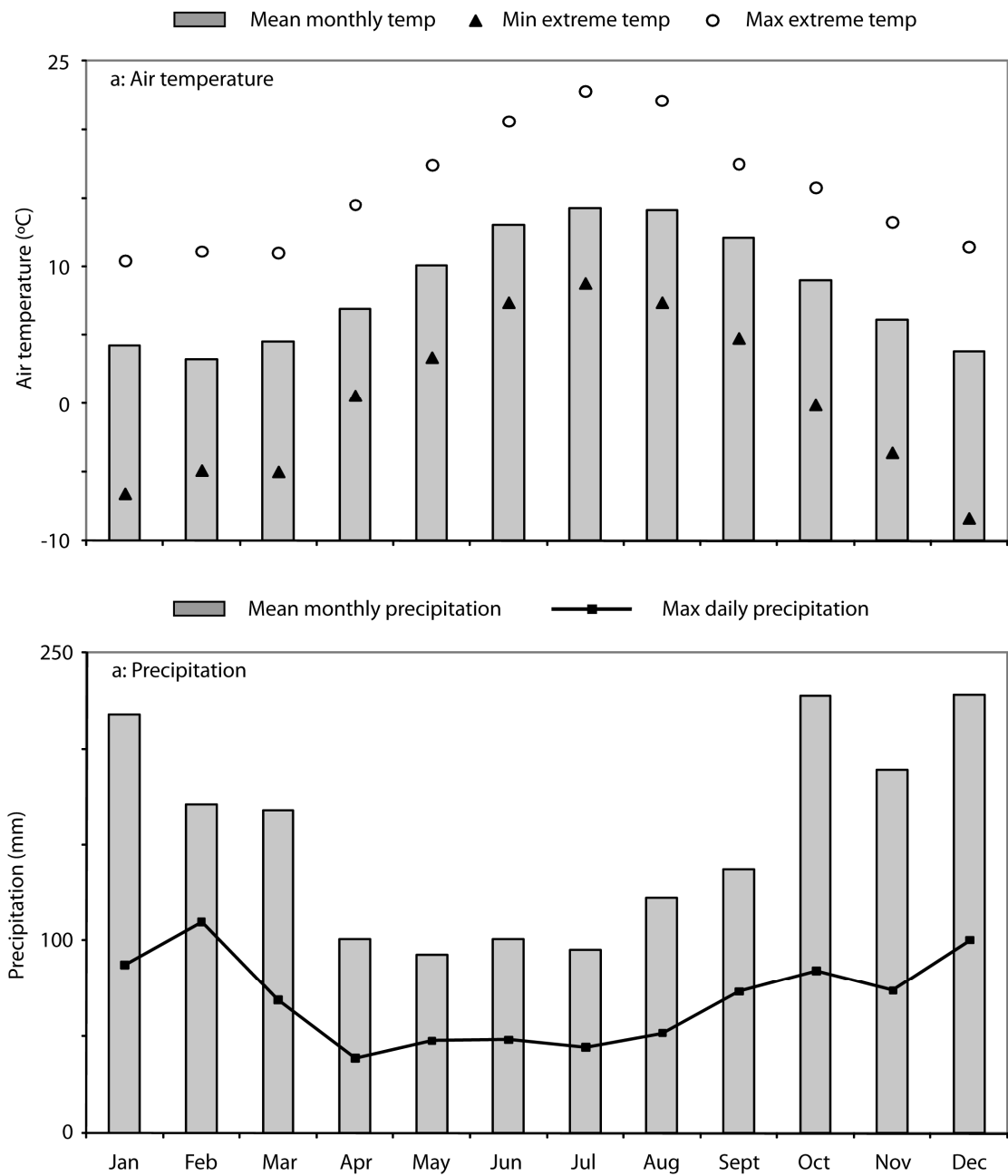


**Figure 3.3:** Afon Twymyn catchment elevation

### 3.1.2 Climate

The mean annual temperature in lowland Wales varies from 9.5 – 10.5°C. This average decreases to 6 – 8°C in upland central Wales (Met Office, 2009). Recent (2000 - 2008) air temperature data for upland Wales is illustrated in **Figure 3.4a** and derived from Dolydd weather station, approximately 3.8 km south-south-east of Dylife (297 mAOD; SN 873 904). February is normally the coldest month with a mean daily temperature of 3.2°C. July is usually the warmest month with a mean daily temperature of 14.2°C. The average monthly temperature usually falls above 0°C, however, extreme cold values have been recorded for January (-6.6°C) and December (-8.4°C). The mean annual temperature between 2000 and 2008 was 8.6°C.

A 29-year (1979 – 2008) record of rainfall was also obtained from Dolydd rain gauge (**Figure 3.4b**). Rainfall tends to be associated with frontal systems advancing eastwards from the Atlantic. In upland Wales, precipitation is dominated by orographic cooling when air is forced to rise over the mountains, resulting in greater precipitation intensity at high altitudes (Rudeforth *et al.*, 1984; Arnell, 2002). The months from October to January are usually significantly wetter than those between February and September (Met Office, 2009). Close proximity to Atlantic weather systems and extensive areas of upland can lead to large daily and monthly rainfalls (Shaw, 2004). Daily precipitation totals can exceed 50 mm and even 100 mm (e.g. 110 mm, February 1991). The total annual rainfall (1979 – 2008) ranged between 1439 mm (1996) and 2839 mm (1994) with a mean value of 2010 mm.



**Figure 3.4:** a) Mean monthly and extreme air temperatures (2000 – 2008) and b) mean monthly and extreme precipitation (1979 – 2008) from Dolydd weather station

### 3.1.3 Geology

The upper Afon Twymyn catchment lies on Upper Silurian (443 – 428 Ma) argillaceous sediments, mainly comprised of shales, siltstones and mudstones

**(Figure 3.5)** (British Geological Survey, 2007). These rocks are generally classified as impervious (Archer, 2007) and were formed from detritus and living organisms in the seas covering Wales during the Lower Palaeozoic era (570 – 410 Ma) (O’Grady, 1980). During the late Silurian period (428 – 416 Ma), the landmasses separated by the Iapetus Ocean slowly collided and the Welsh Basin was forced into a new mountain range – the Welsh Caledonides. Under the intense pressure, some of the clay minerals making up the mudstones recrystallised, becoming aligned at right angles to the direction of maximum pressure, forming shales and slate. The mudstones contain large quantities of dioctahedral mica and quartz (32%), illite (37%) and iron-magnesium chlorite (26%), with lesser amounts of feldspar, iron oxides, albite, orthoclase and rutile (Hornung *et al.*, 1986). The chemical composition of the rocks is primarily silica (58%) and aluminium oxide (22%) with low concentrations of base materials (e.g. CaO = 0.05%) (Evans and Adams, 1975).

Igneous activity during the Caledonian (444 – 416 Ma) and Hercynian (390 – 310 Ma) mountain building periods gave rise to mineralisation. Rising hydrothermal solutions, upon meeting the shales, cooled and precipitated baryte and fluorospar and sulphides of zinc, lead, copper and iron (Evans, 1987). Calcite and dolomite are rare, as are secondary minerals (Jones, 1922). The resulting mineralised faults trend east-north-east through the Ordovician and Silurian sediments (Fuge *et al.*, 1991).

Three mineral lodes are associated with Dylife mine **(Figure 3.8)**. The Esgairgaled and Llechwedd Ddu lodes are located within the Afon Twymyn catchment. Dylife lode is located to the south of Dylife mine at Pen Dylife in the Afon Clywedog catchment. The Dylife lode trends east to west. The Esgairgaled lode trends east-north-east and unites at its western end with the Llechwedd Ddu lode which is situated between the other two lodes and trends north-east. The principal lode constituents are coarsely-crystallised quartz, galena, sphalerite and chalcopyrite (Jones, 1922).

#### 3.1.4 Soils and land cover

The soils of upland central Wales have been studied extensively as part of the Plynlimon catchments project (Kirkby *et al.*, 1991). The high precipitation, low temperatures, steep slopes and low permeability geology of the region have resulted in the widespread accumulation of stagnopodzols and stagnohumic gleys (Brandt *et al.*, 2004). In the Afon Twymyn catchment, strongly-layered Podzols are present mainly on the flat hilltop areas above Dylife (National Soil Resources Institute, 2009) (**Figure 3.6**). The surface peat horizon (c. 25-50 mm), high in organic matter, acts much like a sponge ensuring the soil is seasonally waterlogged. Underlying the surface horizon is a highly impermeable and acidic clay/silt layer (c. 50-200 mm) which forms a barrier to infiltration, deflecting water to run sideways downslope as throughflow (lateral or pipe flow) (Bell, 2005). At the base of the clay/silt layer, a distinct 'iron pan' (c. 0-150 mm) has formed through the concentration of insoluble cations (Fe, Al, Mn) following leaching of more soluble cations (Na, K, Mg, Ca). Soil fertility in the upper catchment is very low and drainage is impeded by the saturated upper horizons. In general, rainwater passes rapidly into the river, particularly in the winter. The steeper valley sides of the catchment are composed of freely draining acidic, loamy soils with low fertility (c. 200-1000 mm) overlain by a thin topsoil (c.100-300 mm). Bell (2005) classifies these soils as Creep Brown Earths owing to their gradual downslope movement and colour (weathered brown mudstone in a matrix of clay/silt weathering products). The slow movement of these soils under gravity ensures they are well mixed and experience better drainage than the Podzols. On the steeper slopes, the cleavage planes of the rocks can be seen. Extensive weathering and fracturing of these exposed rocks may act to transfer rainwater to deeper weathered bedrock (Shand *et al.*, 2005). Central Wales was glacierized during the Pleistocene, however, in the Afon Twymyn catchment, drift is either extremely thin or absent. Slowly permeable Peaty Gleys (c. 300-1500 mm) dominate the lower concave slopes bordering the river channel and may overlay Boulder Clay in places (Bell, 2005).

The land cover of the Afon Twymyn catchment is illustrated in **Figure 3.7** and based on the Land Cover Map of Great Britain 1990 (Fuller *et al.*, 1994). The

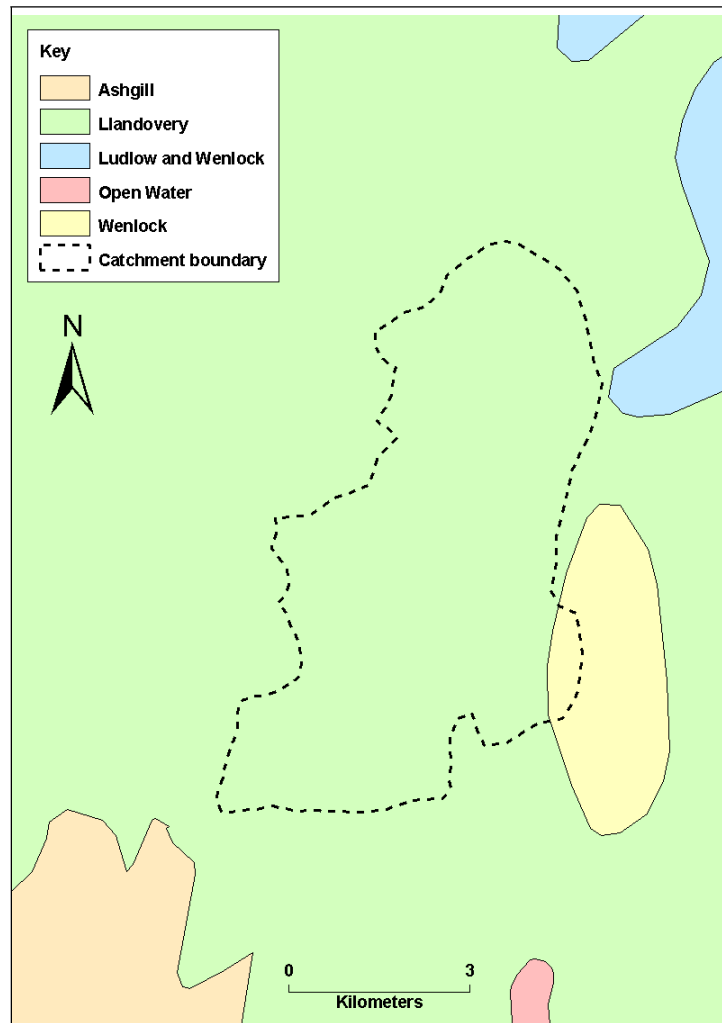


percentage of the Afon Twymyn catchment area in the main land cover categories is shown in **Table 3.1**. The Afon Twymyn rises in high moorland comprising rough grassland, heath, marsh and bracken. Small-scale pastoral farming is the main land use. Two small reservoirs (SN 8475 9400 and SN 8530 9430) are located to the west of the mine and are associated with the mine workings. The mine site is abandoned and currently comprises numerous spoil tips with abandoned shafts, adits and a collapsed stope (**Figure 3.8**). Several shafts and adits are present in the Twymyn valley. Very little remains of the works buildings and many may be buried beneath the spoil (**Figure 3.9**). Due to the contaminated substrate at the mine, vegetative cover is limited to pollution tolerant mosses, liverworts and lichens. The wider catchment is predominantly rough grassland.

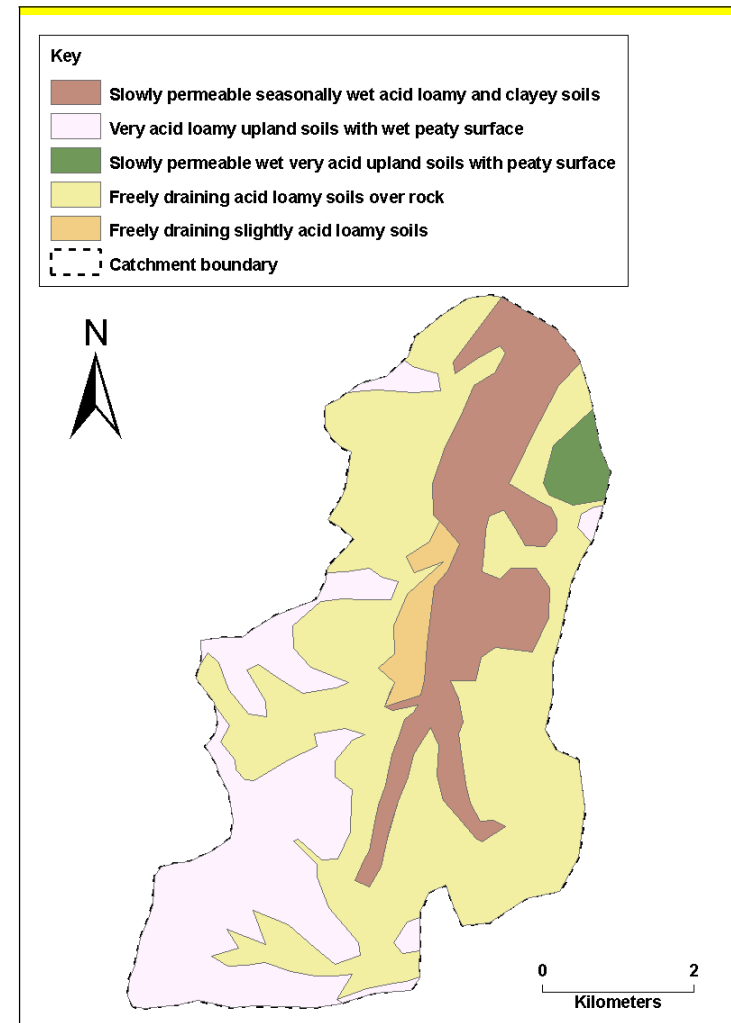
Downstream of Ceunant waterfall, the gorge known as Ceunant Twymyn is designated a Site of Special Scientific Interest (**Figure 3.10**). From this point downstream, the land cover is predominantly rough grassland and heath with pockets of woodland, bracken and bog on higher ground. Pastoral farming, with sheep and cattle, and coniferous plantations are the main land uses. Two small villages are located on the river - Pennant (SN 875 975) and Bont Dolgadfan (SN 885 005). Further small-scale mining activity in the form of spoil is evident at Ty-isaf (SN 878 982) and Ceulan (SN 871 975).

**Table 3.1:** *Percent of Afon Twymyn catchment area in major land cover categories*

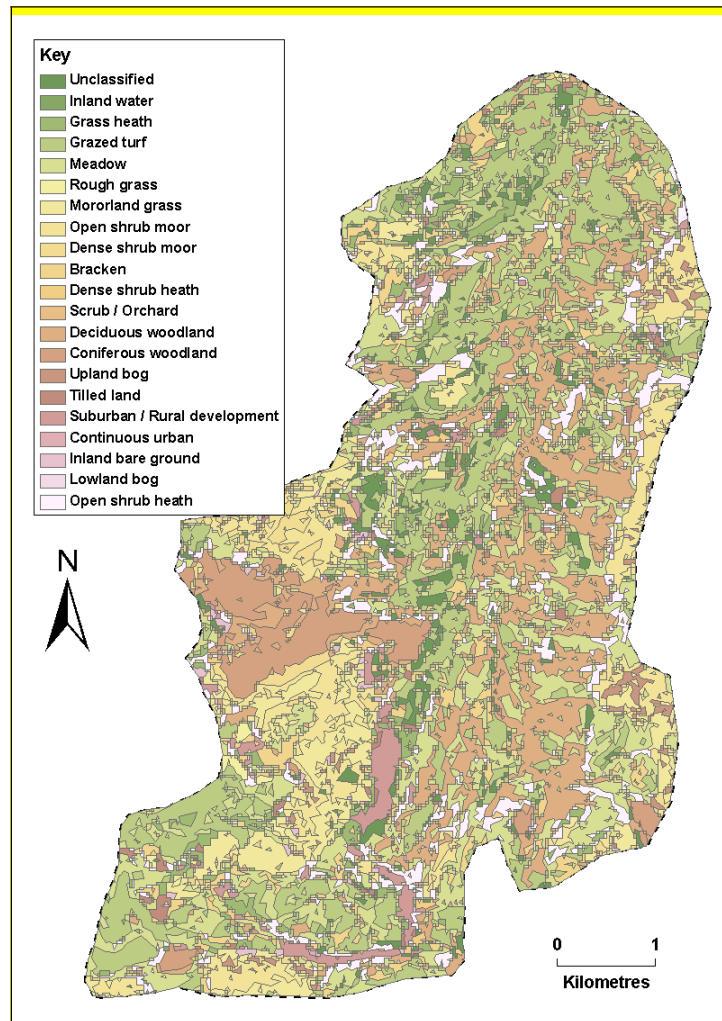
Land cover category	Percent (%)
Grazed turf	20.1
Meadow/semi-natural	18.5
Deciduous woodland	15.9
Open shrub moor	7.6
Open shrub heath	6.9
Moorland grass	5.8
Bracken	5.6
Other	19.6



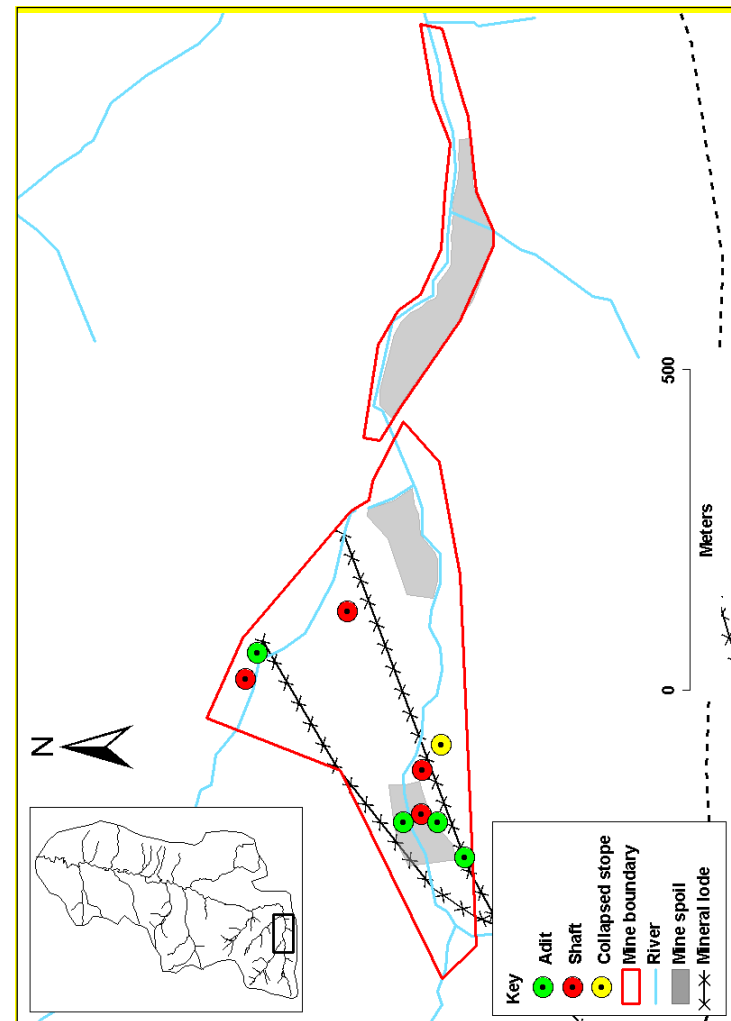
**Figure 3.5:** Afon Twymyn catchment in relation to solid geology



**Figure 3.6:** Soil classification of the Afon Twymyn catchment



**Figure 3.7:** Land cover map of Afon Twymyn catchment



**Figure 3.8:** Location of major mine workings at Dylife mine



***Plate 3.1: Afon Twymyn, Dylife, with spoil tips in background***



***Plate 3.2: Afon Twymyn, Ceunant, Site of Special Scientific Interest***

### 3.1.5 Hydrology

The surface hydrology of the Afon Twymyn catchment is shown in **Figures 3.11** and **3.12**. Two streams, the Afon Twymyn and Nant Dropyns rise to the west of the mine site and enter small reservoirs (SN 8480 9397 and SN 8529 9449) approximately 1 km from their source. These reservoirs once fed leats which ran along the valley sides conveying water to the mine shafts where waterwheels were used to dewater the mine. The two streams enter the mine site at its western border over small waterfalls (SN 8536 9388 and SN 8536 9441).

Past the waterfall, the Nant Dropyns flows through a steep sided valley composed of spoil in parts. The stream passes the Esgairgaled shaft (SN 8579 9420) and Pencerig adit (SN 8584 9419) on its left bank before disappearing into the substrate where the Llechwedd Ddu lode crosses under the stream. Under normal flow conditions (March to October), the Nant Dropyns does not flow at the surface past this point. When the stream does flow past this point, it is diverted under the Machynlleth road through a culvert (900 mm diameter). The downstream end of this culvert discharges with a steep drop onto a rock outcrop which is the site of the old mine dressing floor. The Nant Dropyns/Afon Twymyn confluence occurs at SN 8609 9394.

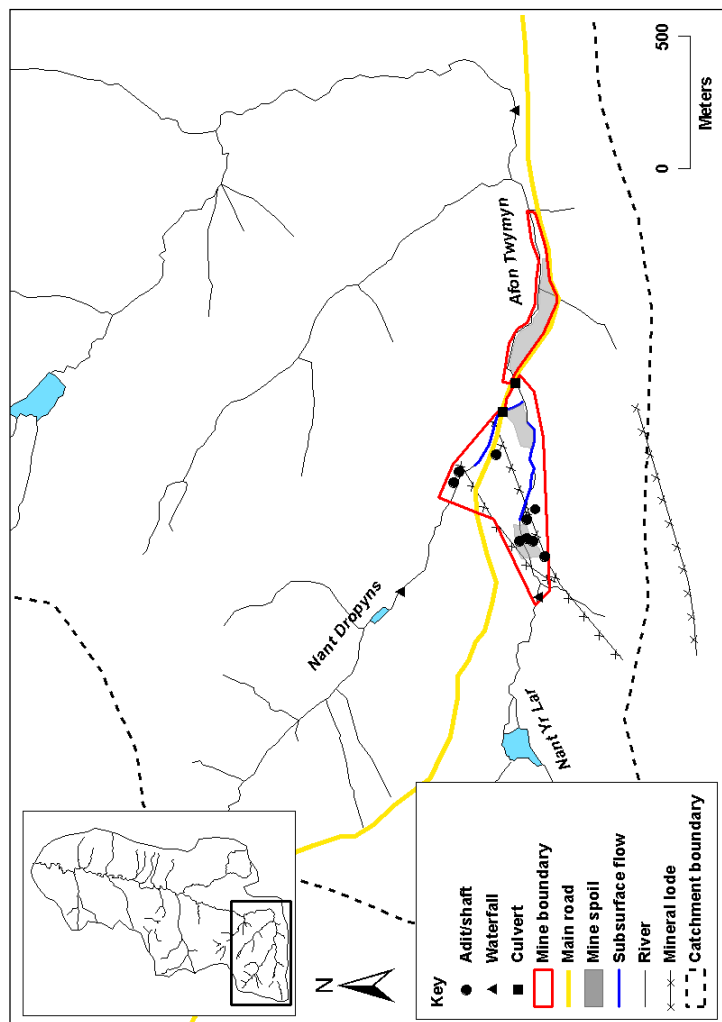
The Afon Twymyn is joined by a small tributary from the south just after the waterfall (SN 8541 9387). Approximately 100 m downstream of the tributary, the Afon Twymyn enters an area of mine workings and mine spoil. The valley sides are steep (c. 45°) with patches of mine spoil on the left bank. Several mine features are to be found on both banks along this stretch. The stream passes Dylife adit (SN 8551 9386) and Level Goch adit (SN 8557 9390) on the right bank and Gwaith Gwyn adit (SN 8557 9396) on the left bank. Llechwedd Ddu engine shaft (SN 8558 9393), Footway shaft (SN 8565 9393) and a collapsed stope (SN 8569 9390) are located on the right bank. A tramway culvert once ran across the watercourse adjacent to the Llechwedd Ddu shaft. The culvert has collapsed into the river forming a low dam and raising the river bed level upstream. The flow disappears under low flow conditions at SN 8565 9396 next to the Footway shaft, and re-emerges from the gravel approximately 100 m downstream where the

stream crosses the underlying Llechwedd Ddu mineral lode. The stream continues through mine spoil past the old mine dressing floor (SN 8606 9397) where, during times of high flow, it may be joined by the Nant Dropyns. The river is then diverted under the Machynlleth road through a rock cut tunnel (1.65 m wide, 1.37 m high) (SN 8613 9395).

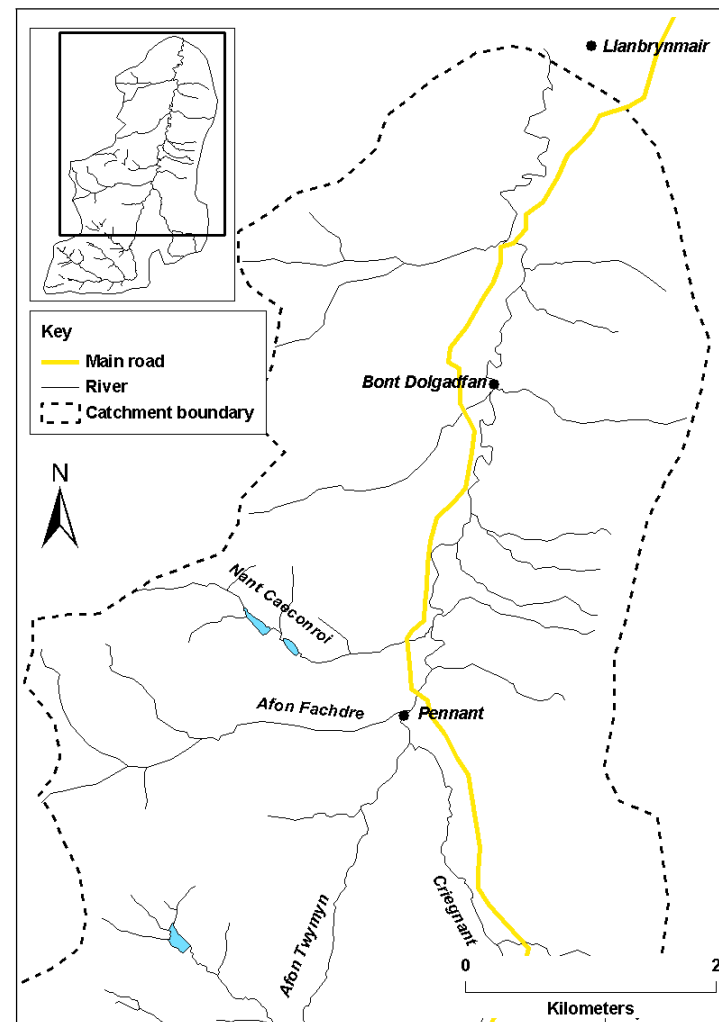
The area between the Machynlleth road and Ceunant waterfall is the location of the main spoil tips area, and designated as a Regionally Important Geodiversity Site (RIGS) for mineralogy (Brown, 2006). Downstream of the tunnel, a gravel bund has been constructed to keep the watercourse away from the spoil heaps on its southern margin. Two visible springs are present in the mine spoil near the rock tunnel (SN 8621 9399) and at the midway point of the mine spoil (SN 8639 9391). A minor tributary enters the river from the south (SN 8652 9388) and crosses the mine spoil.

Beyond this point the river has eroded to bedrock, the result of a knick point working its way upstream from Ceunant waterfall. The valley sides are steep at this point (c. 60°). Approximately 1 km from the Machynlleth road (SN 8718 9398), the river plunges 50 m into an area known as Ceunant Twymyn. This area comprises a two kilometre long section of the Twymyn valley and is designated a Site of Special Scientific Interest (SSSI). It is an excellent example of a process known as river capture, where the original course of the river lay eastwards to the Afon Clywedog catchment but was intercepted through headwater retreat of the Afon Twymyn (Brown, 2006). After Ceunant Twymyn, the Twymyn flows northwards for approximately 8 km passing through the villages of Pennant and Bont Dolgadfan before its confluence with the Afon Laen, near Llanbrynmair (SH 8907 0273). The river is joined by three major tributaries on its passage: Creignant (SN 8796 9734), Afon Fachdre (SN 8795 9761) and Nant Caeconroi (SN 8813 9827). There is evidence of some minor mine workings in both the Afon Fachdre and Nant Caeconroi catchments (Brown, 2006).





**Figure 3.9:** Hydrology and main features of upper Twymyn



**Figure 3.10:** Hydrology and main features of lower Twymyn

### 3.1.6 Mine history

Dylife mine was historically and industrially amongst the foremost metal mines in Wales (Bick, 1977), being worked principally for lead and for smaller quantities of zinc, copper and silver. Small-scale mining occurred during Roman times, however, the principal industry took place from the 17<sup>th</sup> century onwards. Initially, shafts and adits were constructed to access Dylife lode at Pen Dylife. This was followed by 17<sup>th</sup> and 18<sup>th</sup> century workings on the Esgairgaled lode in Nant Dropyns catchment. In the 19<sup>th</sup> century, the Llechwedd Ddu lode was mined in the Afon Twymyn valley. The Esgairgaled and Llechwedd Ddu lodes were connected underground and were dewatered by a 63 ft diameter waterwheel located on the Llechwedd Ddu shaft. Some time around 1850, the Dylife adit was constructed to drain the Dylife lode to below 350 mAOD and, therefore, allow it to be mined to this depth. In 1862 Dylife produced the greatest annual output of lead (2,751 tons) of any mine in mid-Wales (Brown, 2006). By the mid 1870's, the metal mines of Montgomeryshire accounted for 10% of British lead, zinc and silver production (Bick, 1977). Mining activity at Dylife ceased in 1901 although some reworking of the spoil occurred until 1930. The total ore output of the mine for the period 1845 – 1901 was 35,505 tons Pb, 391 tons Zn, 1,342 tons Cu and 126,286 oz Ag (Jones, 1922).

### 3.2 Chapter summary

The Afon Twymyn in central Wales has been chosen as a study catchment to investigate the impacts of metal mining on an aquatic ecosystem. The river drains Dylife mine which is ranked in the top 50 most severe metal mine discharges in Wales. Several features of the Afon Twymyn catchment mark it out from neighbouring catchments as an area of outstanding beauty and historical significance, including its geological history, varied topography and mining legacy. Investigation of the environmental impact of this mining legacy will help inform decision makers as to the best ways to protect and improve the Afon Twymyn ecosystem and other mining-impacted river ecosystems.



## 4. Methods and Materials

### 4.0 Introduction

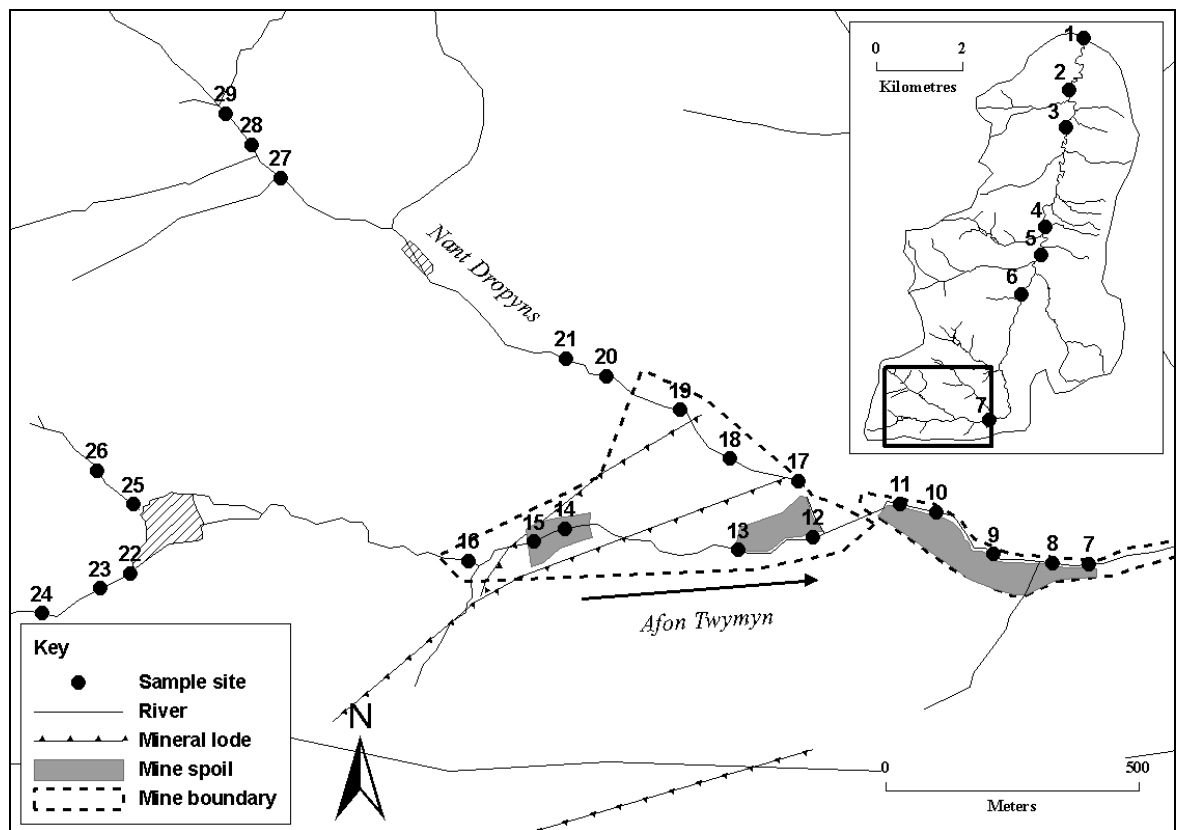
This chapter introduces and assesses the methods and materials used in the present study. As far as is possible, the methods used are standard practice to allow them to be comparable with similar research. The merits of measuring particular parameters as well as the use of particular field, laboratory and statistical techniques are discussed.

### 4.1 Sampling approach

The principle objective of the sampling framework was to assess the impact of Dylife mine on the water and sediment quality, and ecological status of the Afon Twymyn. A total of 40 sampling sites were established for this study (**Figure 4.1**). The number of sampling sites used reflects the degree of heterogeneity in river hydrogeochemistry and macroinvertebrate communities likely to occur in different sections of the Afon Twymyn. Sampling sites were spaced more closely together in the upper part of the catchment where mine workings and mine spoil may result in rapid changes in macroinvertebrate community structure and in the chemical composition of sediments and the water column. Downstream of Dylife mine, sampling sites were more widely spaced reflecting a decrease in features which may impact sample parameters. Sampling sites were positioned upstream and downstream of features which may impact the measured criteria. These features include minor and major tributaries, mine shafts and adits, and mine spoil. For the general classification of river reaches, the Afon Twymyn was divided into control sites (29-22), mine sites (21-7), downstream sites (6-1) and tributary sites. The use of control sites is ideal for tackling the problems associated with spatial and temporal variability (Haines-Young and Petch, 1986).

Twenty-nine of the forty sampling sites were located on the main river channel. These sites were allocated for sediment, macroinvertebrate (surber) and water quality samples. Six sites (3, 8, 12, 16, 18, 21) were also selected for the metal bioaccumulation study (section 4.5.4). Water only, non-channel samples were

collected at 11 other sites of interest within the catchment which might act as sources of pollution or dilution or yield important information on hydrogeochemical processes operating in the catchment. Some small tributaries were omitted from the study as they were estimated to have relatively insignificant flow contributions to the main channel, and there was no evidence of mining in their catchments.



**Figure 4.1:** Sample points in the Afon Twymyn catchment

Water column and macroinvertebrate samples were collected in June 2007, October 2007 and March 2008 in order to represent the low, high and medium phases respectively of the river hydrograph, and the impact this may have on water quality and macroinvertebrate communities. The sampling period also allowed for the collection of macroinvertebrates covering the different stages of their life histories. Sediment samples were collected in June 2007 only, as seasonal variation in deposited sediment quality are, generally, not thought to be significant (Pierre-Stecko and Bendell-Young, 2000). Further water quality and macroinvertebrate samples were collected in October 2008 and March 2009 to

investigate the bioaccumulation of trace metals in early and late instar macroinvertebrates (**Table 4.1**). Further information on the type and location of each sample site is given in **Appendix 4.1**.

**Table 4.1:** *Samples collected and sampling occasions*

Date	Water column	Bed sediment	Macroinvertebrate	
			Surber	Kick
June 2007	Y	Y	Y	
October 2007	Y		Y	
March 2008	Y		Y	
October 2008	Y			Y
March 2009	Y			Y

Y = sampled

## 4.2 Selection of water and sediment quality parameters

Sampling parameters were selected based on the types of data required to enable the study objectives to be met. Mine water is a multi-factor contaminant. Therefore, the parameters selected for analysis in this study reflect those which are likely to be most impacted by metal mine drainage or will yield the most information on the character of this pollution.

Conductivity, pH and temperature are standard physico-chemical measurements used in many studies to broadly estimate the state of water quality (Gray, 2003). Temperature varies diurnally and seasonally and is an important variable influencing physical, chemical and biological processes in rivers; including the respiration and decomposition of plants and animals, and the volatilisation of substances in water (Walling and Webb, 1992; Chapman and Kimstach, 1996). Conductivity is the ability of water to conduct an electric current and measures the amount of dissolved solids in water (Bartram and Balance, 1996). It varies in river systems according to lithology, soil type, land use, topography and precipitation characteristics (Walling and Webb, 1975). As such, it is a good general descriptor of the chemical state of a river system. pH is a measure of the acid/base balance of a river system and influences many biological and chemical processes,

including metal solubility and uptake by aquatic organisms (Rowland and Grimshaw, 1989).

The heavy metals selected for analysis in this study were lead (Pb), zinc (Zn), copper (Cu), cadmium (Cd), iron (Fe) and manganese (Mn). These are the principal heavy metals associated with metal mine drainage in central Wales (Environment Agency, 2002). The major cations analysed include potassium (K), calcium (Ca), sodium (Na) and magnesium (Mg), which are amongst the most abundant elements in natural waters (Reeve, 1994). Calcium and magnesium are the major contributors to water hardness and are derived principally from the weathering of rocks containing calcium and ferro-magnesium minerals (Chapman and Kimstach, 1996; Holloway and Dahlgren, 2001). Permanent water hardness was calculated from calcium and magnesium concentrations using a standard equation (Lenntech, 2009):

$$(\text{CaCO}_3) = 2.5(\text{Ca}^{2+}) + 4.1(\text{Mg}^{2+})$$

Potassium is derived naturally from the weathering of rocks but may be elevated in rivers due to industrial and agricultural effluent. Sodium salts are highly soluble and abundant and are, therefore, present in high quantities in natural waters. Sodium in natural waters occurs principally from precipitation of sea salt and cattle salt supplements (Holloway and Dahlgren, 2001).

The major anions analysed were sulphate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), chloride ( $\text{Cl}^-$ ) and phosphate ( $\text{PO}_4^{3-}$ ). The major source of nitrate and phosphate (and potassium) is soil, and increased concentrations can be expected in areas of intensive agriculture. Sulphate measurements provide an indication of the sulphidic mineral content and acid-generating capacity of mine spoil and mine workings (Younger *et al.*, 2002). In upland Wales, sulphate concentrations are also reflective of rainfall chemistry (Neal, 1997). Chloride (and sodium) originates principally from oceanic aerosols and, in the absence of pollution, can be expected to reflect the concentration of chloride in precipitation (Walling and Webb, 1981). Total organic carbon (TOC) was also measured. TOC measures the total organic loading of

water which occurs in river systems from organic material or from industrial and agricultural effluents (Reeve, 1994). Heavy metals have a high affinity for organic material and so TOC is an important parameter when investigating heavy metal mobility.

### **4.3 Selection of hydrological variables**

River stage is the most commonly measured and useful hydrological parameter which, together with frequent velocity measurements, allows accurate discharge measurements to be made at low cost (Jones, 1997; Shaw, 2004). Discharge measurements provide an insight into river catchment processes, the origin of water quality variables, and allow the calculation of metal loads in rivers. The operation of hydrological equipment and derivation of stage discharge relationships are discussed in more detail in section 4.6.4.

### **4.4 Field sampling procedures**

All samples on the main river channel were collected moving upstream in order to minimise contamination of other sites by disturbance (Quevauviller, 2002). Major tributaries were sampled for water quality within 100 m of their confluence with the Afon Twymyn. Samples were taken far enough upstream (c. 50 m) to avoid sampling river water from the main channel. Water column samples and measurements were collected first, followed by sediment and, finally, macroinvertebrate samples.

#### **4.4.1 Collection of water column samples**

##### *Water column physico-chemistry measurements*

pH, temperature and conductivity were measured concurrent in the field with other sampling operations. Electrical conductivity was measured using a Hanna conductivity/TDS meter (HI198300). Temperature and pH were measured using a Hanna pH meter (HI98108). Both meters were calibrated in the laboratory prior to use using standard calibration solutions. The probes were submerged in flowing water until a constant reading was displayed. Triplicate measurements were taken and the mean recorded. All measurements were temperature-compensated.

#### *Samples for analysis of heavy metals and major cations*

Water samples for analysis of heavy metals (Pb, Zn, Cu, Cd, Fe, Mn) and major cations (Na, K, Ca, Mg) were collected in 125 ml polyethylene bottles. Facing upstream, the polyethylene bottle was rinsed with river water and then filled to the top with the sample. The inclusion of leaves and detritus was avoided where possible. The samples were labelled and transported to the laboratory in plastic cool boxes.

#### *Samples for analysis of major anions and total organic carbon*

Samples for anion ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ ) and TOC analysis were collected in 125 ml glass jars. The same procedure was used as for the collection of cation samples, however, in this case, the glass jar was wrapped in foil to limit microbial activity.

#### 4.4.2 Streambed sediment collection

To minimise potential contamination, a plastic trowel was used to collect sediment samples. Five random samples were taken from riffle locations (sediment supply permitting) to a depth of about 0.05 m below the river bed substrate (after removal of the armour layer) and homogenised to form a composite sample of approximately 2 kg. Samples were double-bagged in airtight polyethylene zip bags and labelled. The trowel was rinsed downstream to minimise contamination. The bags were transported to the laboratory in plastic cool boxes.

#### 4.4.3 Macroinvertebrate sample collection

Macroinvertebrate samples were collected at twenty-nine sites throughout the Afon Twymyn. Surber samples were taken at sites 1 to 29 using a 250  $\mu\text{m}$  mesh with a 0.09  $\text{m}^2$  frame. The Surber sampler allows quantitative analysis of macroinvertebrate communities and is frequently used in routine biological monitoring programmes throughout the UK (Armitage *et al.*, 1983; Extence *et al.*, 1987). Facing downstream, and holding the net opening at a right angle to the flow, five 30-second samples were taken from riffle locations to a depth of

approximately 0.05 m. A plastic trowel was used to disturb the river bed substrate. Larger rocks and woody debris within the sampling area were removed and carefully washed in front of the net. The samples were homogenised in the field after collection to form one composite sample.

## **4.5 Laboratory procedures**

### **4.5.1 Sampling and experimental containers**

All containers used to collect and store water samples were cleaned thoroughly in order to minimise contamination. Containers and equipment were immersed in 2% nitric acid, soaked for 48 hours and rinsed with deionised water prior to use (Quevauviller *et al.*, 1997). Polyethylene containers were used to collect and store samples for heavy metals and major cation analyses. Polyethylene bottles have a very low affinity for ion adsorption compared to glass surfaces and are, therefore, suitable for metal storage and analysis (Reeve, 1994). Glass containers were used for analysis of major anions and TOC. Glass containers are recommended as polyethylene bottles can be porous to the gaseous constituents of anions (Rowland and Grimshaw, 1989). Polyethylene containers were used in metal extractions (Beasley, 2001). Analytical grade acids were used in the present research for all extraction solutions and cleaning procedures to minimise contamination. Sediment and macroinvertebrate samples were stored in airtight polyethylene zip bags.

### **4.5.2 Water samples**

#### *Heavy metals and major cations*

In the laboratory, samples for dissolved metal and major cation analysis were filtered through a Whatman 0.45 µm cellulose membrane filter within 24 hours of collection. The dissolved form of the metal was selected for analysis as this is generally agreed to be the most toxic form (Gundersen and Stiennes, 2001). Additionally, filtration minimises storage problems and prevents blockage of sampler probes and tubing in analytical devices (Rowland and Grimshaw, 1989). After filtration, samples were acidified to pH 2 by adding concentrated nitric acid

(approximately 2 ml per 100 ml sample) in order to preserve the sample and prevent metal adsorption to the sample bottle (Fergusson, 1990; Quevauviller, 2002). Samples were then refrigerated at 4°C and analysed within 6 months (Bartram and Balance, 1996).

#### *Major anions and total organic carbon*

Samples for determination of anions and TOC were filtered using a Whatman 0.45 µm cellulose membrane filter and then refrigerated in darkness at 4°C. Samples were analysed within 48 hrs of collection.

#### 4.5.3 Sediment samples

Sediment samples were stored in darkness at 4°C before processing. The preparation of the sediment samples for extraction tests followed a standard procedure (British Standards Institution, 2006). Firstly, samples were oven-dried at 30°C for five days. To ensure that the samples had dried completely, they were laid out in a dust free laboratory for seven days. Once the sediment had dried, samples were then coned and quartered to select representative sub samples of 200 – 300g. These sub-samples were divided into two size fractions by sieving; <63 µm (clay and silt) and 64 - 2000 µm (fine sand). After sieving each fraction, the sieve was washed thoroughly in de-ionised water. Fractionated samples were then placed in polyethylene zip bags and labelled 'ready for extraction'. No preservative was added to bed sediment samples. Samples were stored in darkness at 4°C until extraction.

#### *Metal speciation*

Metal speciation is essential to assess geochemical phases and the mobility of potentially toxic elements in contaminated sediments (Tokalioglu *et al.*, 2003). Metals associated with river sediment originate either from anthropogenic sources or occur naturally within the crystal lattice of sediment (Beasley, 2001). Metals which occur in the crystal lattice of sediment are not bioavailable. However, metals which have been processed through anthropogenic activity are weakly



bound to sediments and can become bioavailable to aquatic organisms and accumulate in the food chain (Agemian and Chau, 1977). For this reason, sequential extraction techniques capable of producing metal concentrations for each geochemical phase are preferred in this study over total dissolution of the sediment achieved by single extractions.

Various extraction media have been used to extract metals from sediment, including electrolytes ( $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ), pH buffers of weak acids (acetic, oxalic acid), chelating agents (EDTA, DTPA), reducing agents ( $\text{NH}_2\text{OH}$ ), strong acids ( $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$ ,  $\text{HF}$ ) or basic reagents (Tokalioglu *et al.*, 2003). The primary method for extraction of metals in river sediments involves the use of strong acids. A number of doubts concerning the accuracy of selective chemical extraction schemes have been expressed (e.g. Rendell *et al.*, 1980). Particular concerns are whether the chemical extractant may attack phases other than those expected; and whether liberated metals may become associated with another sediment phase rather than staying in solution. The multitude of extraction techniques and media used can also lead to great variability in results and non-comparability between studies.

In this study, a sequential extraction procedure recommended by the Standards Measures and Testing Programme of the European Union (SM&T) was utilised. The SM&T 3-step extraction procedure evolved from that developed by Salomons and Forstner (1984) during interlaboratory trials initiated by the BCR (Community Bureau of Reference) in 1987, in an attempt to harmonise metal speciation by extraction (Rauret, 1998). The agreed 3-step sequential extraction procedure is used throughout EU member states and separates metals into three geochemical phases:

1. Exchangeable and bound to carbonates.
2. Reducible, bound to iron and manganese oxides.
3. Oxidisable, bound to organic and sulphide compounds.

The SM&T procedure is the only sequential extraction technique with a certified reference material (CRM 601) (Quevauviller *et al.*, 1997) for all three phases of extraction allowing validation of the procedure and comparison of results between studies (**Table 4.2**).

**Table 4.2:** Certified and indicative values for CRM 601 (mg/kg)

Metal	Step 1	Uncertainty	Step 2	Uncertainty	Step 3	Uncertainty
Pb	2.68 <sup>1</sup>	+/- 0.35	33.1 <sup>1</sup>	+/- 10	109 <sup>1</sup>	+/- 13
Zn	264.00 <sup>1</sup>	+/- 5.0	182.00 <sup>1</sup>	+/- 11	137 <sup>2</sup>	+/- 30
Cu	8.32 <sup>2</sup>	+/- 0.46	5.69 <sup>2</sup>	+/- 3.2	116 <sup>2</sup>	+/- 26
Cd	4.14 <sup>1</sup>	+/- 0.23	3.08 <sup>1</sup>	+/- 0.17	1.83 <sup>1</sup>	+/- 0.2

1 = certified value

2 = indicative value

This procedure was applied to the clay/silt (<63 µm) and the fine sand (64 - 2000 µm) fractions. Each batch of 14 samples included five of each size fraction, one duplicate of each fraction, a blank and the CRM. The three extraction steps are outlined in more detail in **Appendix 4.2**. The supernatant produced after extraction was acidified to pH 2 to prevent adsorption or precipitation of metals in storage. All solutions were analysed within a month using a Jarrell Ash ICP-AES.

#### 4.5.4 Macroinvertebrate samples

In the laboratory, macroinvertebrate samples were washed and passed through a 250 µm mesh to remove clay, silt and fine sand sediments and debris. The sieved samples were then placed in a white sorting tray and specimens were placed in Petri dishes for identification to species level (where possible) using identification keys. Identification to species level allows more information to be extracted about species-environment relationships.

Due to the multi-factor nature of metal mine pollution (Robb and Robinson, 1995), a range of diversity and biotic indices are used in this study to characterise the macroinvertebrate community of the Afon Twymyn. Diversity indices are used to

measure community response to stresses in an aquatic environment (Washington, 1984). They reflect three components of community structure, namely richness (number of species present), evenness (uniformity in the distribution of individuals among the species), and abundance (total number of organisms present) (Metcalf-Smith, 1996; Gray and Delaney, 2008). It is considered that the healthiest aquatic ecosystems have high diversity or richness, an even distribution of individuals among the species, and moderate to high counts of individuals. **Table 4.3** lists the advantages and disadvantages of diversity indices.

**Table 4.3:** *Advantages and disadvantages of diversity indices (from Metcalf-Smith, 1996)*

<b>Advantages</b>	<b>Disadvantages</b>
Strictly quantitative	Disregard environmental adaptations of species
Independent of sample size	Some undisturbed environments have low diversity (e.g. streams fed by nutrient-poor groundwater)
No assumptions of tolerances of individual species	May generate 'false negatives' (e.g. moderate pollution may cause an increase in abundance without a decrease in diversity)
	Less useful in complex systems with multiple stresses

Diversity metrics are categorised as either dominance or information statistic indices (Gray and Delaney, 2008). Dominance indices are weighted towards abundance of the commonest species. Berger-Parker dominance ( $d$ ) (Berger and Parker, 1970) considers the number of species and distribution of density among them. It is the total number of individuals of all species divided by the number of individuals of the most common species. The most widely used information statistic (diversity index) is the Shannon-Wiener (or Weaver) index ( $H'$ ) (Shannon, 1948). Values of  $H'$  usually fall between 1.5 and 3.5, with lower values characteristic of polluted conditions. This index is independent of sample size and assumes that all samples have been randomly sampled. Its usefulness in areas impacted by mine drainage has been highlighted by Routledge (1979) and

Keylock (2005). Both the Shannon-Weiner diversity index and the Berger-Parker dominance index are calculated in this study.

Diversity indices do not consider which species inhabit a stream or their particular tolerance to pollution (Washington, 1984). However, biotic indices take account of the physiological response or individual sensitivity/tolerance of organisms to pollution and assigns them a value, the sum of which gives an index of pollution for a site (Mason, 2002). Most biotic indices are only suitable for the area within which they have been developed (Armitage *et al.*, 1983). In England and Wales, the Environment Agency uses the Biological Monitoring Working Party (BMWP) (Biological Monitoring Working Party, 1978) score which describes taxon richness and sensitivity to pollution (Armitage *et al.*, 1983). Identification of taxa is to family level only, families with similar pollution tolerances are grouped together and no account is taken of abundance (Metcalf-Smith, 1996). Taxa are awarded a score between 1 and 10, with the most sensitive species, for example mayflies and stoneflies, being awarded higher scores. The values are then summed to give the BMWP. Values greater than 100 are associated with very clean rivers and values less than 10 are considered severely polluted (Mason, 2002). However, due to effects of seasonality and sampling variation (high BMWP scores may occur where large numbers of families from the lower scoring taxa groups are found at a particular station), it is considered more reliable to use the Average Score Per Taxon (ASPT) (Walley and Hawkes, 1997). ASPT is calculated by dividing the BMWP value by the number of scoring taxa and provides a single score out of 10 (Gray and Delaney, 2008). The BMWP and ASPT scoring systems have been developed primarily to measure organic pollution impacts, and so, are generally not applicable to sites where metal or acidic pollution is present (Gray, 2003). However, these biotic scores have had some success in the assessment of acid mine drainage (Armitage, 1980; Nelson and Roline, 1996; Gray and Delaney, 2008), and are, therefore, considered in this study.

The Acid Waters Indicator Community Index (AWIC) (Davy-Bowker *et al.*, 2005) has been developed to detect the impacts of acidification by the indicative loss of acid sensitive families. It is based on the same taxa as BMWP, but values are

obtained from constrained ordination along an acid-base gradient (Ormerod *et al.*, 2006). Species are scored from one to six, taxa with a score of six being most sensitive to acidity. The AWIC score is the mean score of all the taxa present in a sample. Acidity is a principal component of most mine discharges and, therefore, the AWIC scoring system is also considered in this study.

The final biotic index used in this study is percent EPT taxa (Lenat, 1988). This is simply a measure of the percentage abundance of three generally sensitive macroinvertebrate orders, namely Ephemeroptera, Plecoptera and Trichoptera. Measurements of EPT taxa have been reported to elucidate the effects of acid mine drainage (Garcia-Criado *et al.*, 1999; Malmqvist and Hoffsen, 1999).

All calculations, except AWIC, were made using the Species Diversity and Richness software (Version 2) (Henderson and Seaby, 1998). The AWIC index was calculated using the published equation of the authors (Davy-Bowker *et al.*, 2005).

### *Heavy metal bioaccumulation in macroinvertebrates*

Metal accumulation in macroinvertebrates can be used as an indirect tool to determine environmental degradation of aquatic systems (Sola and Prat, 2006). The tissue metal content of three macroinvertebrate species (*Hydropsyche siltani*, *Baetis rhodani*, *Leuctra hippopus*) are analysed in this study to assess metal bioaccumulation in these species, and to infer the impact of metal pollution on the aquatic ecosystem as a whole. These species were selected so as to represent different feeding groups and contaminant exposure routes. *H. siltalai* is an omnivore filterer, feeding on detritus and living organisms in the water column. *B. rhodani* and *L. hippopus* are algal scrapers, feeding on algae and biofilm on river bed sediments. These organisms are also known for their ability to tolerate significant variations of water quality (Kiffney and Clements, 2003; Sola and Prat, 2006), and so it is possible that they can be used as bioindicators in even the most contaminated rivers.

Macroinvertebrate samples were collected in October 2008 and March 2009 at sites 3, 8, 12, 16, 18 and 21 (**Figure 4.1**). Samples were collected in two seasons to evaluate metal accumulation in two life stages of macroinvertebrates, namely early instar and late instar. A kick sampler (250 µm mesh) was used to collect 20 – 30 individuals from each species at each site. Samples were sorted in the field. The species of interest were collected using a pipette and placed in wide mouth 1L polyethylene bottles filled with river water. Physico-chemical measurements (pH, conductivity, temperature) and water samples for heavy metals (Pb, Zn) analysis were taken at each site.

In the laboratory, samples were transferred to a beaker with distilled water. The larvae were starved for 48 hrs to allow gut contents to clear, as only metals accumulated in tissues are in a bioavailable form and can affect organisms (Sola and Prat, 2006). After starvation, excess water was removed from specimens by placing them on filter paper for 1 minute. The wet weight of specimens was recorded to the nearest 0.001 mg. Samples were then oven-dried at 60°C for 24 hours and the dry weight was recorded.

The digestion process followed the method of Martinez *et al.* (2003). Samples were placed in 50 ml polyethylene beakers and digested under a hood in 5 ml concentrated nitric acid (70%). The samples were heated to 50°C on a hot plate and this temperature was maintained for 4 hours. Hydrogen peroxide was added if the sample was not fully digested after this time. Once the sample had cooled, it was filtered through a 0.45 µm cellulose nitrate paper and diluted with deionised water to 50 ml. Samples were analysed by ICP-AES as soon as possible after digestion. Blanks and reference materials were used in the analyses.

#### 4.5.5 Methods of analysis

##### *ICP-AES*

Atomic emission spectroscopy (AES) using inductively coupled plasma (ICP) was used to analyse all water and digested sediment and macroinvertebrate samples. Analyses were carried out on a Thermo Jarrell Ash AtomScan 16 ICP-AES. ICP-AES uses a plasma flame to excite atoms within a sample. ICP-AES was chosen over other popular analytical methods (e.g. Atomic Absorption Spectroscopy; Anodic Stripping Voltammetry) in the present research given its many advantages (Reeve, 1994), including:

- Shorter operational time over AAS.
- Multi-element analysis.
- Chemical bonds cannot survive in the ICP.
- Background signal from plasma is comparatively low, ensuring good detection limits.

##### *Ion Chromatography*

Major anions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ ) were measured on a Metrohm 792 ion chromatograph within 48 hours of sample collection. Ion Chromatography offers many advantages over other anion analysis techniques (Rowland and Grimshaw, 1989), including:

- Multi-ion analysis.
- High sample throughput.
- Ease of automation.
- Less interference.
- Low detection limits.

The technique pumps the sample through a separation column containing specific eluents (separation agents) where ions compete for exchange sites and are separated into discrete bands. Different ions have different retention times in the exchange column and this allows them to be identified (Metrohm, 2004).

#### *Total Organic Carbon*

A Shimadzu TOC analyser was used to analyse water samples for total organic carbon. The process oxidises the organic matter of a sample to carbon dioxide. The gas is then cooled and dehydrated in an electronic dehumidifier and analysed by an infrared gas analyser. The area of the peak concentration is then compared to a calibration curve produced from a standard solution (Shimadzu, 2001).

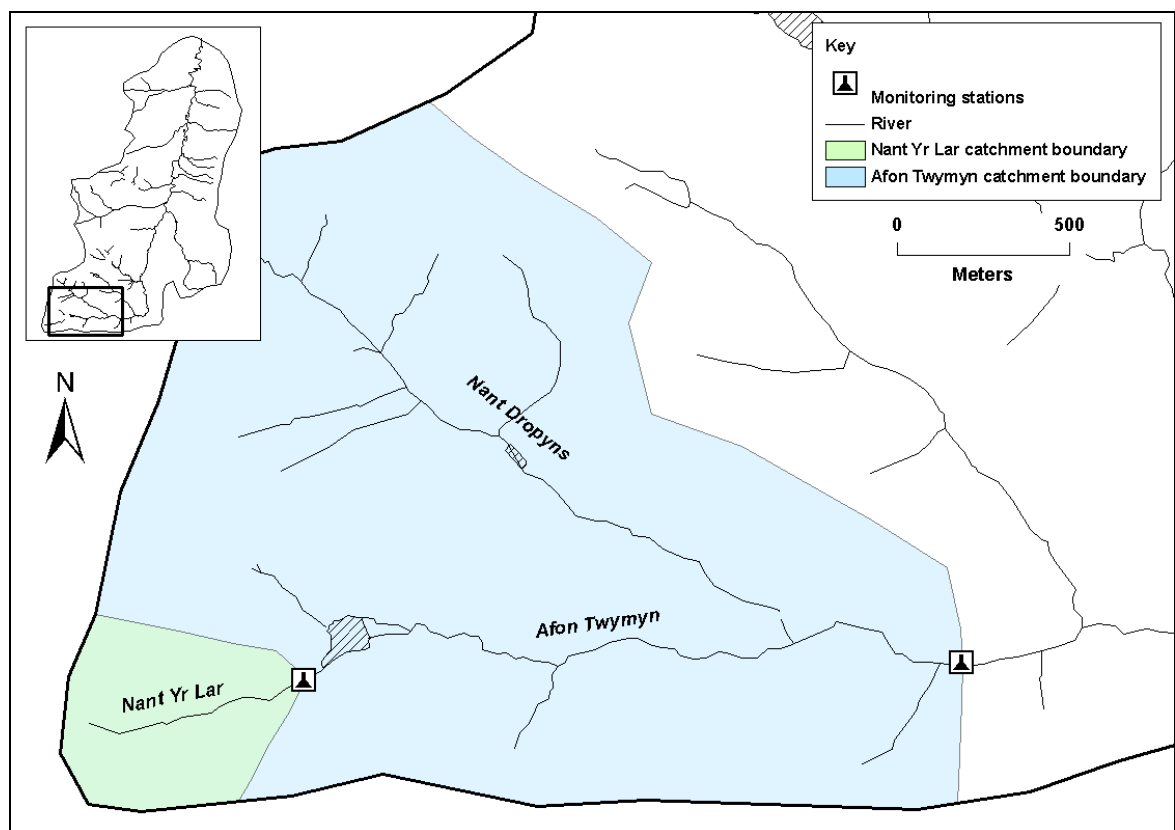
### **4.6 Experimental monitoring stations**

Permanent water sampling and monitoring stations were installed upstream of (SN 8467 9384) and at (SN 8658 9389) Dylife mine in October 2007 in order to investigate heavy metal fluxes and river hydrochemistry during rain-fed flood events (**Figure 4.2**). The control site 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<sup>2</sup>. The mine site monitoring station was located on the Afon Twymyn, just downstream of the main spoil tips area at Dylife, with a catchment area upstream of this point of 3.6 km<sup>2</sup>. Each monitoring station incorporated equipment to measure river stage, pH, temperature and conductivity. In addition, automatic water samplers were used to collect water samples during flood events. Four 12V 17 Amp lead-acid batteries were used to power the equipment.



#### 4.6.1 Station housing

Each station housing (97 x 60 x 50 cm) was constructed of marine plywood (**Figure 4.3**). The housing was bolted to, and supported by, four mild steel stakes driven approximately 30 cm into the ground. A corrugated plastic sheet was secured to the top of the housing to protect it from rainfall. Cables and tubes for the measurement probes and water intake were routed out of the housing through a small 5 cm diameter hole near the base of the structure. Outside of the housing, the cables and tubing were encased in black plastic piping 5 cm in diameter and routed to the river bed. The probes and water intake were secured together inside a mild steel cylinder (**Figure 4.4**), approximately 13 cm in diameter, which was secured to the bed of the river by iron road pins driven through the cylinder and into the bedrock.



**Figure 4.2:** Location of water sampling and monitoring stations in the Afon Twymyn catchment



**Plate 4.1:** Monitoring station at Dylife mine



**Plate 4.2:** Protective probe casing and sample actuator (mine station)

#### 4.6.2 Automatic water samplers

The dissolved heavy metal content of river water during flood events was sampled using ISCO 6712 automatic water samplers with SDI-12 data loggers and 1540 liquid level sample actuators (**Figure 4.5**). The ISCO sampler was programmed to respond to a signal from a sample actuator which was fixed above the water level. The sample actuator was secured next to the stream bank in a mild steel cylinder (5 cm diameter) driven vertically into the bedrock. Holes were drilled into the cylinder to allow the actuator to be raised or lowered in response to changing baseflow conditions, in order to sample quick-return flow. Rising water completes the circuit in the actuator and begins a user-defined sampling programme. The sampler can be programmed to take 24 water samples over any time period. Sample bottles were washed in 2% nitric acid and rinsed with distilled water before use. Upon activation, 500 ml water samples were pumped through a 10 m vinyl sampling tube at the specified intervals. Before and after taking a sample, the equipment was automatically purged with river water to avoid cross-contamination. Samples were taken over periods from 12 to 36 hours depending on weather patterns. In some cases, samples were collected two to three weeks after a sampling programme had been initiated. It is accepted that metal adsorption and precipitation could occur within the sample bottle during this time resulting in inaccurate metal concentrations. However, acidification of the sample in the laboratory should result in desorption and dissolution of any sorbed or precipitated metals.

#### 4.6.3 Water chemistry

A YSI 600 multi-parameter Sonde was used to record conductivity, pH and temperature at 15 minute intervals at each site. This information was logged on the SDI-12 data logger connected to the ISCO sampler and downloaded on site visits. All measurements were temperature-compensated to 25°C. Conductivity and pH probes were regularly calibrated using appropriate solutions and verified using hand held probes.





**Plate 4.3:** ISCO 6712 water sampler (mine station)

#### 4.6.4 River stage and discharge

Stage was measured at each monitoring station using a Druck 175 mb pressure transducer. The pressure transducer works on the principal that the hydrostatic pressure at any given point in the water column is proportional to the height of water above that point (Shaw, 2004). The pressure transducer converts changes in water pressure to electrical signals (volts). Pressure transducers for both monitoring sites were calibrated in the laboratory before being installed in the field. Voltage readings were converted to stage values by using a calibration equation. The pressure transducers were programmed to sample water depth every minute and log an average of this value at 15 minute intervals. The data was logged on a Grant Squirrel 2020 data logger.

The velocity-area method using a current meter is the principal method for direct discharge measurement (Shaw, 2004). Discharge was calculated as:

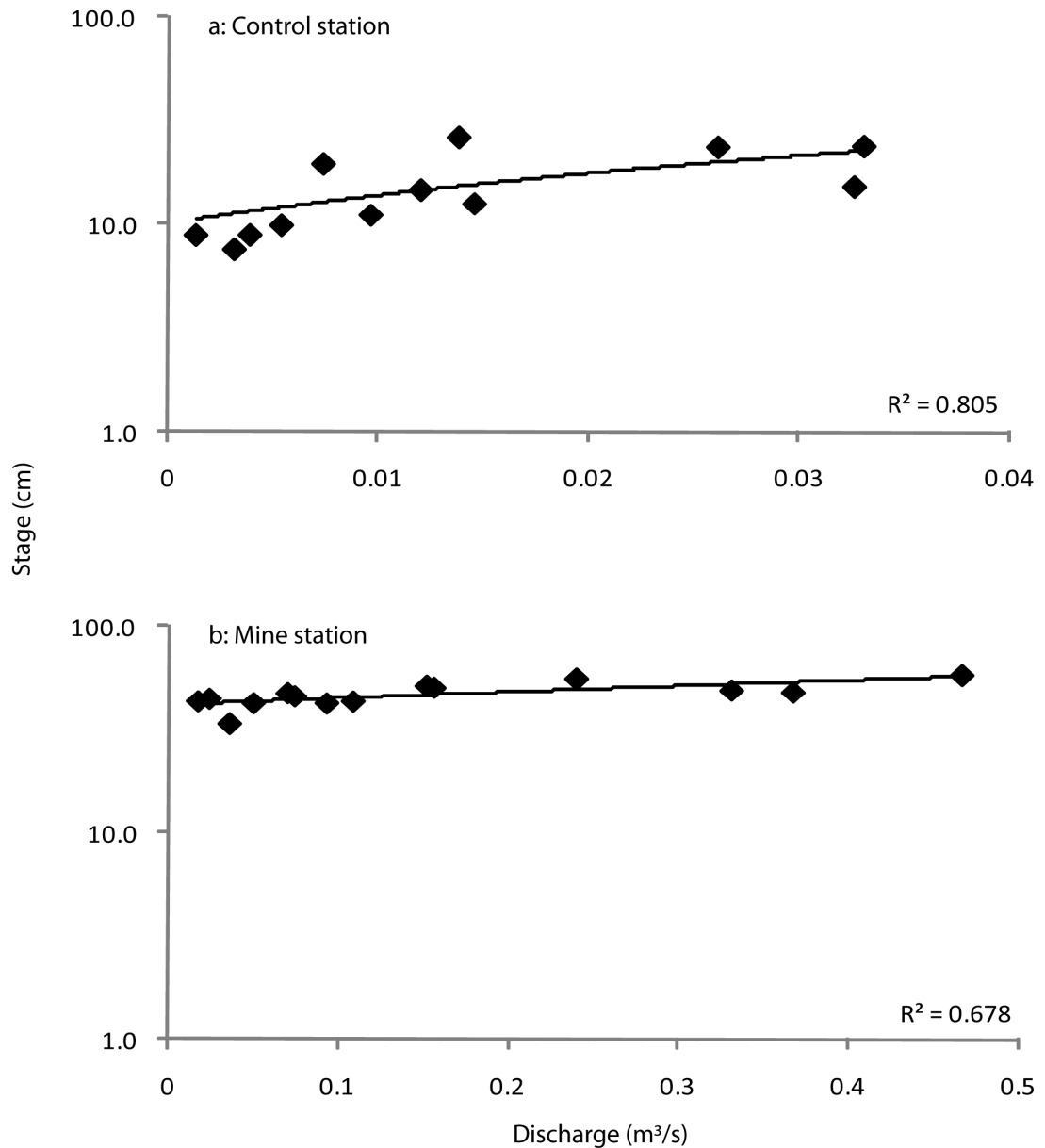
$$Q = VA$$

where  $Q$  is the discharge ( $\text{m}^3/\text{s}$ ),  $V$  the velocity ( $\text{m/s}$ ) and  $A$  the wetted area ( $\text{m}^2$ ). Discharge was measured on site throughout the monitoring period using a Valeport Model 801 electromagnetic current meter. The current meter was calibrated prior to each field visit. Meter readings were taken in the stream adjacent to both monitoring stations from a straight reach with relatively uniform slope and velocity. Where necessary, rocks were removed from the channel to make conditions more uniform and eliminate backwater areas.

The mid-section method of discharge measurement was used. Vertical measurements of flow velocity were taken from the mid-point of 5 – 10 segments across the channel depending on the channel width. Velocity was measured at 0.6 of the depth from the water surface. The meter was allowed to stabilise over 60 seconds before recording an average reading. A measure of river stage at the time of discharge measurement was taken from the pressure transducer and verified using a stage ruler. A stage-discharge curve was produced for each monitoring station from the stage and discharge data (**Figure 4.6**). A rating equation was fitted to each curve of the form:

$$Q = a(h - z)^b$$

where  $Q$  is the discharge ( $\text{m}^3/\text{s}$ ),  $h$  is stage (m),  $z$  is stage at zero flow (m) and  $a$  and  $b$  are coefficients. The equation of the stage-discharge curve was used to transform the 15 minute continuous pressure transducer stage data to river discharge values at both monitoring sites. The equations for the control and downstream sites were  $Q = 0.00004(h-z)^{2.062}$  and  $Q = 0.0000000004(h-z)^{5.032}$ , respectively.



**Figure 4.3:** Stage discharge relationships at a) control station and b) mine station

#### 4.6.5 Precipitation

Precipitation data was provided by the Environment Agency Wales tipping bucket rain gauge at Dolydd (297 mAOD, SN 873905). Rainfall at this gauge is recorded every 15 minutes. The tipping bucket is set to 0.2 mm. One of the principal problems associated with the measurement of precipitation is that rainfall over an area can only be sampled at a single point (Shaw, 2004). When many rain gauges

are present in a river catchment, this point data can be converted to areal data using Thiessen Polygons or other space-averaging methods. The accuracy of the data will depend on the distance between sample points and also on variations in topography which might influence local rainfall patterns. Dolydd rain gauge was selected due to its proximity to the two monitoring stations in the upper Twymyn catchment. The rain gauge is located approximately 3.8 km south-south-east of Dylife. It is situated at an altitude of 297 mAOD which falls within the elevation range of the upper Twymyn catchment (250 – 500 mAOD). Generally, frontal rainfall in the UK falls over several tens of square kilometres and inter-correlations between stations at 10 km distance are good (Arnell, 2002). More likely in upland central Wales, due to the dominance of orographic cooling, are short-lived, localised higher intensity cells of rainfall over two to three square kilometres (Austin and Houze, 1972). Some degree of uncertainty between rainfall recorded at Dolydd and what actually fell on the upper Twymyn catchment is expected. As a result, the Afon Twymyn may have received a larger or smaller amount of rainfall than indicated by the rain gauge at Dolydd.

#### 4.6.6 Dissolved metal load calculations

In Chapters 6 and 7, daily and annual (2008), and storm event metal loads are calculated, respectively. Metal fluxes (g/s) were calculated by multiplying the discharge (l/s) at each monitoring site by the instantaneous metal concentration ( $\mu\text{g/l}$ ). This was extrapolated to hourly metal fluxes (g/hr) by multiplying by 3600 (seconds per hour). Daily and total storm metal loads (kg/day) were calculated by multiplying this figure by 24 (hours per day) or the length of the storm in hours.

### 4.7 Statistical methods

#### 4.7.1 Kruskal-Wallis tests

Kruskal-Wallis tests and bivariate correlation techniques are used to test for significant differences in water, sediment and macroinvertebrate data. Calculations were performed using the program SPSS 16.0. Data for analysis of variance (ANOVA) were tested for normality prior to analysis using the Kolmogorov-Smirnov test. These investigations revealed the majority of variables

were not normally distributed. Several transformations were attempted, however, in all cases, these failed to normalise the data. Additionally, Levene's Tests revealed the data had unequal variances in the majority of cases. Therefore, the non-parametric Kruskal-Wallis one-way analysis of variance test was applied to sediment, water and macroinvertebrate data. Where significant differences occurred, post-hoc tests (multiple Mann Whitney U tests) were used to see where the differences lie. In all cases, a Bonferroni adjustment was performed.

In Chapter 6, the main effects investigated for heavy metals in the water column are sample location (four levels – control, mine, downstream and tributaries) and season (three levels – March, June and October). For heavy metals in sediment, the main effects are sample location (three levels – control, mine and downstream), sediment size fraction (two levels -  $<63\mu\text{m}$  and  $64 - 2000\mu\text{m}$ ) and sequential extract {three levels – exchangeable/carbonate (extract 1), Fe/Mn oxide (extract 2) and sulphide/organic (extract 3)}. In Chapter 8, the main effects investigated are sample location (three levels – control, mine and downstream sites) and season (three levels – March, June, October).

Where bivariate correlation is used to investigate the association between variables, the data is tested for normality prior to analyses. Product-Moment (Pearson) correlation is used when the data are normally distributed. Spearman Rank correlation are used when the data is not normally distributed.

#### 4.7.2 Ordination

Ordination is used in Chapter 8 to investigate macroinvertebrate species-environment relations. The technique condenses a large number of variables into a lower number of indices while still retaining the original meaning of the data set (Randerson, 1993). As such, ordination can provide insights into the structure of biological communities and into the impact on them of natural and anthropogenic disturbances (Beasley, 2001). Ordination analysis was performed using the program CANOCO 4.5 (ter Braak and Smilauer, 2002). This program contains four main classes of ordination method within which there are three possible



response models: a linear model, a unimodal model, and a unimodal model with detrending. There are three main steps to ordination analysis.

#### *Type of analysis and method specification*

The first step in setting up an ordination project is to select the correct data and ordination method (ter Braak and Smilauer, 2002). All datasets were first converted into a CANOCO 4.5 format using the utility program Canolmp. Two ordination methods are used in this study.

*Detrended Correspondence Analysis (DCA)* (Hill and Gauch, 1980) is used to investigate the macroinvertebrate data and identify relationships between species/families and sites. DCA is a method of eigenanalysis-based indirect gradient analysis which was developed to overcome two major problems inherent in some other ordination techniques (PCA, CA), namely the arch effect and compression of the ends of the gradient (Hill and Gauch, 1980). The arch effect is caused by monotonic species distributions (i.e. species which either increase or decrease, but not both, as a function of environmental factors) in which the second axis is a distorted or arched function of the first axis. However, macroinvertebrates show maximum abundances around optimal or unimodal conditions, exhibiting a Gaussian response to environmental gradients (ter Braak and Smilauer, 2002). DCA performs best for species which have unimodal response curves (i.e. species have one optimal environmental condition). Compression at the ends of the gradient means that the spacing of samples (and species) along the first axis is not necessarily related to the amount of change along the primary gradient. DCA corrects these problems by adding detrending (which removes the arch effect) and rescaling (which ensures that distance or space in the ordination diagram is constant).

*Canonical Correspondence Analysis (CCA)* (ter Braak and Prentice, 1988) is used to examine the influence of environmental gradients on the macroinvertebrate data. The Gaussian response of macroinvertebrates to environmental gradients selects the unimodal response model. Direct gradient analysis was preferred over indirect gradient analysis as it allows integrated analysis of species and

environmental variables and it shows those patterns in the species data that can be explained by the available measured environmental variables (Gower *et al.*, 1994; Beasley, 2001). The combination of a unimodal response model with direct gradient analysis automatically dictates the use of CCA. CCA builds on the method of weighted averaging of indicator species by performing weighted averaging to the simultaneous analysis of many species and many environmental variables, and by incorporating regression and correlation within the ordination analysis (ter Braak and Verdonschot, 1995). Correlations between species scores and sample scores are maximised and sample scores are constrained to be linear combinations of explanatory variables (ter Braak and Smilauer, 2002).

For both models, species abundances were log transformed to prevent outliers from unduly influencing the ordination. Down weighting of rare species was also attempted, however, this did not significantly alter their influence. Therefore, all species with an abundance less than or equal to 4 were removed from the final analyses.

#### *Plotting results – ordination diagrams (biplots)*

Results of the analyses using the top ranking environmental variables were plotted as ordination diagrams using the program CanoDraw 4.13. Modifications to the ordination diagrams in terms of clarity improvement were made using the program Adobe Illustrator 13. Information on the interpretation of biplots is provided in section 8.2.2.

#### *Ranking of environmental variables and species tolerances*

CCA analyses are completed by removing variables with high inflation factors, which permits the ranking of environmental variables in the order of their importance for determining the species data. In automatic selection, the K best variables are selected sequentially on the basis of maximum extra fit. The statistical significance of each selected variable is judged by a Monte Carlo permutation test (999 permutations) (Randerson, 1993).

#### **4.8 Chapter summary**

This chapter has outlined the field, laboratory and statistical techniques and equipment used in this study to investigate the impact of Dylife mine on the Afon Twymyn. A detailed description of the experimental monitoring stations has been provided. The following chapters will present the results obtained from the field and laboratory studies.

## 5. Evaluation of Precipitation and Discharge Patterns in the Afon Twymyn

### 5.0 Introduction

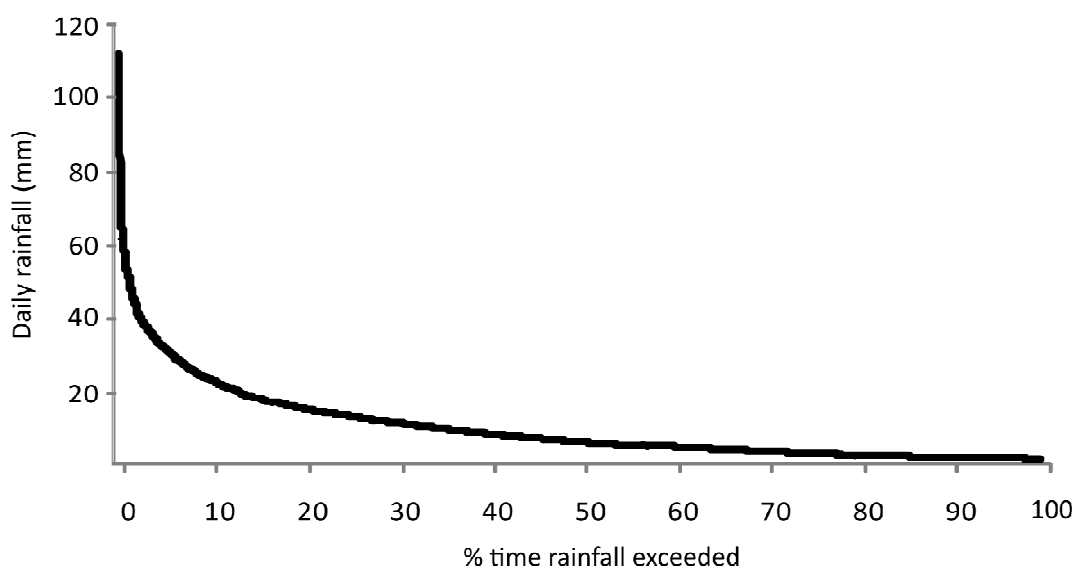
The aims of this chapter are to analyse and evaluate long-term precipitation and discharge patterns (c. 30 years) in the Afon Twymyn catchment and to compare them to the patterns observed during the present study period (2008). The purpose is to set the meteorological and hydrological context for the evaluation of succeeding results chapters.

It must be stressed that relatively short datasets commencing in the last 30-40 years can provide only limited insight into past meteorological and hydrological trends. The UK climate is naturally very variable, with flood-rich and flood-poor periods, and annual rainfall and runoff patterns for England and Wales do not generally exhibit a long-term trend (Jones *et al.*, 2006; Marsh *et al.*, 2007). Over the last 30 years, there have been increases in winter rainfall totals for England and Wales over previous averages, and decreases in summer rainfalls (Wilby *et al.*, 2008). However, during the 19<sup>th</sup> century, summer rainfall generally exceeded winter rainfall, and clusters of drier winters were common (Marsh *et al.*, 2007).

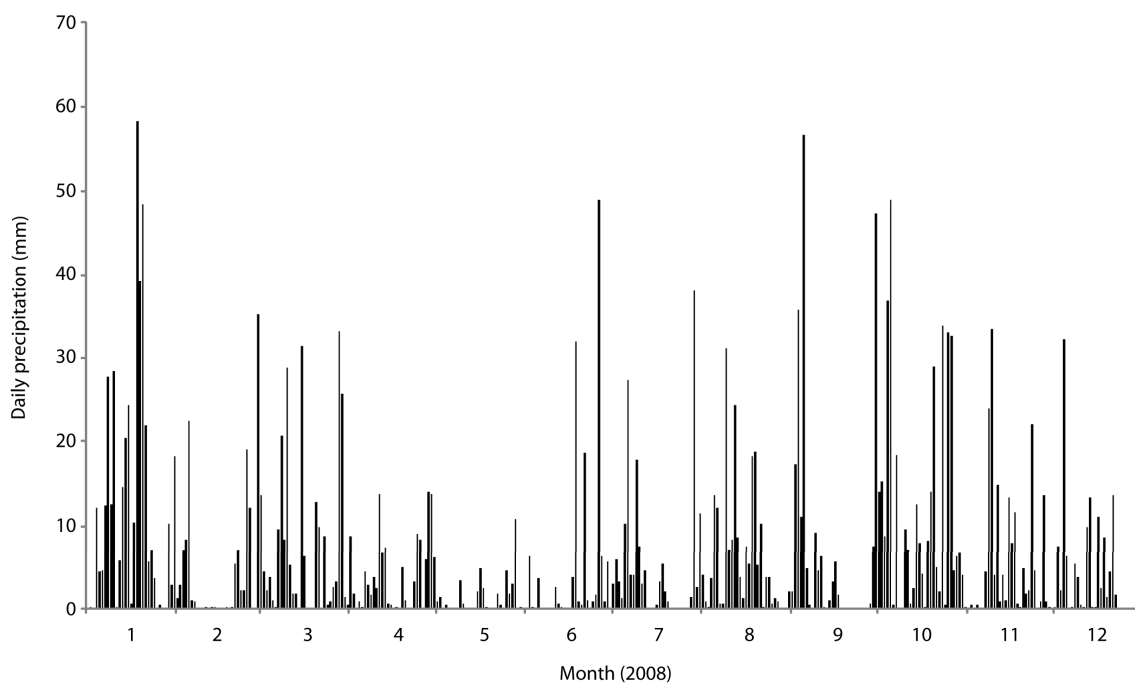
### 5.1 Precipitation

Long-term (1979-2008) precipitation data for the Afon Twymyn catchment were obtained from the Environment Agency rain gauge at Dolydd, approximately 3.8 km south-south-east of Dylife. The rainfall frequency pattern at Dolydd over the 29-year record indicates the dominance of lower-intensity orographically enhanced frontal rainfall (**Figure 5.1**). Precipitation intensity is typically below 1 mm/hr occurring 95% of the time. Over the study period, daily rainfalls in excess of 30 mm and 50 mm occurred 4% and 0.6% of the time, respectively. Daily rainfall over 100 mm occurred on two occasions (22/02/1991 and 26/12/1994). Daily precipitation (**Figure 5.2**) at Dolydd over the present study period exceeded

30 mm/day 5.5% of the time and rainfalls exceeding 50 mm/day occurred on two occasions (18/01 and 05/09).



**Figure 5.1:** Relative frequency of daily rainfalls at Dolydd (1979-2008)



**Figure 5.2:** Daily precipitation values at Dolydd (2008)

Monthly precipitation data from the study period are tabulated in **Table 5.1** and compared with the long-term averages. The pattern of precipitation in 2008 was not representative of a typical (1979 – 2008) year for the region. 2008 was the sixth wettest year of the record at Dolydd, with a total annual precipitation of 2291 mm compared to the 29-year mean of 2010 mm per annum. Typically, a seasonal precipitation pattern dominates with nearly 50% of the annual total falling in the four months of October to January. This general pattern was evident in 2008, although some monthly totals (e.g. January, October) were significantly higher than the average. Summer precipitation (May-Sept) in 2008 was greater than the long-term mean. High summer values were recorded in August which experienced greater rainfall than February, November and December. Precipitation in May 2008 was notably lower than the long-term mean (92 mm). In most months of 2008, the number of days with rainfall was greater than the mean based on the long-term record. Most notably, August 2008 had 28 days with rainfall compared to the long-term mean for this month of 17 days.

**Table 5.1:** *Monthly rainfall totals and number of days per month with rainfall at Dolydd (2008) compared with mean values from the long-term record (1979 – 2008)*

Month	Total rainfall (mm)	Mean rainfall (mm)	Number of days with rainfall	Mean number of days with rainfall
	2008	1979 - 2008	2008	1979 - 2008
January	395	218	25	21
February	128	172	19	18
March	238	168	26	20
April	122	101	30	27
May	39	92	15	15
June	134	101	16	16
July	157	95	21	15
August	198	122	28	17
September	215	137	18	17
October	367	227	29	21
November	172	189	24	20
December	125	228	21	20
Nov-Apr (winter)	1181	1076		
May-Oct (summer)	1110	774		

## 5.2 Discharge

### 5.2.1 Derivation of stage-discharge curves

Discharge data derived from stage-discharge rating curves are necessarily less certain than data from channel structures as a river channel can change its shape over time and from storm to storm, thus changing the relationship between stage and discharge (Hersch, 1995). Measurements of high flows are usually absent from stage-discharge curves due to the difficulty of measuring them. As a result, to obtain discharge values for high flows, it is often necessary to extrapolate the rating curve beyond the range of the maximum measured flow, and this can be a source of considerable error in the stage-discharge relation (Beven, 2000). The maximum 15 minute flows estimated for the Nant Yr Lar ( $0.065 \text{ m}^3/\text{s}$ ) and Afon Twymyn ( $0.926 \text{ m}^3/\text{s}$ ) monitoring stations during the study period were roughly

twice the measured maximum flows used to construct the stage-discharge relationships. Therefore, these extrapolated extreme values are less reliable than those which fall in the range covered by the stage-discharge curves, especially since the extreme flows are overbank (Shaw, 2004). Overbank flow was likely to occur on occasion at the control station, where the channel is narrow, shallow and constrained (c. 0.8m x 0.3m). As a result, such flows will be significantly underestimated. However, the uniform shape of the channel means that predicted values for channel flow are likely to be more accurate ( $r^2 = 0.805$ ,  $\alpha = <0.01$ ). At the control station, the river channel was relatively stable throughout the study period. However, re-working of the channel bed occurred frequently at the mine station. The channel cross-section at the mine station is irregular, wide and shallow (c. 4m x 0.3m), with no distinct banks. Therefore, a weaker relationship between stage and discharge ( $r^2 = 0.678$ ,  $\alpha = <0.01$ ) was observed at this site and greater errors are expected in the stage-discharge relationship.

#### 5.2.2 Derivation of long-term discharge records

In the absence of long-term discharge records for the Afon Twymyn, long-term (1973 – 2008) records from the nearby Afon Gwy (SN 824 853) are used as a surrogate of long-term daily mean flows in the Nant Yr Lar and Afon Twymyn. Discharge in the Afon Gwy catchment has been measured since 1973 as part of long running hydrological and hydrochemical studies in the Plynlimon catchments by the Centre for Ecology and Hydrology (Kirkby *et al.*, 1991). The Afon Gwy catchment was chosen as a surrogate due to its close proximity to the Afon Twymyn (approximately 10.5 km between discharge measurement points) and because it is geographically and hydrologically very similar to the Afon Twymyn catchment (above Dylife mine) (Brandt *et al.*, 2004). The two catchments share similar geology, soil type, land cover and land use. The altitude range of the Afon Gwy catchment is greater than that of the Afon Twymyn and this is reflected in the greater mean slope (**Table 5.2**).



**Table 5.2:** Similarities between physical features of the Afon Gwy and Afon Twymyn catchments

Catchment characteristics	Gwy	Afon Twymyn
Catchment area (km <sup>2</sup> )	3.9	3.6
Geology	Lower Palaeozoic slates, mudstones and sandstones, generally classified as impervious	
Soil type	Widespread accumulation of peats and peaty soils, limited boulder clay	
Land cover/use	Principally semi-natural grassland with small scale pastoral farming	
Altitude range (mAOD)	380 – 700	349 – 537
Level of station (mAOD)	405	420 (control station) 351 (mine station)
Mean slope (°)	15.6	9.6

Analysis of daily flow patterns in 2008 for the Afon Gwy and Afon Twymyn revealed total annual flow in the Afon Gwy exceeded that in the Afon Twymyn by approximately 30%. Given the similar catchment characteristics, flow volumes in the two catchments would be expected to be reasonably similar. Much of the observed differences will be related to the greater precipitation and relief in the Afon Gwy. At the time of writing, no precipitation data were available for 2008 for the Afon Gwy, however, the long-term average (2499 mm from 1972 – 2004) (Marc and Robinson, 2007) is 20% greater than that at Dolydd (2010 mm from 1979 – 2008). There is also some debate over the delineation of the Afon Gwy catchment related to flat areas of the lower valley which are distributed evenly between interfluvial areas and valley bottoms (Kirkby *et al.*, 1991; Hudson *et al.*, 1997; Marc and Robinson, 2007). It is thought that the lower Afon Gwy catchment might extend further east and west into the Iago and Cyff catchments, respectively. However, probably the greatest potential source of error will be in the stage-discharge relationships, especially during overbank flow.

Regardless of the differences in flow volumes between the two catchments, there exist good correlations between daily discharge in 2008 in the Afon Gwy/Afon

Twymyn ( $r = 0.727$ ,  $\alpha = <0.01$ ) and in the Afon Gwy/Nant Yr Lar ( $r = 0.734$ ,  $\alpha = <0.01$ ). Unexplained variance in the data most likely derives from differences in incidence and amount of rainfall, catchment geomorphology and soils, snow-melt, and errors in the stage-discharge relations. However, the correlations between datasets are good enough to give confidence in the use of the Afon Gwy as a surrogate for long-term discharge patterns in the Afon Twymyn.

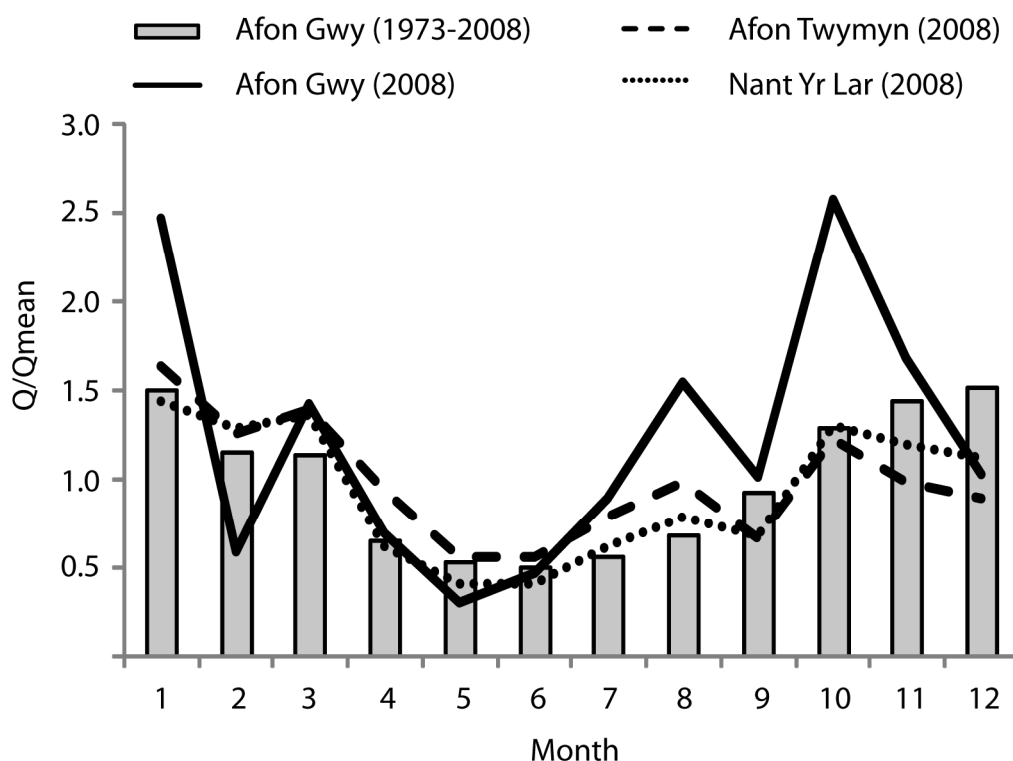
Discharge records from the present study (2008) and the historical Afon Gwy dataset (1973 – 2008) were evaluated and checked for missing records and erroneous readings. Some short gaps in the 2008 data (e.g. 2 – 3 hrs during maintenance and data download) were filled by interpolation.

### 5.2.3 Catchment response

Long-term discharge data for the Afon Gwy are used in this section to set the context for the hydrological behaviour of the Nant Yr Lar and Afon Twymyn in 2008. Discharge data are non-dimensionalised ( $Q/Q_{\text{mean}}$ ) for ease of comparison between catchments. Summaries of actual discharge data (2008) for the Afon Gwy, Nant Yr Lar and Afon Twymyn are provided in **Appendices 5.1, 5.2 and 5.3**. These data are represented graphically in **Figure 5.4**.

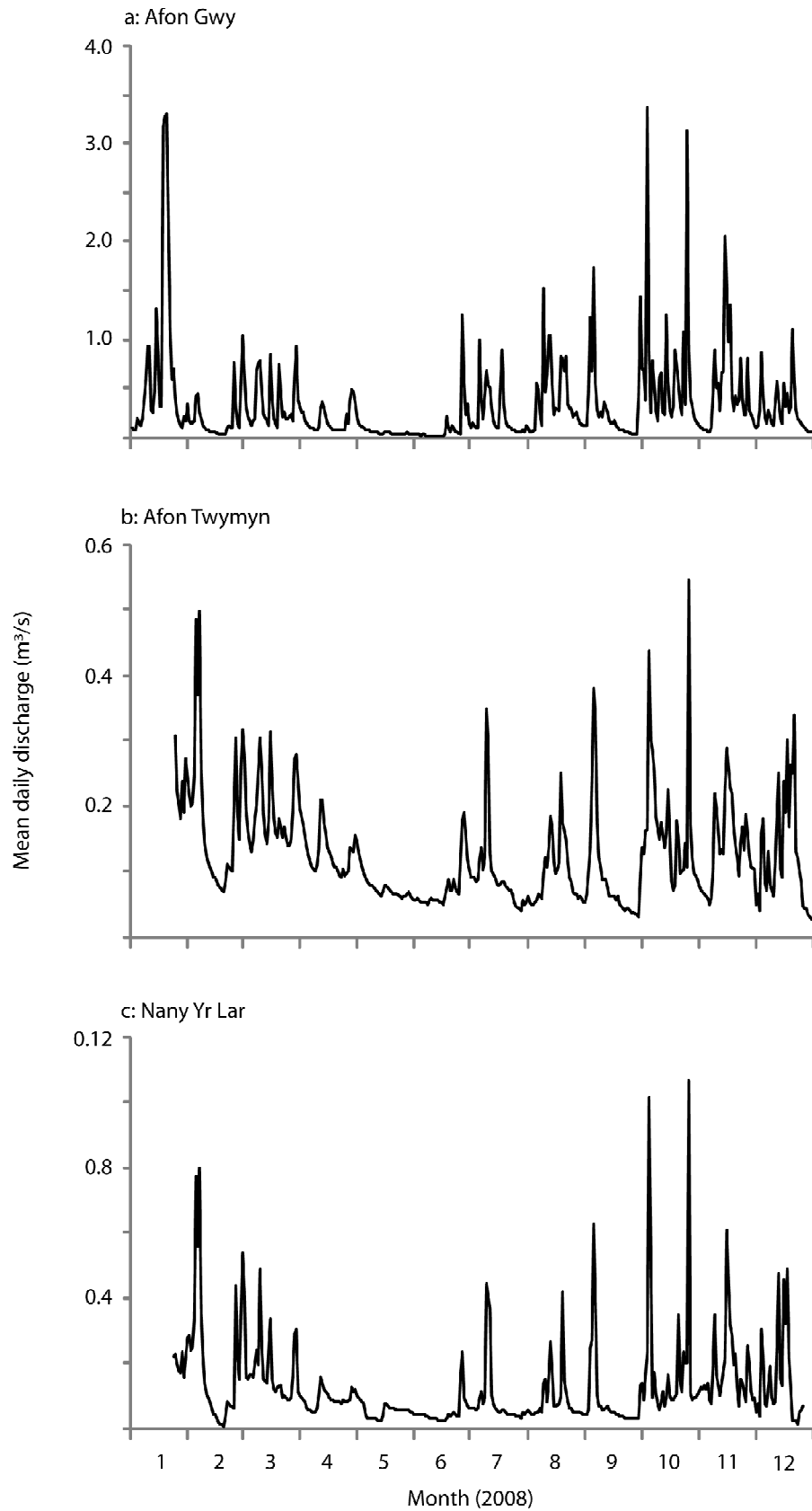
Mean monthly relative discharge values for the long-term Afon Gwy data are illustrated in **Figure 5.3**. These data provide an insight into the annual hydrological regime of the river. Monthly discharge exhibits a distinctive seasonal characteristic of temperate oceanic regions, with the highest values occurring in the winter months. Lower summer values are a result of decreased rainfall and higher evaporation. However, some large flood peaks occur in the summer months as a result of convective activity (**Figure 5.4**). In general, monthly mean discharge values for the Gwy in 2008 were greater than those of the long-term means, confirming 2008 as an atypical year in the hydrological record. As with the precipitation data, some exceptionally high values occur in January, August and October. Exceptions to the trend of increased flows were the months of February and May which both received significantly lower rainfall than the long-term average (**Table 5.1**). The Nant Yr Lar and Afon Twymyn exhibit the same general

discharge pattern as the Afon Gwy in 2008, although they show less variability between months (**Figure 5.3**).



**Figure 5.3:** Afon Gwy river regime 1973-2008 compared to 2008 values for the Afon Gwy, Afon Twymyn and Nant Yr Lar

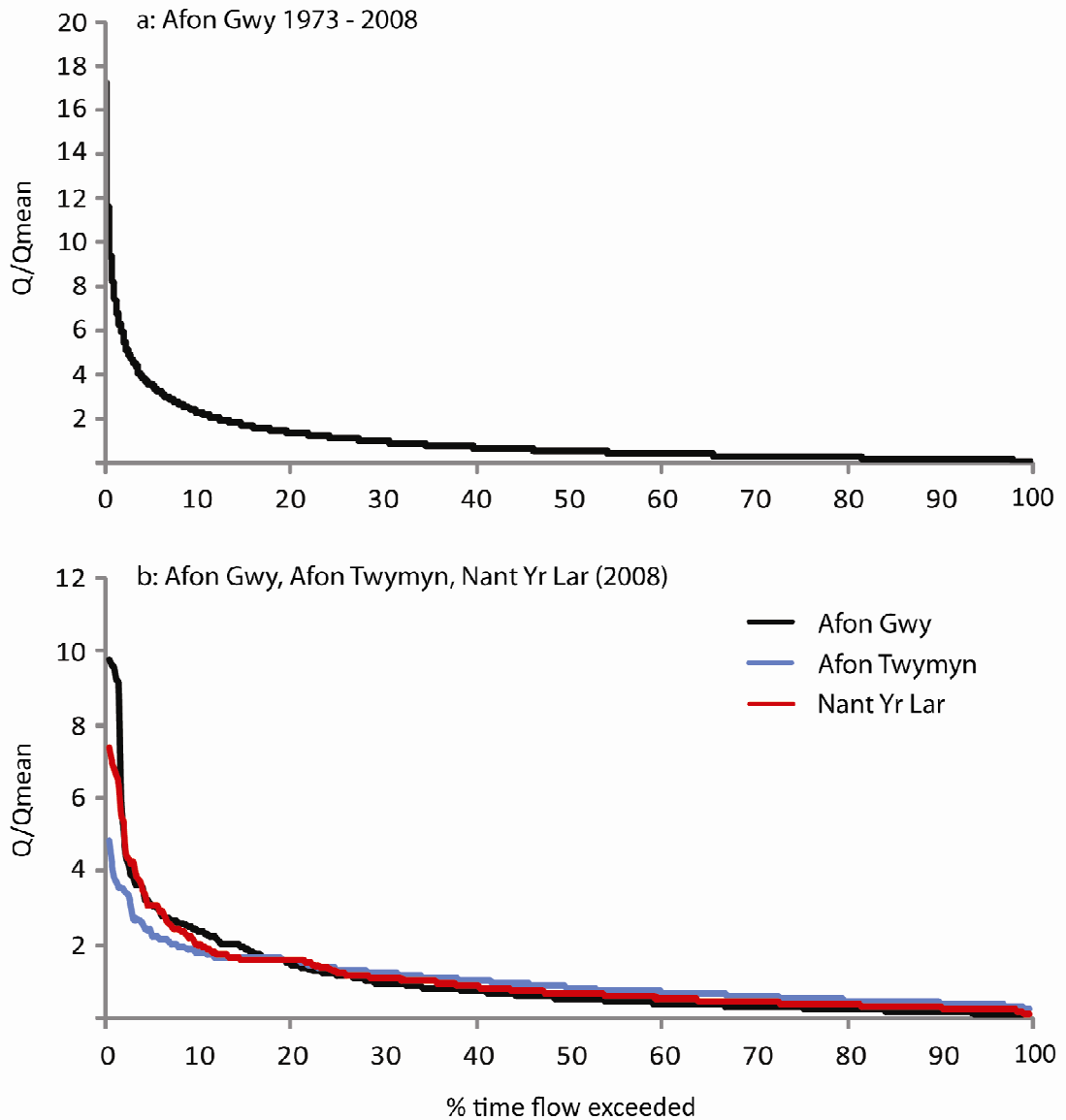
The average rainfall runoff ratio for the long-term Afon Gwy record is 0.90 indicating, on average, 90% of rainfall reaches the river as runoff. However, this value assumes an average daily discharge with no extremely low or high values and uniform rainfall throughout the catchment. Such a high runoff coefficient is not unexpected from a small upland catchment with high incidence of rainfall, steep slopes and peaty soils (Kirkby *et al.*, 1991). Actual evapotranspiration data for the Gwy catchment confirms this high incidence of runoff (Marc and Robinson, 2007). At the time of writing, no rainfall data was available for 2008 in the Gwy catchment for comparison with the long-term mean. However, rainfall in 2008 was likely to have been greater than the long-term mean of 2547 mm, resulting in increased runoff.



**Figure 5.4:** Mean daily discharge (2008) in a) the Afon Gwy, b) the Afon Twymyn (mine station) and c) the Nant Yr Lar (control station)

The long-term flow duration curve for the Afon Gwy is illustrated in **Figure 5.5a**. The initial steep slope results from a very variable discharge and indicates little catchment storage where streamflow closely reflects the rainfall pattern. This pattern is indicative of minimal groundwater flow in the catchment. Flow duration curves for the Afon Gwy, Nant Yr Lar and Afon Twymyn in 2008 are compared in **Figure 5.5b**. Flow patterns are very similar for all three catchments. However, the Afon Gwy and Nant Yr Lar show greater range in flow variability than the Afon Twymyn with apparently higher incidence of both low and extreme flows. The higher incidence of extreme flows in the Afon Gwy, despite its similar size to the Afon Twymyn catchment, probably reflects the higher relief of the catchment, higher annual rainfall and a greater extent of peat cover (with well developed soil pipe networks) which helps to quickly convey water from the catchment to the river (Bell, 2005).

Rainfall runoff ratios illustrate the differences in runoff efficiency between the Nant Yr Lar and Afon Twymyn predicted by the flow duration curves. The rainfall runoff ratio for the Nant Yr Lar sub-catchment in 2008 was 80%. The value for the Afon Twymyn catchment at the mine station was 67%. This indicated that greater storage occurs in the Afon Twymyn catchment. Part of this difference might be attributed to the misrepresentation of overbank flows at the mine station. Another explanation might be the greater importance of overland flow (and possibly pipe flow) in the Nant Yr Lar sub-catchment. Even under dry antecedent soil moisture conditions, the hydrophobic characteristics of the humic content of the peat can lead to overland flow in heavy rainfall (Kirkby *et al.*, 1991). A smaller proportion of the Afon Twymyn catchment is composed of peat. Downstream of the two reservoirs, the soils of the catchment are composed predominantly of well-drained Creep Brown Earths (National Soil Resources Institute, 2009), allowing more time for infiltration of water into the soil and slower movement of this water downslope as subsurface lateral flow. The increase in storage in the Afon Twymyn catchment is also probably a function of catchment size, the Afon Twymyn catchment being larger (x10) with more storage and less flow variability.



**Figure 5.5:** Flow duration curve for a) daily relative discharge in the Afon Gwy (1973 – 2008) and b) daily relative discharge in the Afon Gwy, Afon Twymyn and Nan Yr Lar (2008)

#### 5.2.4 Flood response

This section attempts to identify the main runoff and flow generating processes in the upper Afon Twymyn catchment. Rainfall and discharge data from 14 storms occurring in the 12 month study period were analysed for both monitoring stations. Storms were selected according to the criteria specified by Evans *et al.* (1999):

- Storms were selected to span a range of peak discharge values. A number of larger storms were excluded on the grounds that they were too complex in form.
- Where possible, the storms selected were single-peaked. Minor secondary peaks amounting to less than 10% of the total storm peak discharge were allowed.
- At least one storm from each month of the record was used, excluding May, which was the driest month of the year with no useful storm events.
- Hydrographs were separated using the constant slope method, drawing a straight line from the beginning of rise in discharge to the inflection point on the recession limb.

Summary data for the 14 storms for each monitoring station are presented in **Appendices 5.4 and 5.5**. The mean characteristics of important variables are shown in **Table 5.3**. Notable features are the short lag times between peak rainfall and peak discharge indicating the importance of overland and near-surface flow in the catchments. Examination of Pearson correlation coefficients reveals a strong relationship between flow and rainfall variables (**Appendices 5.6 and 5.7**). Storm discharge, peak discharge, maximum 15 minute rainfall intensity and total rainfall are all significantly positively correlated with each other. These results confirm the rapid movement of water from the catchment to the channel. The negative correlation between lag time and peak storm discharge suggests that, at lower rainfall intensities, movement of water to the channel is delayed, particularly at the mine station. This is consistent with infiltration and subsurface storage and transfer of water (Evans *et al.*, 1999).

**Table 5.3:** Mean characteristics of storm variables at monitoring stations

Storm characteristics	Control station	Mine station
Storm Q (m <sup>3</sup> )	2005	34389
Pk Q (m <sup>3</sup> /s)	0.036	0.373
Time Pk (hours)	7.27	6.98
Lag (hours)	2.14	3.1

Storm Q = Total storm discharge (m<sup>3</sup>)

Pk Q = Peak discharge (m<sup>3</sup>/s)

Time Pk = Time between first recorded rainfall and peak discharge (hrs)

Lag = Time between peak rainfall intensity and peak discharge (hrs)

Results from the analyses of storm hydrograph characteristics are consistent with the findings of Bell (2005) regarding flow generating processes in the geologically and hydrologically similar Plynlimon (peatland) catchments. Because of the heterogeneous nature of the hillslopes, downslope flow processes are complex. During storm conditions, water falling on the hilltops causes a rise in the water table. This increases the hydraulic gradient and results in increased subsurface flows to the steep slope areas. If rainfall intensity is maintained, some hilltop areas may become saturated resulting in saturated excess overland flow. The importance of grassy vegetation in generating overland flow (the 'thatch' effect) on convex, upper slopes has been shown to be significant in the Plynlimon catchments (Kirkby *et al.*, 1991). Infiltrating water reaches an impeding 'clay pan' layer where it is transported laterally downslope. If the rainfall is exceptional, saturation excess overland flow can occur onto the middle and lower concave slopes as a result of upwelling of water from pathways lower in the soil profile. Increased drainage water can also be intercepted by soil pipes which transport the water to saturated areas.

Overland flow and throughflow appear to be the dominant components of runoff during storm events in the upper Afon Twymyn catchment. However, inspection of the 2008 discharge records for the Afon Gwy, Afon Twymyn and Nant Yr Lar (**Figure 5.3**) indicate that, although the hydrographs are irregular and flashy, baseflow appears to be seasonal and have greater importance during the winter

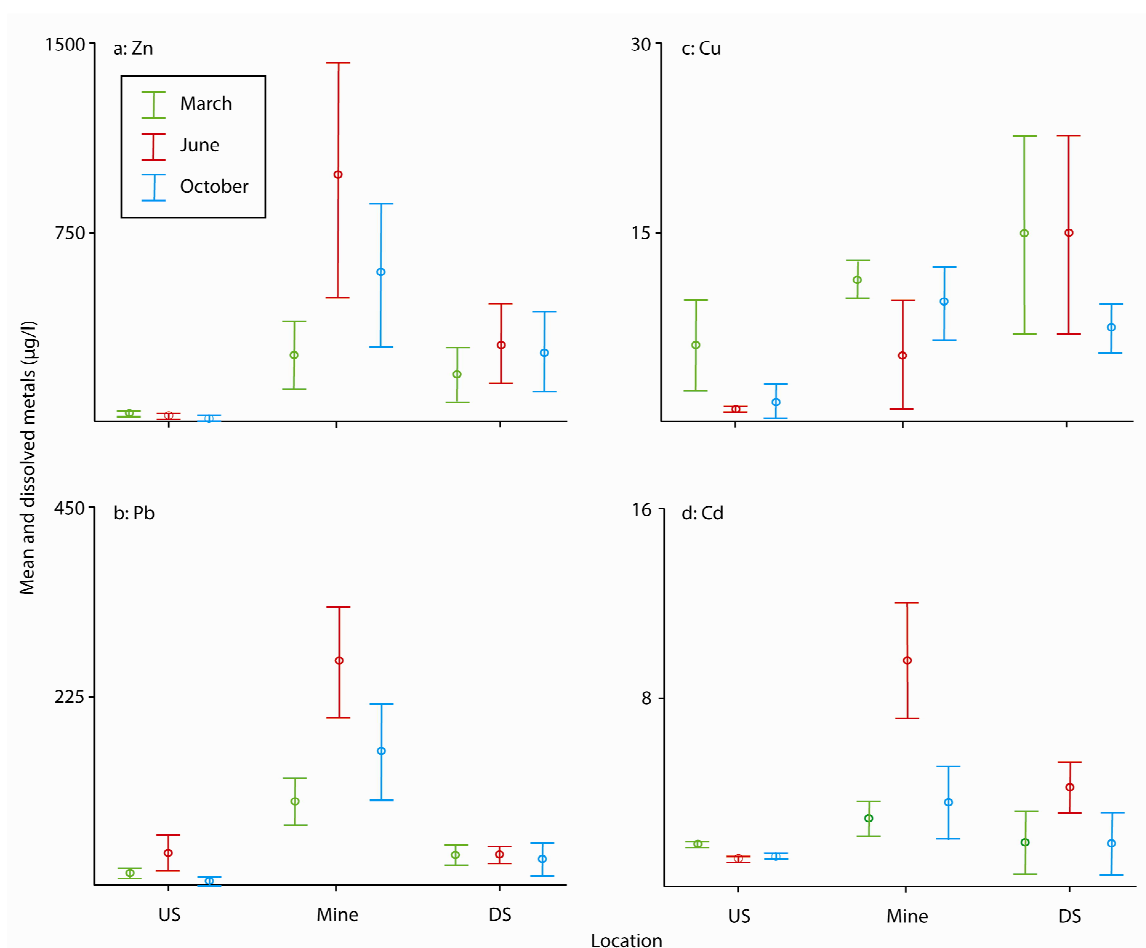


and autumn months. Generally, the lithological formations of upland central Wales have been considered to be impervious to water, thereby limiting the contribution of baseflow to rivers and streams in the region (Kirkby *et al.*, 1991). However, it is becoming increasingly apparent that many upland catchments in central Wales contain groundwater which may play an important role in streamflow generation (Neal *et al.*, 1997; Shand *et al.*, 2005). Several studies using conservative solutes and stable isotopes have indicated significant storage (long enough to dampen tracers) in the Plynlimon catchments and also that pre-event water (derived from rainfall which fell prior to event and not soil water) may constitute much of the storm hydrograph (Neal *et al.*, 1997; Shand *et al.*, 2005). Whether the storage is as bedrock groundwater or deeper soil water has not been determined to date.

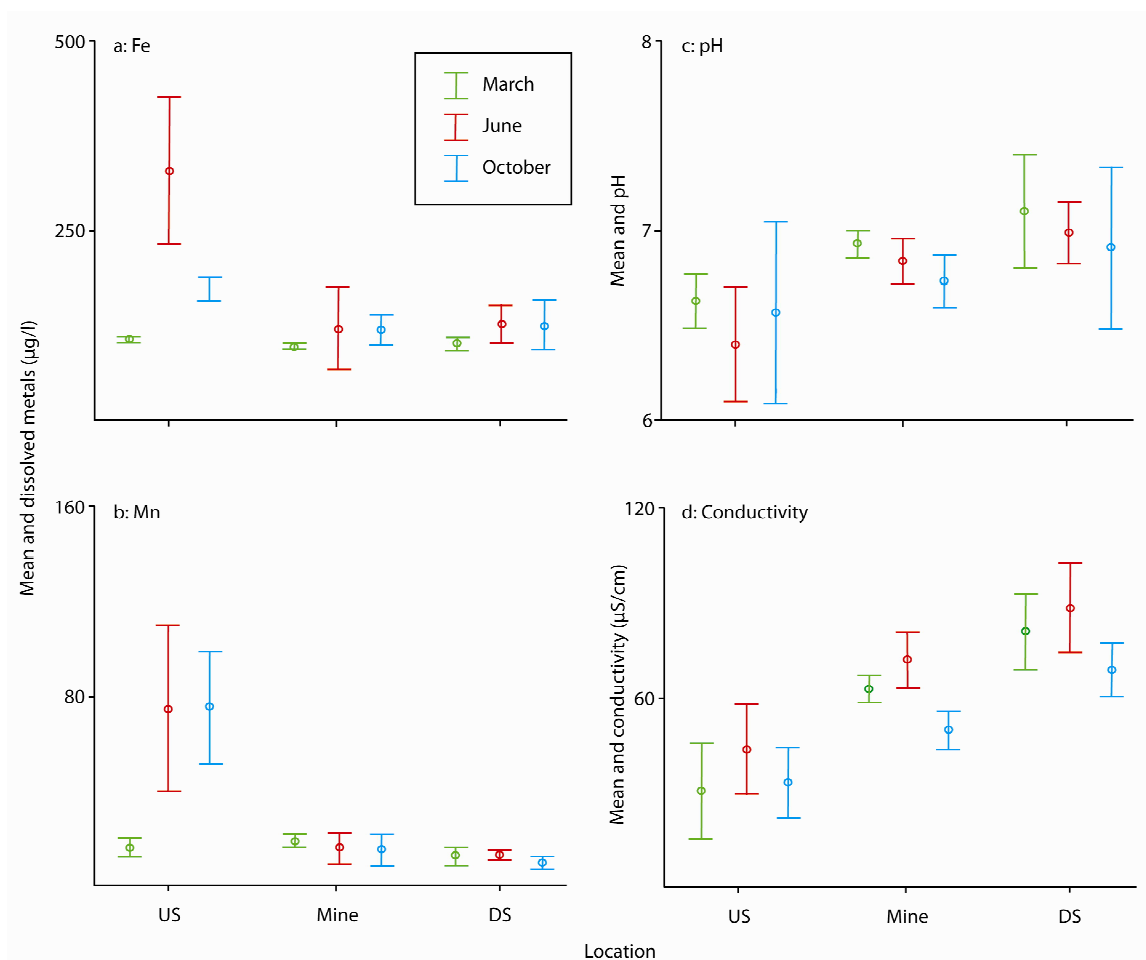
### **5.3 Chapter summary**

Precipitation and discharge data for the Afon Twymyn catchment in 2008 reveals this year was atypical of the long-term records. In general, precipitation and river discharge were greater than the long-term means, particularly in January, August and October. The most important runoff processes in the Afon Twymyn catchment appear to be overland flow and throughflow and this is reflected in the generally rapid response of the river hydrograph to rainfall events. Soil pipes in the upper Afon Twymyn catchment may also account for the rapid response. Evidence from recent hydrological studies of the Plynlimon catchments suggest that baseflow may be more important than the local geology would lead us to believe, particularly during the winter months.

concentrations were still elevated suggesting sources of readily soluble metals still existed at the mine at this time. The lowest metal concentrations were observed in March reflecting increased dilution and the exhaustion of available metal sources at the mine. pH showed a trend of high values in March and lower values in June and October. Lower values in June and October may reflect increased acidity generated by hydrolysis of metal ions at the mine site. Increased carbonic acid generated through plant and animal decomposition in October may also be a factor (Neal, 1997). Conductivity was lowest in October and highest in June reflecting decreased dilution and higher concentrations of dissolved metals and major ions during the summer.



**Figure 6.2:** Temporal variability in mean dissolved Zn, Pb, Cu and Cd in the Afon Tywmyn



**Figure 6.3:** Temporal variability in mean dissolved Fe, Mn, pH and conductivity in the Afon Twymyn

### 6.1.3 Estimating dissolved heavy metal fluxes under steady flow conditions

The observed differences in metal concentrations between control and mine sites and between seasons highlight the impact of mining activity on water quality. However, measurements of metal fluxes and loads present a clearer picture of metal mobilisation from mine sites and provide information which informs the selection and design of remediation technologies. Daily and annual (2008) dissolved heavy metal fluxes and loads are estimated for two sites, one upstream of (site 22) and one at Dylife mine (site 8) (**Table 6.3**). Site 22 has been identified as an effective control site with low concentrations of dissolved Pb, Zn, Cu and Cd. Site 8 is considered the most heavily polluted mine site (section 6.1.1). Mean

daily dissolved metal fluxes (ML<sub>d</sub>) at these sites for March 2008, June 2008, and October 2008 are estimated using the following equation:

$$ML_d \text{ (kg/d)} = MC_w * Q * s/h * h/d$$

where MC<sub>w</sub> is the instantaneous metal concentration (µg/l); Q is the instantaneous stream discharge (m<sup>3</sup>/s – measured on-site); s/h is seconds per hour; h/d is hours per day. Mean metal concentrations for the three sample months and continuous discharge data from January to December 2008 (Chapter 7) are used to estimate total annual metal loads. Using single metal concentration measurements to create an annual load is unwise given the likely inter and intra-monthly variation in load. Nevertheless, it is felt this approach is justified with the data available and is aimed simply at establishing a general estimate.

**Table 6.3:** Mean daily and annual (2008) metal loads upstream of and at Dylife mine

Time period	Control (site 22)				Downstream (site 8)			
	Pb	Zn	Cu	Cd	Pb	Zn	Cu	Cd
March '08 (kg/d)	0.02	0.02	<0.01	<0.01	2.79	8.71	0.23	0.07
June '08 (kg/d)	0.02	0.02	<0.01	<0.01	2.79	11.74	0.06	0.09
October '08 (kg/d)	<0.01	<0.01	<0.01	<0.01	4.13	15.92	0.15	0.10
Annual total (2008) (kg)	11.96	7.13	2.80	0.76	1294	5023	50	37

Metal flux estimates indicate that contaminated drainage from Dylife mine generates dissolved Zn loads of between 8 and 16 kg/d, and an estimated 5023 kg/yr, comparable to other metal mining-impacted rivers in the UK (Mighanetara *et al.*, 2009). Notably, daily metal loads (except Cu) increase through the year reaching maximum levels in October. Despite the highest metal concentrations occurring in June, when river dilution is reduced and metal availability appears to

be greatest, the combination of high dissolved metal concentrations and high river flows in October produces the highest metal loads.

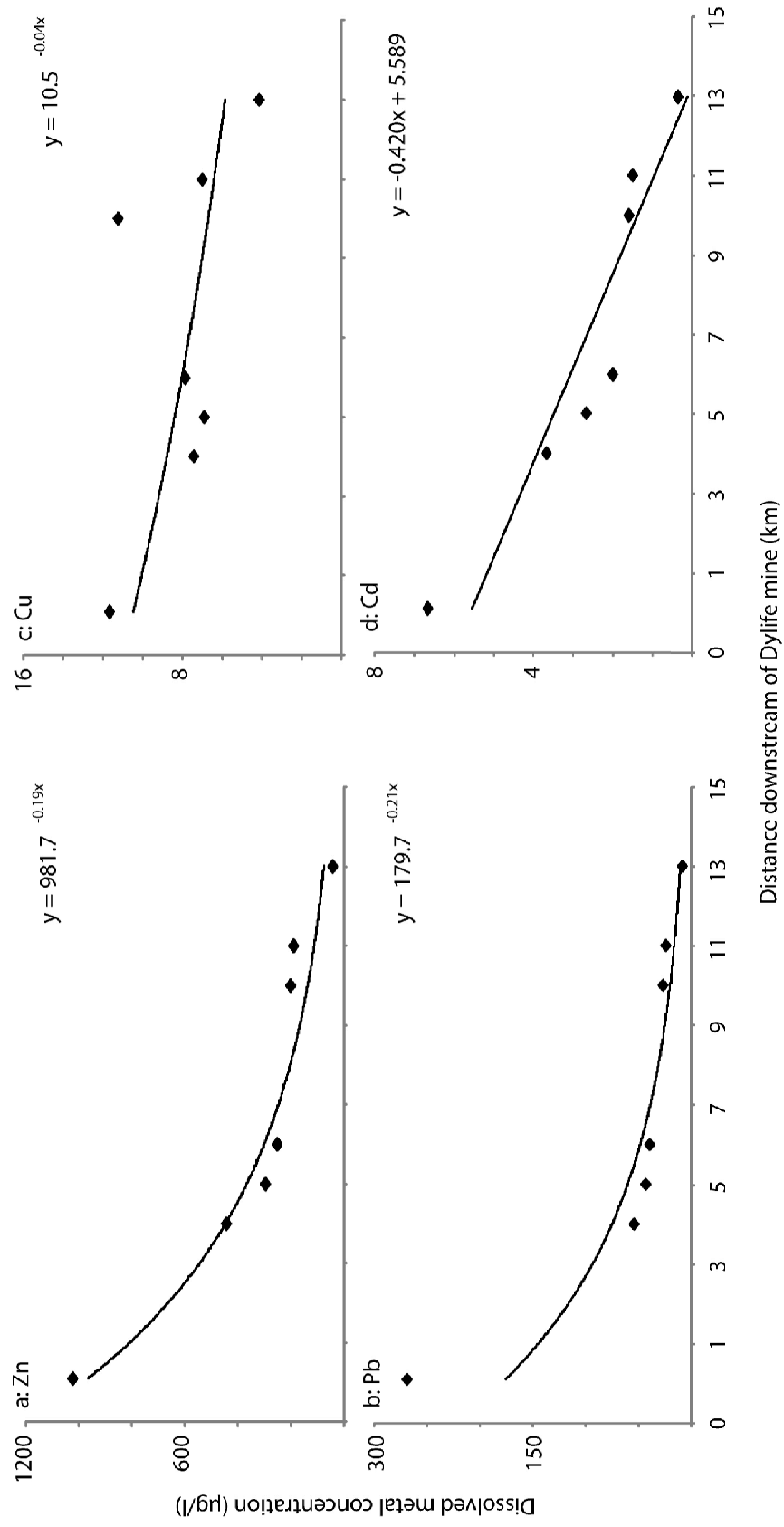
#### 6.1.4 Modelling downstream patterns of dissolved heavy metal attenuation

Dissolved metals appeared to disperse or decay at a steady rate downstream of Dylife mine, reaching their lowest concentrations at the Afon Laen confluence. This section attempts to develop functional quantitative relationships between the toxic heavy metals (Pb, Zn, Cu, Cd) and distance downstream by fitting longitudinal, exponential and power function least-square regressions. Mean metal concentrations for the study period are considered so as to reduce the variation caused by seasonal data. **Figure 6.4** illustrates the best-fit curves and regression equations for each of the metals and **Table 6.4** summarises the model results.

**Table 6.4:** Regression model summaries for mean dissolved metal concentrations downstream of Dylife mine

Regression model		Pb	Zn	Cu	Cd
Longitudinal	$r^2$	0.774	0.614	0.321	<b>0.840</b>
n = 7	$\alpha$	0.009	0.037	0.185	<b>0.004</b>
Power	$r^2$	0.623	0.835	0.358	0.642
n = 7	$\alpha$	0.035	0.004	0.156	0.168
Exponential	$r^2$	<b>0.850</b>	<b>0.887</b>	<b>0.359</b>	0.638
n = 7	$\alpha$	<b>0.003</b>	<b>0.002</b>	<b>0.155</b>	0.031

Note: Best fit model and significance are in bold



**Figure 6.4:** Relationships between dissolved metal concentrations and distance downstream in the Afon Twymyn

Lead, Zn and Cu are best approximated by exponential models, and the best fit for Cd is achieved by using a longitudinal model. The exponential model best suits a gradual decrease in concentration as recorded with the majority of metals in this study. The regression relationships for Pb, Zn and Cd are statistically significant, indicating a strong relationship between dissolved metal concentrations and distance downstream of the contamination source. The exponential model does not indicate a strong relationship between dissolved Cu and distance from contamination source. Copper exhibited some unpredictability in its concentrations downstream of Dylife mine, which may be related to inputs of Cu from left-bank tributaries.

## **6.2 Sediment chemistry**

### **6.2.1 Longitudinal variation in sediment chemistry**

It is hypothesised that sediment contamination in the Afon Twymyn as a result of historical metal mining is extensive and that, in the absence of multiple contamination sources, metal concentrations in sediment attenuate gradually with distance downstream of Dylife mine. Investigations of sediment contamination are not usually undertaken in the standard monitoring programmes of environmental regulators. Quite often, total metal concentrations are measured as part of more detailed remediation investigations. However, non-residual or bioavailable metals may be the most significant barrier to the long-term success of remediation strategies and the EU Water Framework Directive, and these can only be quantified by an assessment of metal partitioning between sediment geochemical phases.

#### *Control sites*

There is a great deal of longitudinal variation in non-residual (summed total of extracts 1 – 3 for each individual metal) metal concentrations in the sediment of the Afon Twymyn. The pattern of variation for fine sediment (<2000  $\mu\text{m}$ ) is illustrated in **Figure 6.5**. Individual metal concentrations for Pb and Zn are represented graphically on maps in **Figure 6.6**. Non-residual metal concentrations at control sites ranged from 222 to 1858 mg/kg. Low levels of Pb, Zn, Cu and Cd were

recorded indicating these sites are free of mine contamination. Control sites were dominated by Fe (maximum 1042 mg/kg) and Mn (maximum 1148 mg/kg) (**Table 6.5**). These metals are strongly associated with reducing and acidic conditions found in marshy areas (Xavier, 1990), such as those that characterize the headwaters of the Afon Twymyn. When Fe and Mn-rich groundwater that is low in dissolved oxygen emerges from headwater springs, it is readily oxidised to form insoluble metal hydroxides in the oxic surface water environment of the marsh. Precipitated Fe accumulates in deeper water environments where it is concentrated by anaerobic bacteria, often forming deposits of 'bog iron' (Kaczorek and Sommer, 2003). In addition, Fe and Mn adsorb preferentially to organic surfaces that are abundant in marshy environments (Misra and Mishra, 1969). Sites 27, 28 and 29, located in the headwaters of the Nant Dropyns tributary, recorded the highest Fe and Mn concentrations. Here, the extent of the marsh is considerably greater than in the headwaters of the Afon Twymyn (22, 23, 24, 25, 26). The peat horizon in the Nant Dropyns tributary also appears to be more developed, which would also account for the higher concentrations of these two metals. High metal concentrations observed at site 22 probably reflect the displacement of enriched material from the plunge pool of a small waterfall upstream of this site. Reducing conditions are maintained at sites 20 and 21 on the Nant Dropyns and are a likely explanation for the high concentrations at these sites.

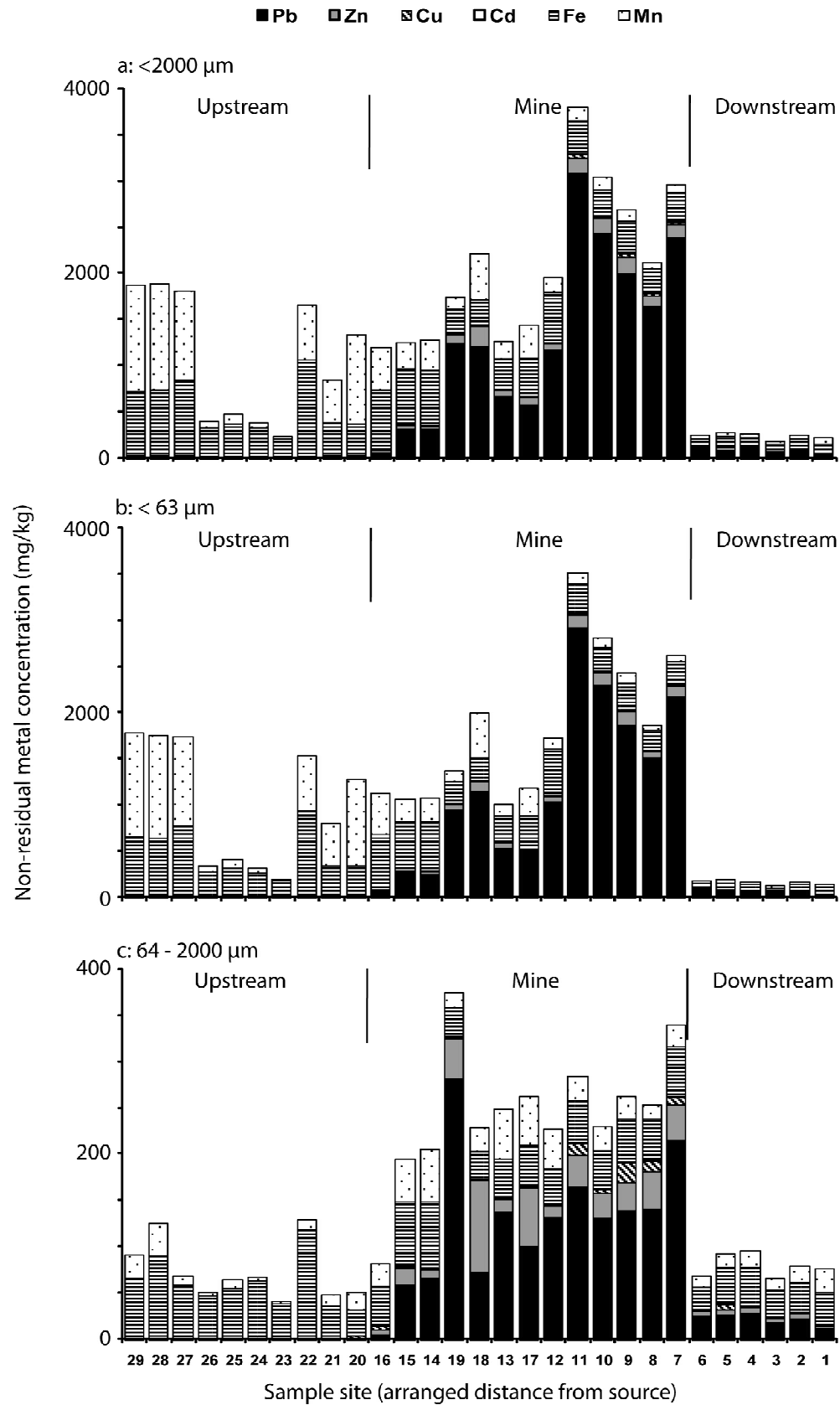
### *Mine sites*

The bed sediment of the Afon Twymyn is severely polluted at Dylife mine and all of the metals analysed with the exception of Fe and Mn were significantly different ( $\alpha = <0.01$ ) in concentrations between control and mine sites (**Appendix 6.2**). Non-residual metal concentrations ranged from 1192 to 3786 mg/kg and were dominated by Pb (**Table 6.5**). However, as with dissolved metals, there was considerable spatial variability (**Figure 6.5**). Pb and Zn concentrations increased gradually on the Afon Twymyn between sites 16 and 12 (**Figure 6.6**), where the Afon Twymyn flows past a number of mine workings. A large proportion of the river bed on this stretch is composed of displaced mine spoil from the adjacent hill sides. The old mine dressing floor opposite sites 12 and 13 is composed of very

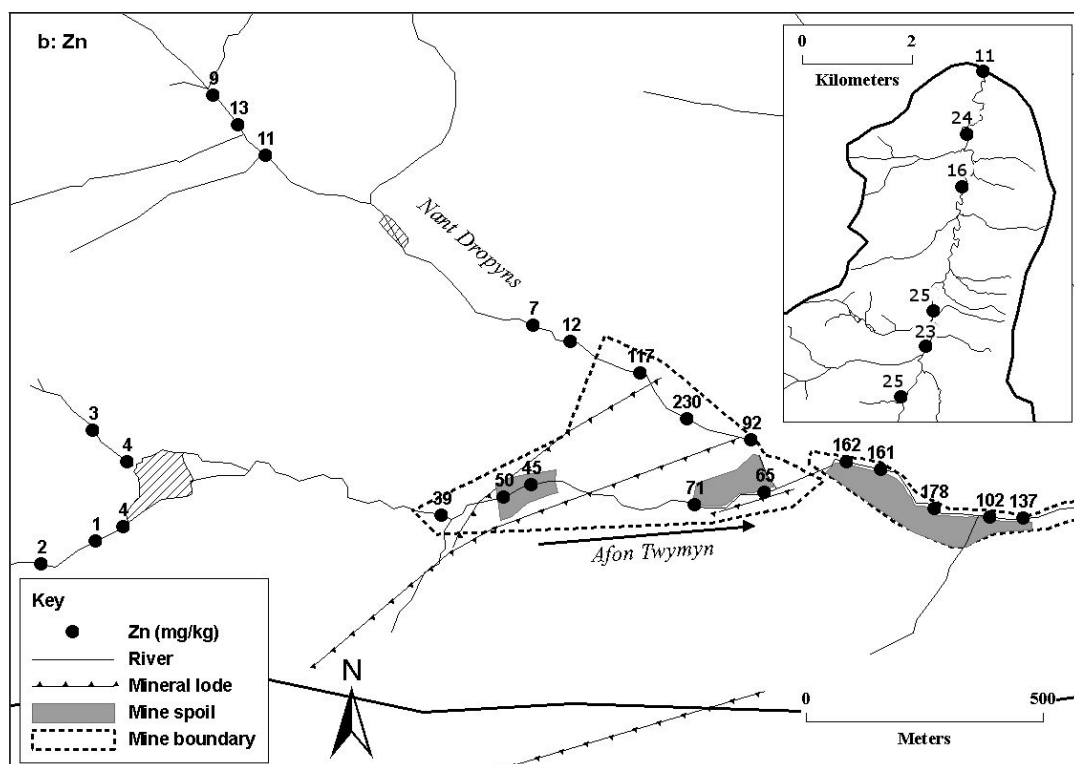
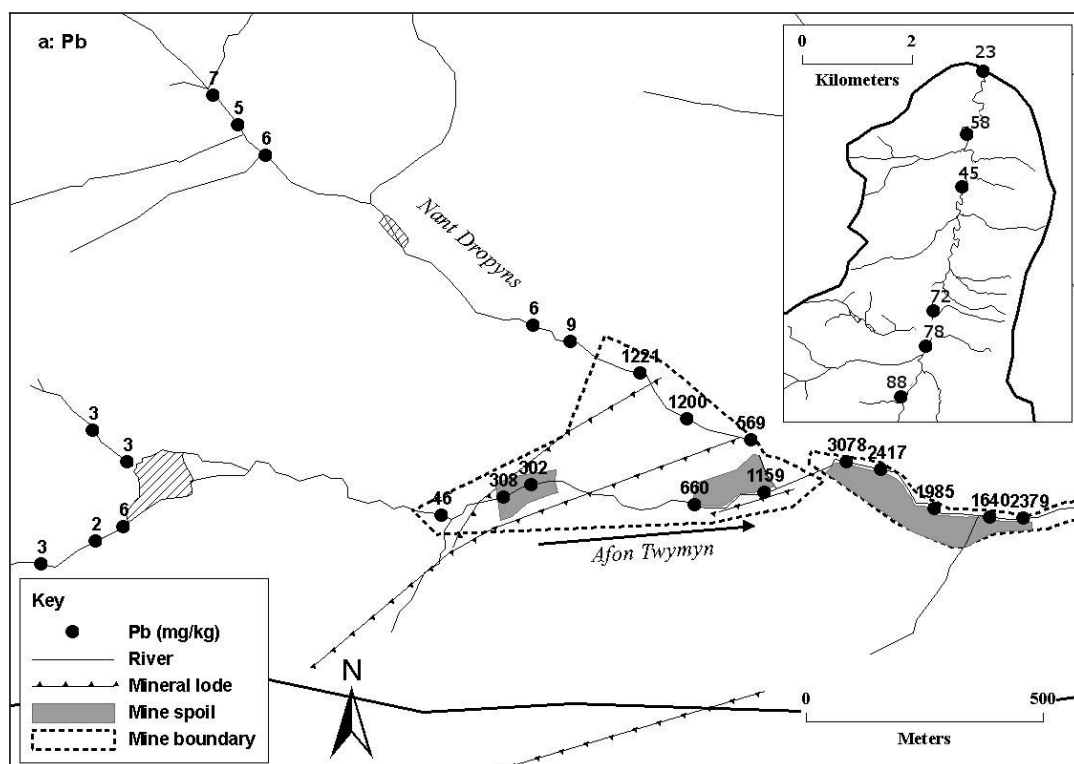


fine material highly elevated in reactive sulphides. The Nant Dropyns flows through the dressing floor from the north before merging with the Afon Twymyn and is likely to flush this material especially during overbank flow, resulting in enrichment of the river bed sediment. On the Nant Dropyns, sites 18 and 19 were the most contaminated sites. The highest Zn and Cd levels in the study were recorded at site 18 (230 mg/kg Zn; 1.65 mg/kg Cd). There are pockets of mine spoil on the Nant Dropyns and a number of mine workings. The two mineral lodes which cross this site are also a potential source of enriched material. There is a decrease in total metal concentrations at site 17 after a gradual increase from sites 21 to 18. For much of the year (March to October), river flow disappears into the river substrate upstream of site 17, possibly entering the Llechwedd Ddu lode. Disconnected from running water for much of the year, site 17 is unlikely to be enriched in contaminated sediment to the same extent as sites upstream. Fe and Mn concentrations generally decreased at mine sites (range 167 – 466 mg/kg Mn and 325 – 633 mg/kg Fe). However, concentrations similar to control site values were recorded at site 16, on the Afon Twymyn, where reducing conditions predominate.

The eastern part of Dylife mine from the road culvert (under the Machynlleth road) to Ceunant waterfall recorded the highest non-residual metal concentrations in the Afon Twymyn, where values ranged from 2103 to 3786 mg/kg (**Table 6.5**). Site 11 recorded the single highest non-residual metal concentration (3786 mg/kg) and Pb concentration (3078 mg/kg) in the study (**Figure 6.5**). This Pb value is over 310 times greater than the control site mean for this metal. Metal concentrations began to attenuate from site 11 to the eastern boundary of the mine, although they remained highly elevated throughout. An increase in concentrations at site 7 can possibly be explained by additional contaminated sediment delivered to the river upstream of this point by the unnamed tributary (MineT) flowing through mine spoil and entering the mine site from the south. More likely, however, is the preferential deposition of contaminated sediment of high density at site 7 in a placer-like deposit, due the creation of a dead-zone by bedrock obstructing river flow.



**Figure 6.5:** Longitudinal patterns in sediment-bound non-residual metal concentrations in the Afon Twymyn – a) <2000  $\mu\text{m}$ , b) <63  $\mu\text{m}$ , c) 64 – 2000  $\mu\text{m}$



**Figure 6.6:** Non-residual a) Pb and b) Zn concentrations in bed sediments of the Afon Twymyn

**Table 6.5:** Mean and range (in parenthesis) of non-residual sediment-bound heavy metals (mg/kg) at site groups

Variable	Mean		
	Control sites	Mine sites	Downstream sites
<b>Zn</b>	6.70 (1.10	111	21
<b>(range)</b>	– 13)	(39 – 230)	(11 – 25)
<b>Pb</b>	4.86 (1.52 –	1305	61
<b>(range)</b>	7.10)	(46 – 3078)	(23 – 88)
<b>Cu</b>	0.67 (0.23 –	18 (0.70 –	3.62 (1.29 –
<b>(range)</b>	1.39)	46)	9.64)
<b>Cd</b>	0.07 (<0.01 –	0.64 (0.35 –	0.14 (0.08 –
<b>(range)</b>	0.16)	1.65)	0.19)
<b>Fe</b>	513	399 (256 –	101
<b>(range)</b>	(200 – 1042)	633)	(82 – 113)
<b>Mn</b>	553	229	43
<b>(range)</b>	(19 – 1148)	(69 – 507)	(29 – 57)
<b>Total metals</b>	1078 (222 –	2063 (1192 –	223 (175 –
<b>(range)</b>	1872)	3786)	271)

#### *Downstream of the mine*

All of the heavy metals analysed attenuated gradually downstream of Dylife mine (**Figure 6.5**). All of the metals analysed, except Fe and Mn, were significantly ( $\alpha = <0.01$ ) different between mine and downstream sites, confirming the impact of attenuation (**Appendix 6.2**). However, as with dissolved metals, non-residual Pb, Zn, Cu and Cd concentrations are significantly different between control and downstream sites ( $\alpha = <0.05$ ), indicating these toxic metals remain elevated at downstream sites relative to control sites, despite the impact of attenuation. An initial steep drop in metal concentrations occurred from sites 7 to 6 due to the addition of uncontaminated sediment from the scree slopes which mantle the valley sides. This pattern was also observed in a previous study of total metal concentrations in the Afon Twymyn (Wolfenden and Lewin, 1978). Metal concentrations continued to decrease after this initial drop, but at a reduced rate. Minimum downstream concentrations (except Fe) were reached at site 1, where

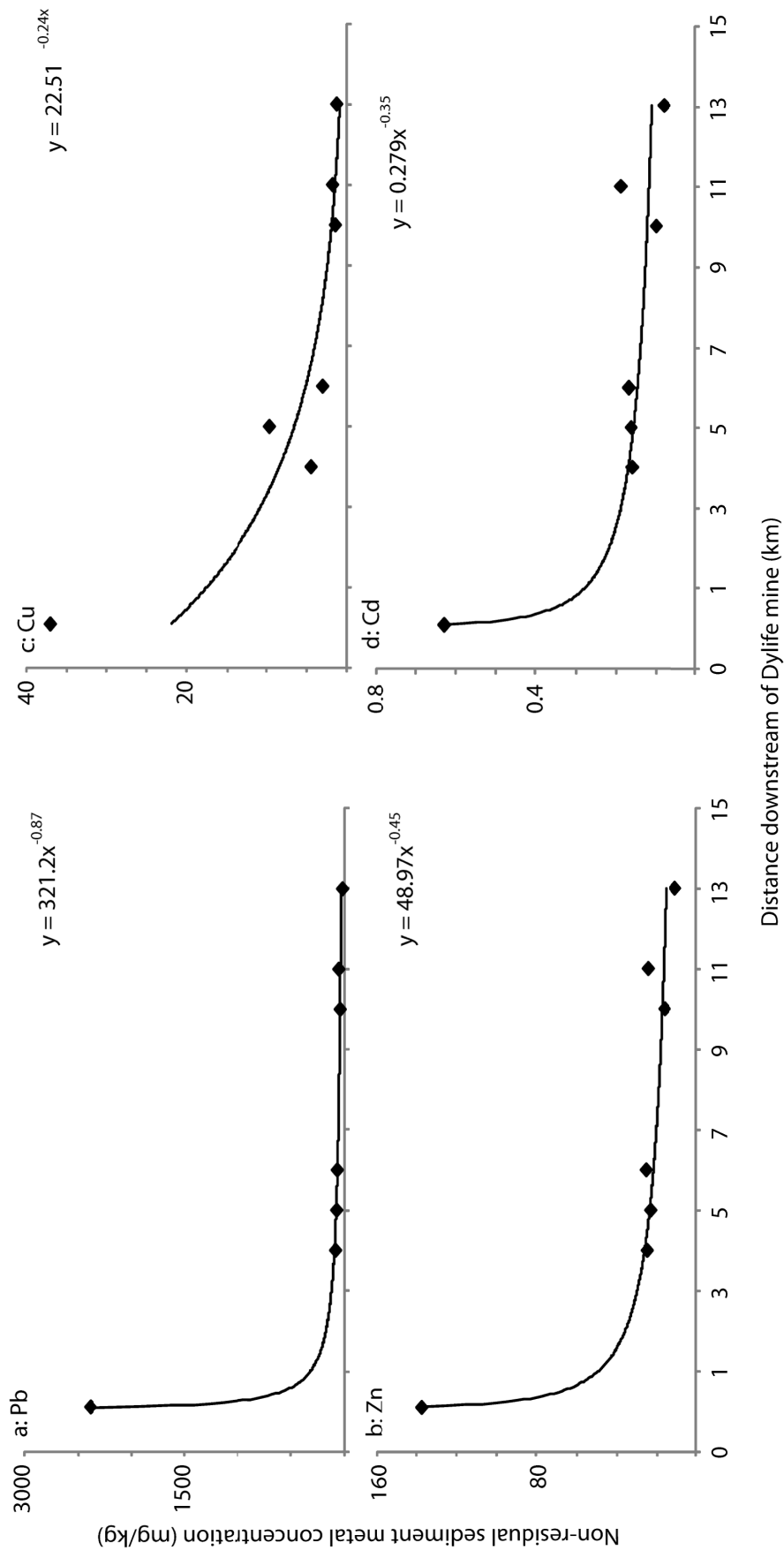
the Afon Laen delivers inputs of clean sediment to the Afon Twymyn. Some variation in Cu, Cd, Fe and Mn concentrations occurred downstream of Dylife which may be related to contaminated sediment inputs from the left bank tributaries. Sediment Cu concentrations were slightly elevated at sites 2 and 5, possibly related to entrapment of bedload by vegetation at these points.

#### 6.2.2 Modelling downstream patterns of sediment-bound heavy metal (non-residual) attenuation

Previous attempts at modelling the rate of decay of sediment-bound metals downstream of input sources have utilised measurements of total heavy metals rather than bioavailable metals (Wolfenden and Lewin, 1978). Generally, quantitative models have achieved a good fit between total metal concentrations and distance from a single metal input (Lewin and Macklin, 1987). It is argued here that measurements of bioavailable metals provide more information on the toxicological risk to aquatic ecology of heavy metals, and the risk of contaminant mobilisation. Therefore, this section seeks to identify whether the dispersion of bioavailable metals downstream of a mining input can be modelled in a similar manner to total metals. The best-fit regression curves and equations for each of the metals are illustrated in **Figure 6.7** and summarised in **Table 6.6**.

Lead, Zn and Cd patterns are best approximated by power function relations, while an exponential function fits Cu patterns slightly better. In all cases the relationships are statistically significant. The b coefficients of the regression equations can be used to illustrate gradients of slope for the four metals and an order of dispersion of metals of the form  $Cu > Cd > Zn > Pb$  (**Figure 6.7**). The low dispersion of Pb can be explained by the greater density of this metal compared to the other metals. Copper is denser than Cd and Zn but experiences greater dispersion due to increases in the concentration of this metal at some sample sites. The better performance of the power function model is possibly explained by the lack of floodplain in the Afon Twymyn. Exponential models are better fitted to rivers with large floodplains where contaminant storage and reworking can lead to more gradual declines in metal concentrations (Lewin and Macklin, 1987). The quantitative relationships developed in this study are stronger than those for total

metals derived in studies of the same river by Wolfenden and Lewin (1978) and Lewin and Macklin (1987). When one is interested in contamination of sediment by mining or other human impacts, measurement of total metals (i.e. residual and non-residual metals) may confound the picture of contamination. This is because residual metals from unmined parts of a mineralised catchment might bolster total metal concentrations in the river channel, giving an incorrect picture of mine waste dispersal. It is more reasonable to assume that bioavailable metals are derived from the mine since the vast majority of bioavailable metals result from human activity. Therefore, non-residual metal concentrations provide a more complete picture of mine waste dispersal and its pattern of attenuation.



**Figure 6.7:** Relationships between sediment-bound non-residual metal concentrations and distance downstream in the Afon Twymyn

**Table 6.6:** Regression model summaries for non-residual metal concentrations downstream of Dylife mine

Regression model		Pb	Zn	Cu	Cd
Longitudinal	$r^2$	0.478	0.543	0.602	0.554
n = 7	$\alpha$	0.085	0.059	0.040	0.055
Power	$r^2$	<b>0.976</b>	<b>0.926</b>	0.838	<b>0.845</b>
n = 7	$\alpha$	<b>0.000</b>	<b>0.001</b>	0.004	<b>0.003</b>
Exponential	$r^2$	0.710	0.703	<b>0.849</b>	0.655
n = 7	$\alpha$	0.017	0.018	<b>0.003</b>	0.028

Note: Best fit curves and significance levels in bold

### 6.2.3 The importance of particle size

The preferential adsorption of heavy metals to smaller sediment size fractions has been demonstrated in many studies and attributed to the greater surface area per unit mass of smaller clay and silt-sized sediments. Longitudinal non-residual metal concentrations in the clay/silt (<63 $\mu\text{m}$ ) and sand (64 – 2000 $\mu\text{m}$ ) size fractions are illustrated in **Figure 6.5**. Concentrations of all of the metals analysed except Pb are significantly greater in the clay/silt fraction than in the sand fraction (**Appendix 6.2**). Lead concentrations are not significantly different between size fractions due to the physical and chemical properties of this metal. The greater density of Pb (11.34 g/cm<sup>3</sup>) compared to other metals makes it more difficult to entrain and transport during high flows. Lead is the most chemically stable of the toxic metals analysed, and adsorbs easily to many mineral surfaces, including Fe, Al and Mn oxides. Therefore, it is less likely than other metals to be chemically dispersed from sediment. Considering the sum of all six metals, the percentage of metals in the clay/silt fraction at control, mine and downstream sites is 92%, 78% and 65%, respectively, and, overall, 80% of metals in the Afon Twymyn system are bound to the clay/silt fraction (**Table 6.7**). The large percentage of metals in the smaller fraction at control sites reflects the dominance of clay and silt-sized particles in the marshy upper catchment. At mine sites, the vast majority of Pb (90%), Fe (88%) and Mn (85%) are found in the clay/silt fraction.



A similar longitudinal pattern was observed for metals in the fine sand fraction, with Fe and Mn dominating control sites and Pb dominating mine sites. Differences in metal concentrations between individual sites and site groupings were not as obvious in the sand fraction as they were in the clay/silt fraction. This is due to the vast majority of heavy metals being scavenged by the smaller size fraction and accentuating the pattern. A notable increase in Pb concentrations occurred at site 19 where the Esgairgaled lode crosses the river. This is undoubtedly a source of sand-sized particles enriched in galena.

**Table 6.7:** *The percentage of heavy metals in the clay/silt and fine sand fractions in the bed sediment of the Afon Twymyn according to site groups*

Variable	Control sites		Mine sites		Downstream sites		All sites	
	Silt	Sand	Silt	Sand	Silt	Sand	Silt	Sand
<b>Zn</b>	88	12	70	30	73	27	71	29
<b>Pb</b>	88	12	90	10	66	34	90	10
<b>Cu</b>	94	6	68	32	53	47	69	31
<b>Cd</b>	93	7	66	34	72	28	68	32
<b>Fe</b>	89	11	88	12	67	33	88	12
<b>Mn</b>	98	2	85	15	61	39	93	7
<b>Total metals</b>	92	8	78	22	65	35	80	20

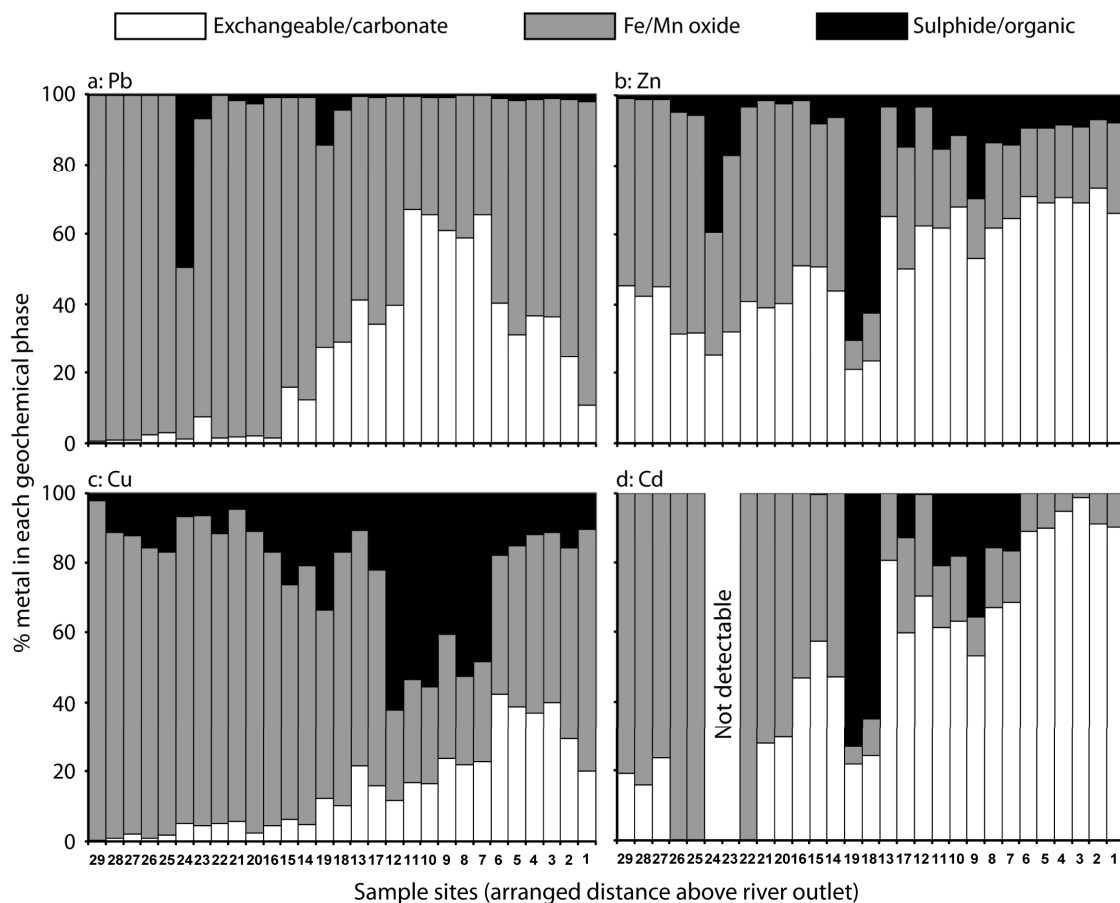
#### 6.2.4 Heavy metal geochemistry

The previous sections have investigated spatial patterns in non-residual metal concentrations, i.e. the sum of three distinct geochemical phases. This section investigates metal concentrations in each of the three geochemical phases and assesses the potential mobility and toxicity of metals as a consequence of its geochemical form. It is hypothesised that a high proportion of sediment-bound metals exist in the most mobile geochemical phase and that these metals represent a significant secondary diffuse source of pollution.

Significant differences exist in heavy metal concentrations between extract phases (**Appendix 6.2**). At control sites, the majority of Pb, Zn, Cu and Cd in the clay/silt fraction were bound to Fe/Mn oxides (**Figure 6.8**). The greatest proportion of Pb was found in this phase confirming the high affinity of this metal for Fe and Mn oxides. Proportions of Zn and Cu bound to sulphide/organics reflect the frequent occurrence of these metals in this geochemical phase (Dawson and Macklin, 1998; Galan *et al.* 2003).

Through Dylife mine, there was a progressive increase in the proportion of all four metals in the easily exchangeable/carbonate-bound geochemical phase. At the mine, the majority of Pb (54%), Zn (53%) and Cd (51%) are found in this phase however, Cu (49%) is found mainly in the sulphide/organic phase (**Table 6.8**). There are increases in the proportion of Zn, Cu and Cd in the sulphide/organic phase, reflecting the high prevalence of zinc sulphide (sphalerite) and copper sulphide (chalcopyrite) which had been discarded (as uneconomic) in preference to galena. Notable increases in Pb, Zn and Cd in the sulphide/organic phase at sites 18 and 19 probably reflect the presence of sulphidic minerals in the underlying Esgairgaied lode. Downstream of the mine, the proportion of Pb (65%) in the easily exchangeable and carbonate-bound phase decreased at the expense of the Fe/Mn oxide phase (33%), due to the high chemical stability of Pb in river systems. However, the concentration of Pb in this phase was still substantial. Copper initially increased in the easily exchangeable/carbonate (37%) and Fe/Mn oxide (48%) phases at the expense of the sulphide/organic phase (15%). This shift is possibly explained by a decrease in sulphidic and organic material downstream of the mine, or perhaps by increased oxidation of sediments below the mine forcing migration of Cu to more bioavailable geochemical phases. However, much like Pb, exchangeable/carbonate-bound Cu decreases after this initial increase, due to its high density ( $8.02 \text{ g/cm}^3$ ) and moderately stable hydrochemistry (Mance *et al.*, 1984). Downstream of the mine, the proportion of Zn (70%) and Cd (92%) in the exchangeable/carbonate phase continues to increase, reflecting the unstable nature of these two metals in river systems (Licheng and Guijiu, 1996).

The general pattern of geochemical partitioning was much the same for metals in the fine sand fraction (**Figure 6.9**). However, there were notably larger relative amounts in the sulphide/organic-bound phase at all sites. Increases at control sites reflect anoxic and acidic conditions in the marsh (favouring metal reduction), the presence of organic material and, possibly, the presence of naturally-weathered ore minerals. At the mine site, the majority of Zn (67%) and Cd (78%) were found in the sulphide/organic fraction and the proportion of Cu (82%) in this phase had increased, reflecting the prevalence of discarded and unprocessed sphalerite and chalcopyrite at the mine. In contrast, Pb (50%) remained high in the exchangeable/carbonate-bound phase. Downstream trends in the sand fraction were similar to trends in the clay/silt fraction, with exchangeable/carbonate-bound Pb (44%) decreasing gradually, and Zn (30%) and Cd (54%) increasing. An increase in exchangeable/carbonate-bound Cu between sites 5 and 2 may explain similar patterns observed in dissolved Cu concentrations at the same sites (section 6.1.1), the process being ion-exchange between the sediment and water column. The reason behind elevated exchangeable/carbonate-bound Cu at these sites may be processing of Cu ore in the headwaters of the left bank tributaries.



**Figure 6.8:** Geochemical partitioning of chalcophile metals in clay/silt fraction of Afon Twymyn bed sediment – a) Pb, b) Zn, c), Cu, d) Cd

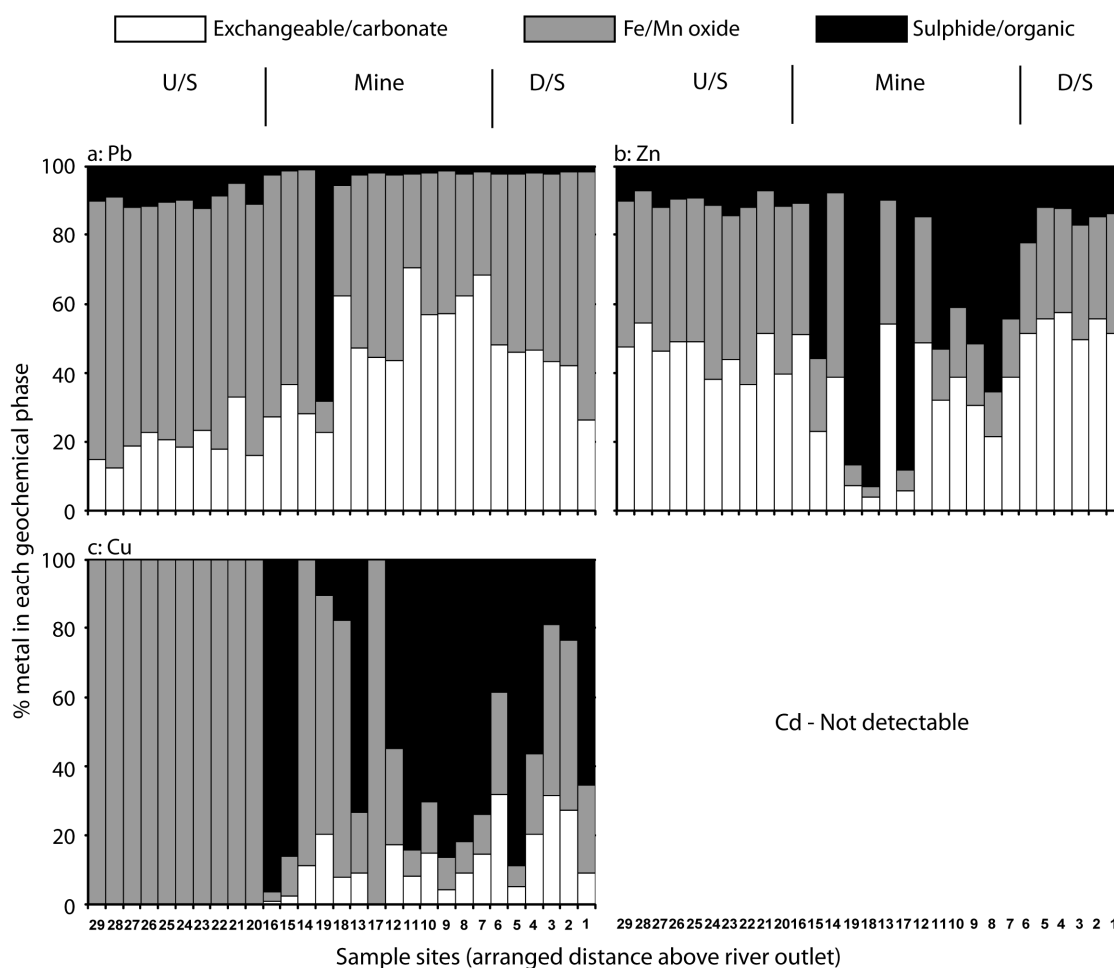


Figure 6.9: Geochemical partitioning of chalcophile metals in fine sand fraction of Afon Twymyn bed sediment – a) Pb, b) Zn, c), Cu

The percentage of each metal in each geochemical phase of the sand fraction (<2000µm) was calculated for the entire Afon Twymyn reach by averaging and summing metal concentrations for stream segments between sample points (Table 6.8). The vast majority of heavy metals in the bed sediment of the Afon Twymyn are found in the most mobile geochemical phase, as easily exchangeable ions or bound to carbonates. The second most common geochemical fraction is the Fe/Mn oxide phase.

**Table 6.8:** *Percentage of metals from the sand fraction (<2000  $\mu\text{m}$ ) in each geochemical phase in the Afon Twymyn*

<b>Geochemical phase</b>	<b>Pb</b>	<b>Zn</b>	<b>Cu</b>	<b>Cd</b>
Exchangeable/ carbonate	49.72	63.02	28.82	77.46
Fe/Mn oxide	48.48	22.18	40.88	13.18
Sulphide/ organic	1.80	14.81	30.30	9.36

## 6.3 Discussion

### 6.3.1 Principal sources of contamination at Dylife mine

The majority of the deep mine workings at Dylife do not appear to be contributing to river or sediment contamination. The flooded stope, however, was observed to discharge into the Afon Twymyn during high river flows (**Figure 6.10**), and a dry drainage channel was observed linking the Footway shaft with the main river channel. These were the only two point sources of mine water contamination found at Dylife during the present study. Under steady flow conditions, the Afon Twymyn disappears next to the Footway shaft and re-emerges from the gravel approximately 100 m downstream, where the stream crosses the underlying Llechwedd Ddu mineral lode. A number of suggestions have been offered to explain this (Parsons Brinckerhoff Ltd., 2005):

- The river flows beneath the level of the mine debris to re-emerge 100 m downstream.
- It flows through the debris into the Footway shaft and into the Llechwedd Ddu lode below where it re-emerges at the flooded stope.
- It passes into the Esgairgaled lode where it crosses under the stream bed.
- It flows into the Gwaith Gwyn adit during floods; some of the water returning to the stream out of the adit after the flood wave has passed.

If the river were flowing into the Llechwedd Ddu lode it would interact with and leach heavy metals from any exposed sulphides, resulting in elevated metal concentrations. However, extensive collapse of underground mine workings is likely to limit the movement of water underground. The most plausible explanation is that the stream flows beneath mine debris (the collapsed tramway) and re-emerges downstream near the Llechwedd Ddu lode. Mine water that emerges from the flooded stope and (possibly) the Footway shaft during high flows is likely caused by rising groundwater rather than the transfer of water from the river channel. Elevated metal concentrations recorded in the flooded stope suggest that these waters do interact with sulphidic material deep underground and, together with runoff from small pockets of mine waste, are the primary causes of the elevated water column and sediment-bound metal concentrations on this stretch of the Afon Twymyn.



**Plate 6.1:** *Groundwater efflux from collapsed stope during high flow (October 2007)*

No evidence was found supporting the theory of groundwater efflux from mine portals on the Nant Dropyns. Dissolved metal concentrations decreased in the Afon Twymyn at site 12 just downstream of the Nant Dropyns confluence indicating this stream has a diluting affect. This is confirmed by relatively low dissolved metal values on the Nant Dropyns which peak at site 18. Contamination of water and sediment on the Nant Dropyns is most likely a result of runoff from small pockets of mine spoil scattered throughout this reach.

Most of the mine water contamination is likely to arise from diffuse sources, namely through dissolution of efflorescent salts accumulated in the oxic surface layers of mine spoil, and flushing of dissolved metals in deeper anoxic layers. Diffuse sources have been identified to contribute substantially to the heavy metal flux of rivers in other regions of the UK (Pirrie *et al.*, 2003; Mayes *et al.*, 2008; Mighanetara *et al.*, 2009). The major source of diffuse pollution occurs at the main spoil tips area to the east of the mine where at least two springs (Spr1, Spr2) drain this spoil and deliver high levels of dissolved heavy metals to the Afon Twymyn. Estimated dissolved metal loads under steady flow conditions indicate substantial fluxes of Pb and Zn from the mine. Another possible source of diffuse contamination is ion-exchange between the mobile heavy metals in the bed sediment and the water column. Other possible diffuse sources are through erosion of channel banks and the narrow floodplain downstream of the mine.

### 6.3.2 Principal factors controlling the hydrochemical status of the Afon Twymyn

#### *The impact of stream pH*

The pH range of the Afon Twymyn from slightly acidic to neutral is most likely the primary factor limiting the concentration of dissolved heavy metals in the river. This is confirmed by positive correlations between sediment metal concentrations (Pb, Zn, Cu, Cd) and pH (**Appendix 6.5**) – as pH increases, greater proportions of metals adsorb/precipitate onto sediment. Lead is the second most abundant dissolved contaminant in the Afon Twymyn system. However, Pb concentrations in the bed sediment are far higher than any other metal due to the liberation of galena by mining. The pH range (6.0 – 7.5) of the Afon Twymyn limits the



proportion of Pb present in the dissolved phase as, above pH 6, most Pb in freshwater systems will exist as a solid, bound to carbonates, hydroxides, sulphides or organic matter (Mance, 1987). This is confirmed by sediment chemistry results (section 6.2.4). On the other hand, Zn, Cu and Cd are less stable heavy metals with critical pH values for precipitation of about 8.4, 7.2 and 9.7, respectively (Kelly, 1988). As a result, a greater relative proportion of these metals exist in the dissolved phase. Indeed, significant positive correlations between dissolved Zn, Cu, Cd and conductivity suggest that this is the case (**Appendix 6.5**). Lower pH values would undoubtedly result in substantially greater dissolved metal concentrations in the Afon Twymyn. pH values as low as 2.3 have been recorded in the Afon Goch, approximately 1 km downstream of Parys Mountain copper mine in north Anglesey, resulting in massively elevated dissolved metal concentrations (maximum 2590 mg/l Fe, 490 mg/l Mn, 600 mg/l Cu, 420 mg/l Zn) (Boult *et al.*, 1994). The highest dissolved metal levels in the present study were recorded at a spring (Spr1) draining the main spoil tips area. However, the pH of this water did not fall below 6.0 during the study period, limiting the amount of dissolved metals. Other mine waters with low pH in Wales (Fuge *et al.*, 1991; McGinness and Johnson, 1993); Macedonia (Alderton *et al.*, 2005), California (Filipek *et al.*, 1987; Nordstrom *et al.*, 2000), Australia (Edraki *et al.*, 2005) and Spain (Marques *et al.*, 2001; Asta *et al.*, 2007) have been observed to have extremely high dissolved heavy metal and sulphate concentrations, highlighting the acid-producing capacities of many abandoned metal mines in comparison to Dylife mine.

#### *Principal factors controlling pH concentrations*

The pH of the Afon Twymyn means that much of the heavy metal load exists in solid form. Low stream pH at control sites is a result of biological activity and acid deposition. A further decrease in pH due to inputs of sulphuric acid might be expected to occur as the river passes through Dylife mine (Filipek *et al.*, 1987; Fuge *et al.*, 1991; Asta *et al.*, 2007). However, although pH values at the mine remain slightly acidic, mean values increase relative to control sites (**Table 6.1**), suggesting that mine waters are not significantly acidic. The lack of acidic drainage at Dylife is probably a result of two main factors, namely the chemical

composition of the bedrock and mineral sequences, and the length of time the mine spoil and underground workings have been exposed to weathering processes. Where mining has taken place in regions rich in carbonate minerals, neutral to basic mine and river water pH concentrations have been observed to limit dissolved metal concentrations (Routh and Ikramuddin, 1996; Marques *et al.*, 2001; Alderton *et al.*, 2005; Sanchez-Espana *et al.*, 2006; Cidu *et al.*, 2007). The Lower Palaeozoic mudstones of central Wales are low in carbonate minerals and this is reflected in the low concentrations of base cations (K, Ca, Mg) observed in the present study. Calcium and Mg concentrations indicate a total water hardness of between 6.9 and 13.3 mg/l (as CaCO<sub>3</sub>). These results confirm that the Afon Twymyn has a low acid neutralising capability leaving the river at risk to pulses of acidic drainage which could force stream pH to fall dramatically. Many abandoned coal mines experience severely acidic mine drainage due to the presence of iron sulphides (e.g. pyrite, marcasite or pyrrhorite) in large quantities, and the combination of sulphur and iron therein (Singh, 1987; Robb and Robinson, 1995; Johnson, 2003). Pyrite produces the most acidic waters as dissolved ferric iron can continue to oxidise pyrite and produce acid even in anoxic conditions (Robb, 1994). Reduced mine water acidity and relatively low concentrations of dissolved metals have been explained elsewhere by low concentrations of iron sulphides in surface and underground mine workings (Alderton *et al.*, 2005). Low concentrations of dissolved iron and sulphate in the Afon Twymyn at Dylife mine reflect the absence of high concentrations of iron sulphides in the region. The lack of acid producing sulphides at Dylife mine combined with the base-poor geology of the region explains the circum-neutral pH of the mine waters. Furthermore, the weathering (oxidation) of sulphides such as sphalerite and galena does not always produce acid drainage (Younger *et al.*, 2002). The subsequent hydrolysis of metal ions can produce some acidity but this is unlikely to decrease the pH of mine water below 5.5 (Banks *et al.*, 1997). Low sulphate levels in the Afon Twymyn suggest that hydrolysis of metal ions is the principal means of acid production at Dylife mine. The length of time the mine has been abandoned may also be a factor explaining the circum-neutral pH of the river and mine waters. It is possible that when the mine was first operated, freshly exposed bedrock and mine spoil containing greater quantities of sulphides produced significant quantities of

sulphuric acid to reduce the pH of mine waters below 5.9. The gradual weathering and exhaustion of sulphidic minerals over the past century may have been mirrored by a gradual increase in the pH of mine waters.

### 6.3.3 Contaminant dispersal and decay downstream of Dylife mine

Quantitative relationships have been established describing the rate of decay of water column and sediment-bound heavy metals with distance downstream of Dylife mine. An exponential regression model was found to best approximate dissolved metal attenuation, while a power function model proved a best-fit for non-residual sediment-bound metals. The decline in dissolved metal concentrations was more attenuated than the pattern for sediment metal concentrations, explaining the better fit of the exponential model. However, the initial rapid decline in sediment metal concentrations downstream of Dylife, followed by a slower, more attenuated decay, is the reason for the better fit of the power function model. In this study, the rate of decay of the more dangerous sediment compartments (i.e. non-residual metals) appeared to exhibit greater predictability than that of total metals in studies of the same river by Wolfenden and Lewin (1978) and Lewin and Macklin (1987). Therefore, it may be possible, with relatively few sediment samples, to predict both the rate of decay and the potential impact on organisms of the more dangerous sediment-bound contaminants with distance downstream of a single heavy metal source. However, further data would need to be collected from other metal mining impacted rivers before this decay pattern could be verified and applied more generally.

A number of physical and chemical factors will influence the downstream decay of sediment metal concentrations in the Afon Twymyn. The initial rapid decline in metal concentrations below Dylife mine was also observed by Wolfenden and Lewin (1978) and is probably due to dilution with uncontaminated sediment from the steep scree slopes which mantle the valley sides (Marcus, 1987; Hudson-Edwards *et al.*, 2001). Hydraulic sorting of sediment based on size, shape and density is also a factor (Macklin and Dowsett, 1989; Hudson-Edwards *et al.*, 1997). Lead was observed to decay at a faster rate than the other metals due to its greater density. Slight increases in Cu concentrations at sites 2 and 5 might be

explained by inputs of contaminated sediment from tributaries in which mining took place. Another possibility is the occurrence of sediment waves migrating downstream (Gilbert 1917), or elevated metals in lateral accretion deposits (Lewin and Macklin, 1987), although elevated concentrations of other metals might also be expected to occur in such deposits. The greater fit of the power function model suggests that storage of metals in the narrow downstream floodplain is not as significant as in other metal mining-impacted river catchments where exponential models have proved a better fit (Lewin and Macklin, 1987).

Chemical processes of metal dispersion are also likely to play an important role in the Afon Twymyn. The gradual decline in dissolved metal concentrations downstream of Dylife mine is primarily a function of dilution by relatively uncontaminated tributary water and surface runoff, and a gradual increase in pH (Edraki *et al.*, 2005). The increase in pH, combined with similar increases in the presence of complexing ligands, encourage precipitation, adsorption and/or complexation of metal ions (Benjamin and Leckie, 1981; Filipek *et al.*, 1987). The attenuation of trace metals by Fe/Mn oxide/hydroxides has been studied extensively (Bowell and Bruce, 1995; Ford *et al.*, 1997; Lee *et al.*, 2002). Low concentrations of sulphate, chloride and carbonate ions in the Afon Twymyn, and negative correlations between sediment-bound Fe and Mn and dissolved Zn, Pb, Cu and Cd (**Appendix 6.5**), indicate that the main attenuation process for these metals may be adsorption and/or co-precipitation with Fe/Mn oxide/hydroxides.

#### 6.3.4 Heavy metal mobility and bioavailability

Investigations of sediment geochemistry have revealed that the vast majority of sediment-bound metals in the Afon Twymyn exist in a highly mobile and bioavailable state, posing serious concerns to ecological integrity. The dominant sinks for Pb, Zn and Cd were the most mobile, easily exchangeable and carbonate-bound geochemical phases. Therefore, the scenario under which most metals are likely to be released from storage is that of acidic environmental conditions, possibly occurring during flood events. Several other studies (Licheng and Guijiu, 1996; Morillo *et al.*, 2002; Galan *et al.*, 2003; Jain, 2004) have noted high concentrations of Zn and Cd in these phases. However, as far as is known,

the concentrations and proportions of Pb in these phases in the Afon Twymyn are unparalleled in other investigated metal mining-affected rivers. This may indeed reflect the severe level of Pb contamination at Dylife, however, it is probably also a reflection of the paucity of studies investigating the geochemical partitioning of sediment-bound metals.

The reducible geochemical phase (Fe/Mn oxides) constituted the next largest sink for heavy metals confirming metal sorption onto these metal oxides as an important attenuation mechanism. Therefore, oxidising conditions (e.g. high river flows, dredging operations, drainage of the riverbed) have the potential to release large amounts of contaminants from storage. Several studies have noted the mobilisation of stored sediment-bound metals to the water column under changing conditions of water chemistry (Petersen *et al.*, 1997; Kuwabara *et al.*, 2000; Butler, 2009; Knott *et al.*, 2009). Once released to the water column, metals can move through aquatic environments causing poor water quality and contaminated sediment/floodplains in stretches of river/coast/floodplain that were previously unaffected by mine drainage. The combined exchangeable, carbonate and Fe/Mn oxide phases are considered to be geochemical forms that are highly to moderately available to aquatic organisms as they can interact with organisms more easily than sulphide/organic and residual metals (Pierre-Stecko and Bendell-Young, 2000). This indicates that heavy metals in the sediment of the Afon Twymyn pose a serious threat to the ecological integrity of the aquatic ecosystem. Combining the concentration of metals in the exchangeable/carbonate and Fe/Mn oxide phases, metals in order of potential bioavailability are: Pb > Zn > Cd > Cu.

#### **6.4 Chapter summary**

The Afon Twymyn is found to be highly contaminated as a result of drainage from Dylife mine. The primary source of contamination is diffuse pollution from mine spoil. Secondary diffuse pollution from highly mobile metal fractions in the river bed sediment is a potential source of contamination, especially during conditions of significant variation in river hydrochemistry, e.g. oxidation events. Groundwater efflux from one mine portal has been identified as a point source of contamination

during stormflows. The concentration of dissolved metals in the Afon Twymyn is most likely controlled by pH which, in turn, is controlled by the character of the local bedrock and mineral sequences. Although the Afon Twymyn is seriously contaminated by mine water drainage, the circum-neutral pH of the river prevents contamination reaching levels recorded elsewhere in Wales and abroad. However, the low acid-neutralising capacity of the river leaves it susceptible to acid 'flushes' containing high dissolved metal loads which may occur during short-term flood events. A gradient of contamination was observed with both dissolved and sediment-bound metals peaking at the mine site and decaying at a regular rate with distance downstream of the mine. Quantitative relationships describing the relation between metal concentration and distance downstream have been developed and may be applied to other metal mining-impacted rivers to predict the rate of decay of toxic, dissolved and sediment-bound non-residual metals. However, the relationships described here are only applicable to 'simple' systems where the pattern of contaminant decay is not significantly confounded by the addition of pollutants from many points within the catchment.

Metal partitioning of stream sediment using the SM&T, 3-step, sequential extraction procedure (Salomons and Forstner, 1984) was successfully used to provide insight into the relative mobility and geochemical factors influencing the potential bioavailability of sediment-bound heavy metals. Investigations reveal that the vast majority of heavy metals in the sediment of the Afon Twymyn exist in the most bioavailable geochemical phases, thereby posing a serious threat to ecological integrity. The relative mobility of heavy metals has also been assessed. While Pb was found to decay downstream of Dylife at a faster rate than other toxic metals, it was found to have greater potential mobility due to high concentrations in the acid-soluble geochemical phase. The use of bioavailable rather than total metals in this study has demonstrated metal phase as a significant factor in the context of downstream dispersal of sediment-bound metals. Where assessments of bioavailable metal fractions do not take place, there is likely to be serious misunderstanding of ecological risk and contaminant mobility.

## 7. Flood event variation in river hydrochemistry

### 7.0 Introduction

Chapter 6 analysed spatial and temporal patterns of heavy metal contamination under steady flow conditions in the Afon Twymyn, and identified sources of contamination, patterns of contaminant dispersal and heavy metal mobility. However, standard water quality monitoring programmes, and even the most in-depth hydrogeochemical assessments, are usually limited by the temporal resolution of hydrochemical data (Gundersen and Steinnes, 2001). Monthly, weekly and even daily sampling can miss high flow events during which significant changes in river hydrochemistry can occur. If variations in heavy metal and other chemical parameters are substantial during high flows at abandoned metal mines, then predictions of long-term water quality trends, ecological impacts, pollution risks and the effectiveness of remediation are likely to be misunderstood (Lambing *et al.*, 1999). Therefore, there is a need to monitor flood events in detail in order to quantify accurately contaminant dynamics and to allow resource managers to prioritise areas for remediation.

The aims of this chapter are to investigate variability in river hydrochemistry during rain-fed flood events at Dylife mine and to identify the mechanisms controlling that variability. Additional chapter objectives are to:

1. Study physico-chemical changes in the Afon Twymyn at an annual scale.
2. Estimate mass fluxes of heavy metals during flood events.
3. Identify the importance of antecedent soil moisture in determining flood event metal concentrations.
4. Examine trends in metal attenuation during flood events.

## 7.1 River hydrochemistry

River hydrochemistry is investigated at two temporal scales. Section 7.1.1 is concerned with variability in river physico-chemistry at an annual (2008) scale. Section 7.1.2 focuses on river physico-chemistry and heavy metal concentrations and fluxes during flood events. The selection and location of the experimental monitoring stations is described in detail in section 4.6. River stage and physico-chemical data (pH, temperature, conductivity) were recorded every 15 minutes from 24<sup>th</sup> January 2008 until 4<sup>th</sup> February 2009. Continuous chemical data are absent at the control station from 24<sup>th</sup> January to 16<sup>th</sup> March and from 12<sup>th</sup> to 29<sup>th</sup> August due to some technical problems (see section 4.6). Stream discharge was estimated from stage-discharge curves developed by area-velocity flow gauging at both monitoring stations (section 4.6.4). Precipitation data were obtained from the Dolydd rain gauge (section 4.6.5).

### 7.1.1 Temporal variability in river physico-chemistry

Summary data (mean daily) for pH, conductivity and water temperature are presented in **Table 7.1**. Temporal variability in mean daily pH indicates that the mine station was circum-neutral for most of the year, ranging between 6.2 and 7.2 (**Figure 7.1a**). At the control station, pH values were slightly to moderately acidic, ranging between 5.4 and 6.7. Lower pH values at the control station are a result of acidic groundwater emerging from springs and increased CO<sub>2</sub> production as a result of plant decomposition. pH values followed a similar temporal pattern at both monitoring stations. There was a gradual increase in values from the beginning of February with a peak in mid-June. This slow rise could be related to increases in the consumption of hydrogen protons during the growing season. A similar trend in pH concentrations has been observed in the Upper River Wye, Plynlimon, central Wales (Reynolds *et al.*, 1997). A sharp decline in pH values occurred at the beginning of July around the same time as a notable decrease in conductivity at the mine station (**Figure 7.1b**). pH and conductivity have good positive correlations at the control and mine station (**Appendix 7.1**). The initial sharp decline in July becomes more gradual in August culminating in minimum annual values for both monitoring stations around the beginning of September.



The cause of this decline was, possibly, flushing of accumulated metal salts at this time with increased rainfall – dissolution of metal sulphates releases mineral acidity. However, river pH shows only weak negative correlations with rainfall and discharge at both monitoring stations (**Appendix 7.1**). Another possibility for the gradual decrease in stream pH is the early end to the growing season caused by atypical rains during the summer months (section 5.1). Decreased growth and increased plant decomposition would have increased CO<sub>2</sub> levels (and carbonic acid) in the catchment soils (Neal, 1997). After September, pH values gradually increased to reach values in November/December similar to those values observed in January/February. pH is positively correlated between monitoring stations (**Appendix 7.1**).

For most of the year, conductivity lay between about 15 and 40  $\mu\text{S}/\text{cm}$  at the control station and between 35 and 80  $\mu\text{S}/\text{cm}$  at the mine station (**Figure 7.1b**). These low figures reflect, primarily, the low solubility of the Upper Silurian rocks and the thin and poorly developed soils of the upper Afon Twymyn catchment (Walling and Webb, 1975). The steep relief of the upper catchment might also reduce soil water flow-through times and, hence, opportunity to dissolve soluble material. There was considerable variation in the conductivity data, especially at the mine station. A notable pattern was the gradual increase in values during April, May and June, reaching a maximum daily value of 81  $\mu\text{S}/\text{cm}$  in mid-June. This pattern did not occur at the control station and probably reflects the addition (or concentration) of ionic species due to low flows and increased sulphide oxidation during these months. There may also have been greater availability of dissolved base ions. A sharp decrease in values occurred at the mine station in mid-June, possibly associated with increased rainfall and dilution of ionic species. Thereafter, with successive precipitation events, conductivity at the mine station gradually declined to a daily minimum of 38  $\mu\text{S}/\text{cm}$  in September, whereas discharge continued to increase (section 5.2). Several spikes and troughs are apparent in the data at both monitoring stations from July onwards (although the magnitude of variation is greater at the mine station) which appear to be related to discharge variation, although only a weak correlation exists (**Appendix 7.1**).

Conductivity at the control station was relatively stable throughout the year, with variation generally mirroring variation at the mine station (**Appendix 7.1**).

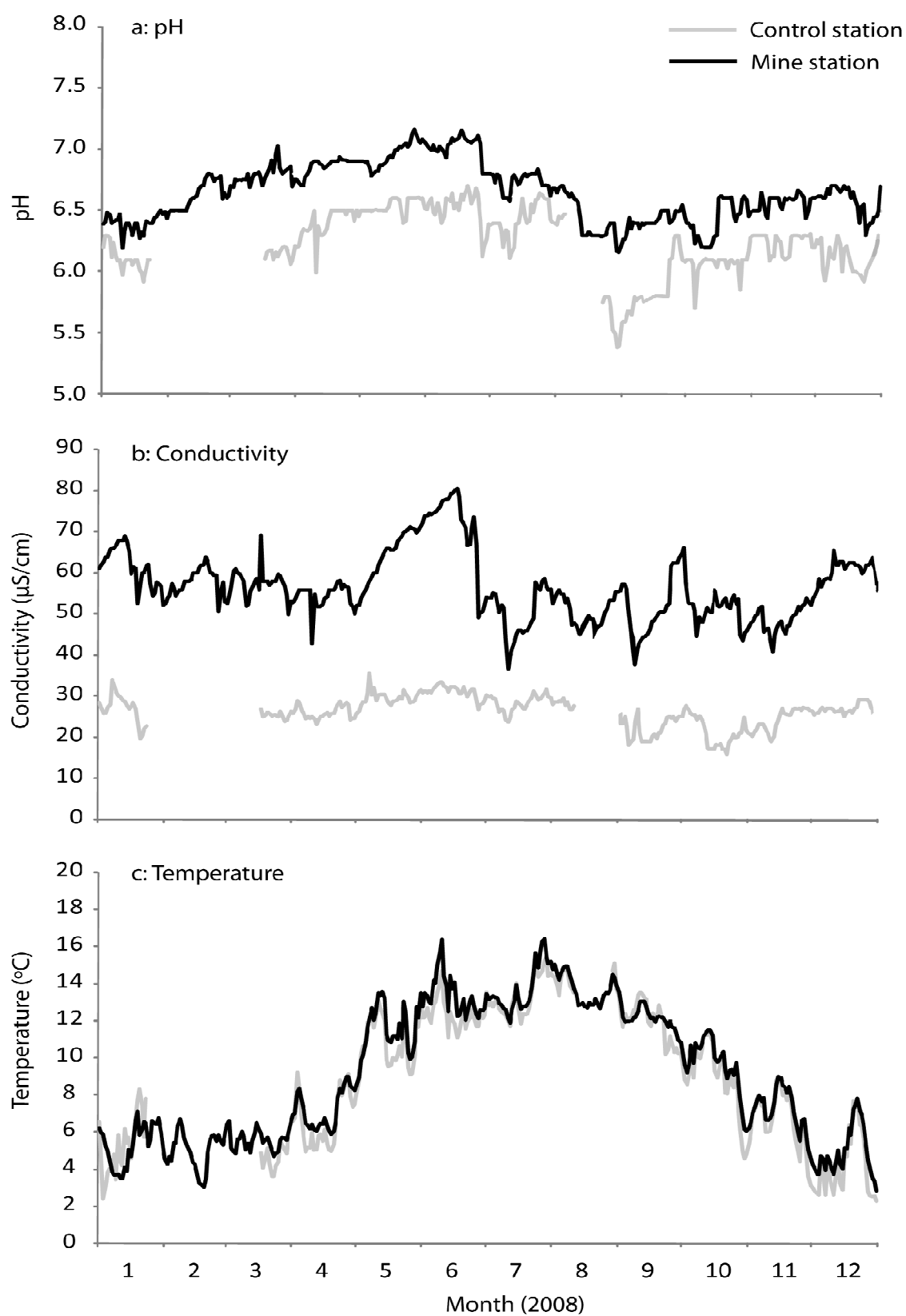
Daily water temperature varied between 2.3°C at the control station (December) and 16.5°C at the downstream station (June) (**Figure 7.1c**). From the 15 minute data, the minimum and maximum temperatures recorded were 0.8°C (December – control station) and 23.1°C (July – mine station), respectively. Some of the high summer values were possibly affected by inadequate shielding of the Sonde and the interception of radiation (through the water column). Temperature fluctuations were identical at both monitoring sites (**Appendix 7.1**). Temperature at the control station was always slightly lower possibly due to the higher elevation of the site and a greater area of shading (Webb and Walling, 1992).

**Table 7.1:** Summary of daily pH, conductivity ( $\mu\text{S/cm}$ ), and water temperature data ( $^{\circ}\text{C}$ ) (2008) at monitoring stations

Variable	Control station			Mine station		
	pH	Conductivity	Temperature	pH	Conductivity	Temperature
Jan	6.1	27	5.3	6.4	62	5.3
(range)	(5.9 – 6.3)	(20 – 34)	(2.4 – 8.3)	(6.2 – 6.5)	(52 – 69)	(3.5 – 7.1)
Feb	-	-	-	6.6	58	5.0
(range)	-	-	-	(6.5 – 6.8)	(51 – 64)	(3.1 – 6.7)
Mar	6.2	26	4.8	6.7	57	5.6
(range)	(6.1 – 6.2)	(24 – 27)	(3.6 – 6.6)	(6.6 – 7.1)	(50 – 69)	(4.7 – 6.6)
Apr	6.4	26	6.5	6.9	54	7.2
(range)	(6.0 – 6.5)	(23 – 29)	(5.0 – 9.3)	(6.7 – 6.9)	(43 – 58)	(5.9 – 9.0)
May	6.5	30	10.9	7.0	64	11.5
(range)	(6.4 – 6.6)	(26 – 36)	(8.1 – 13.1)	(6.8 – 7.2)	(52 – 71)	(8.5 – 13.6)
Jun	6.5	31	12.3	7.0	71	13.4
(range)	(6.1 – 6.7)	(27 – 34)	(11.1 – 14.7)	(6.8 – 7.2)	(49 – 81)	(12.0 – 16.4)
Jul	6.4	29	13.3	6.7	50	13.7
(range)	(6.1 – 6.6)	(24 – 32)	(11.7 – 15.6)	(6.6 – 6.8)	(37 – 59)	(11.9 – 16.5)
Aug	6.3	29	14.3*	6.4	50	13.8
(range)	(5.4 – 6.6)	(27 – 31)	(13.4 – 15.1)	(6.2 – 6.7)	(44 – 56)	(12.7 – 15.2)
Sep	5.8	24	12.0	6.4	50	12.2
(range)	(5.4 – 6.3)	(18 – 28)	(10.2 – 13.6)	(6.3 – 6.6)	(38 – 64)	(10.8 – 13.6)
Oct	6.0	24	9.0	6.4	54	9.7
(range)	(5.7 – 6.1)	(16 – 28)	(4.6 – 11.3)	(6.2 – 6.6)	(45 – 67)	(6.1 – 11.5)
Nov	6.2	26	6.7	6.6	49	7.2
(range)	(6.1 – 6.3)	(20 – 29)	(3.1 – 9.0)	(6.4 – 6.7)	(40 – 55)	(4.6 – 9.0)
Dec	6.2	28	4.2	6.5	61	4.9
(range)	(5.8 – 6.3)	(25 – 30)	(2.3 – 7.7)	(6.3 – 6.7)	(52 – 66)	(2.9 – 7.8)

- No data

\* Value greater than mine station value caused by some missing data at control station in August



**Figure 7.1:** Mean a) daily water temperature, b) conductivity and c) pH at monitoring stations (2008)

### 7.1.2 Analysis of short-term flood events

Flood event sampling programmes were stage-activated and samples were taken over periods from 12 to 36 hours. Discharge, rainfall, pH and conductivity data represent 15 minute averages; and heavy metal samples were collected at intervals from 15 to 120 minutes (**Table 7.2**). Sample intervals were selected so that a greater number of samples were taken during the rising limb 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 less likely (Canovas *et al.*, 2008).

**Table 7.2:** Example of ISCO water sampling programme

No. Samples	Interval
1	Start time
10	15 min
5	30 min
5	60 min
3	120 min

The use of this variable time interval sampling function was restricted to the control station sampler due to technical problems encountered with the mine station sampler during the study period. As a result, sample intervals at the mine station were limited to fixed intervals of 30, 60 and 120 minutes. The sample actuator at each site was set to 2 cm above the water level on each site visit. This height was selected so that minor fluctuations in river stage would not activate the sampler. Analysis of discharge patterns showed that stage fluctuations of +/- 2 cm were common. Therefore, as a general rule, an increase in stage of 2 cm was judged to be sufficient to constitute a significant rainfall runoff event. An obvious limitation of this approach is that part of the rising limb of the hydrograph might not be sampled for heavy metals resulting in an incomplete chemograph. This was seen as unavoidable due to equipment limitations and the distance to be travelled to maintain the site.

It is anticipated that rain-fed floods passing through Dylife mine will exhibit significant flushing of heavy metals on the rising limb of the hydrograph. Metal concentrations and fluxes at the mine station should be significantly greater than that observed at the control station. It is hypothesised that the magnitude of the flood chemograph (i.e. heavy metals) is strongly related to antecedent soil moisture conditions. That is, the largest flushing of metals occurs during dry antecedent conditions as a result of increased metal oxidation and availability at the mine.

#### *Control station flood events*

Two flood events were recorded at the control station, one in August and one in November 2008. Total and peak 15 minute rainfalls were similar in both events (**Table 7.3**). In *Event 1* (09/08/08), an extended period of rainfall caused an initial discharge peak followed by a slow rise to peak storm discharge, approximately 10.75 hours after the peak 15 minute rainfall (**Figure 7.2**). *Event 2* (09/11/08) was characterised by two separate rainfall events (**Figure 7.3**). The first rainfall event caused an initial discharge peak followed by approximately 5 hours of relatively steady flow. A subsequent larger rainfall event caused a more rapid rise to a second discharge peak. This time the lag between peak rainfall and peak discharge was 2.25 hours.

During both events, significant chemical changes occurred during the first 4 hours of sampling. In *Event 1*, Zn, Pb, Cu, Cd, Fe and Mn exhibited a similar trend with a concentration peak before maximum discharge. Concentrations of all four chalcophile elements were high (512 µg/l Zn, 182 µg/l Pb, 64 µg/l Cu, 20 µg/l Cd) and exceeded water quality guidelines (section 2.6) on several occasions. After 4 hours of sampling, metal concentrations had returned to values similar to mean steady flow concentrations (section 6.1.1). Metal concentration peaks coincided with a decrease in stream pH. pH fell from 6.8 to 6.4 during the rising limb of the hydrograph and conductivity also fell slightly during this time. The reduction in pH was probably related to the flushing of hydrogen ions associated with carbonic acid from plant and animal decomposition and, possibly, sulphuric acid from dissolved metal sulphates. The decline in conductivity was probably a result of

dilution by increased flow – a greater concentration of dissolved salts was masked by dilution with increased flow.

**Table 7.3:** Control station flood event characteristics

Event	Total Pcp	Max Pcp	Pre-event Q	Sampler activation	Pk Q	Time Pk	Lag
<b>1</b> <b>(09/08/08)</b>	29.2	2.2	0.005	0.008	0.04	10.5	10.75
<b>2</b> <b>(09/11/08)</b>	26.2	2.4	0.010	0.017	0.13	9.25	2.25

Total Pcp = Total storm precipitation (mm)

Max Pcp = Maximum 15 minute rainfall intensity (mm/15min)

Pre-event Q = Pre-flood event discharge (m<sup>3</sup>/s)

Sampler activation = discharge at which the sampler was activated (m<sup>3</sup>/s)

Pk Q = Peak discharge (m<sup>3</sup>/s)

Time Pk = Time between first recorded rainfall and peak discharge (hrs)

Lag = Time between peak rainfall intensity and peak discharge (hrs)

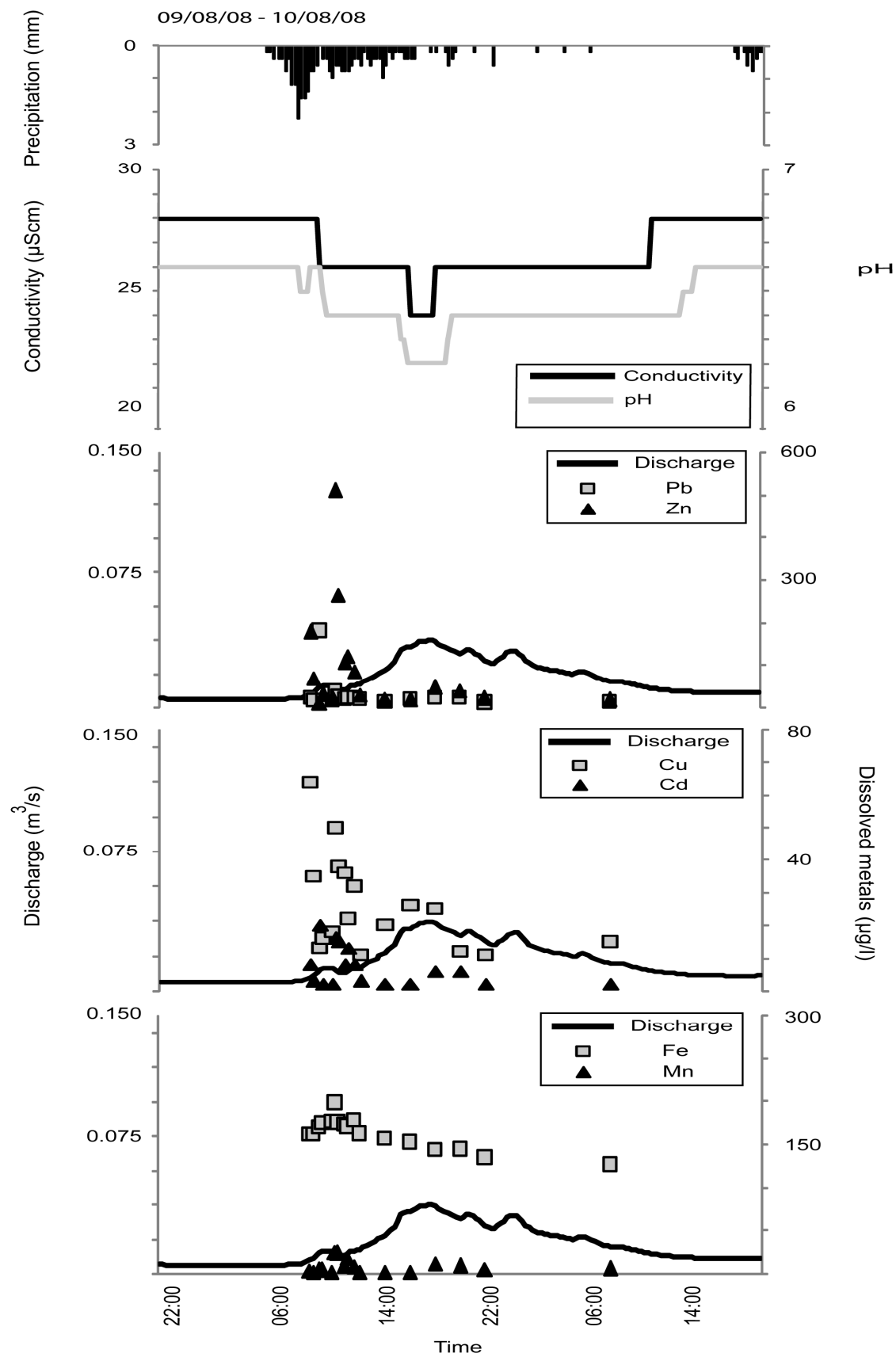
Elevated concentrations of Pb (234 µg/l), Cu (30 µg/l) and Fe (79 µg/l) were similarly observed in the initial stages of runoff in *Event 2* (**Figure 7.3**). Flushing of Zn and Mn was evident but their respective concentration peaks occurred approximately 2hrs after the Pb, Cu and Fe peaks. The different behaviour of the metals was probably related to variations in the dominance of different flow paths throughout the event, and in the chemistry of the flow paths and their source areas. Less soluble metals such as Fe, Pb and Cu might be preferentially enriched in the iron and clay pan below the surface of the peat. More soluble metals like Zn and Mn might be found in shallower soil depths or in dissolved form in pools on the saturated peat surface.

Flushing of heavy metals at the control station was expected, however, some metal concentrations were extremely high (e.g. 512 µg/l Zn, 182 µg/l Pb and 64 µg/l Cu in *Event 1*) and far in excess of those encountered under steady flow conditions (section 6.1.1). A possible explanation is the release, during runoff

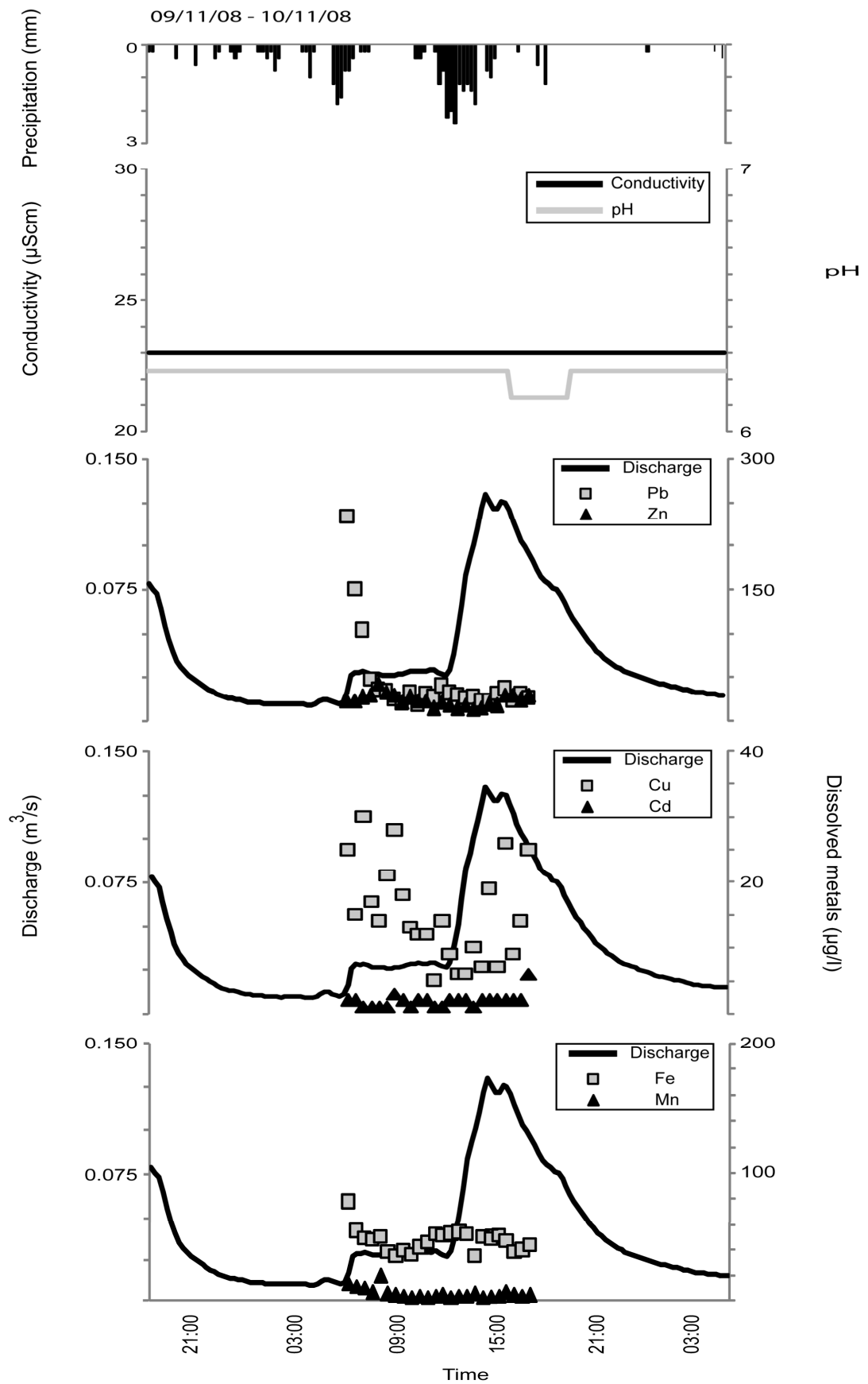
events, of bog iron and associated metals. Lead and Cu are less soluble than Zn and Cd and may, therefore, be preferentially enriched in the 'iron pan' with Fe. Throughflow or pipeflow could leach Pb and Cu in the same manner as with Fe. Peak Pb concentrations in both flood events were greater than peak Fe values. This is possibly a function of the greater solubility of Pb (than Fe) and, hence, its greater release during runoff events. It is unlikely that Zn is enriched in the iron pan to any great extent due to its high solubility. However, continuous leaching of Zn from the soils may result in the enrichment of the upper soil layers and surface pools with this metal. High levels of toxic metals during flood events at the control station might also be accounted for by the pore size ( $0.45\mu\text{m}$ ) of the filter used to separate dissolved and solid-form metals. Organic colloidal material, likely present in high concentrations in the peaty upper catchment, would pass through a  $0.45\mu\text{m}$  filter and might contain high levels of adsorbed heavy metals (Shaw *et al.*, 1984). Another possibility for the high flood event metal concentrations is the occurrence of mine spoil above Dylife mine, although field investigations identified no such deposits nor are they mentioned in the historical literature (Brown, 2006). Displaced mine materials were used in the construction of Rhyd Y Porthmyn reservoir just below the control station. It is possible that, during construction, some of this material was stored or dumped above the monitoring station and that leaching and flushing of metal sulphates from this material causes the elevated metal concentrations.

.





**Figure 7.2:** Control station flood event 09/08/08



**Figure 7.3:** Control station flood event 09/11/08

### *Mine station flood events*

Six flood events were recorded at the mine station during the study period. Characteristics of these six events are summarised in **Table 7.4**.

**Table 7.4:** Mine station flood event characteristics

Event	Total Pcp	Max Pcp	Pre Q	Sampler activation	Pk Q	Time Pk	Lag
<b>3</b> <b>(12/04/08)</b>	14.8	1.2	0.134	0.147	0.259	11	15.5
<b>4</b> <b>(06/07/08)</b>	17.4	2.6	0.103	0.302	0.460	1.5	2
<b>5</b> <b>(13/08/08)</b>	5	1.2	0.142	0.142	0.255	6.5	3.25
<b>6</b> <b>(03/09/08)</b>	32.4	3.4	0.074	0.159	0.465	6	2.75
<b>7</b> <b>(30/09/08)</b>	50.2	2.2	0.024	0.089	0.163	17	8.25
<b>8</b> <b>(08/11/08)</b>	13.4	2.8	0.046	0.046	0.364	1.25	2.75

Total Pcp = Total storm precipitation (mm)

Max Pcp = Maximum 15 minute rainfall intensity (mm/15min)

Pre-event Q = Pre flood event discharge ( $\text{m}^3/\text{s}$ )

Sampler activation = discharge at which the sampler was activated ( $\text{m}^3/\text{s}$ )

Pk Q = Peak discharge ( $\text{m}^3/\text{s}$ )

Time Pk = Time between first recorded rainfall and peak discharge (hrs)

Lag = Time between peak rainfall intensity and peak discharge (hrs)

*Event 3* (12/04/08) was characterised by a twin-peaked hydrograph with an initial rapid rise and decline followed by a slow rise to peak storm discharge (**Figure 7.5**). The form of the hydrograph appears to have been strongly influenced by the intermittent low-intensity rainfall which initiated the event. Throughout the event, metal concentrations were relatively low, possibly as a result of a previous large flood flow (31/03/08;  $Q_p = 0.371 \text{ m}^3/\text{s}$ ) which might have flushed the majority of

available metals. The hydrograph response was also relatively small and slow, suggesting limited overland flow and, possibly, limited dissolution of surface oxidised metals. At the beginning of the sampling event, Pb concentrations were lower (minimum 105 µg/l Pb) than steady flow concentrations, though a general increase in values was recorded throughout. Zinc concentrations were well below steady flow values (minimum 456 µg/l Zn) throughout the event, although a slight flushing (maximum 647 µg/l Zn) occurred after the first discharge peak. Increasing discharge following this initial peak resulted in dilution thereafter. Copper, Cd, Fe and Mn concentrations were relatively stable at near-steady flow values, though there was some variation in Cu and Fe. A slight decrease in conductivity occurred at the beginning of the event, associated with dilution of the dissolved metal load by increased river flow. River pH fluctuated between 6.8 and 6.9 with no obvious pattern or correlation with any of the other variables.

*Event 4* (06/07/08) was characterised by a rapid rise to a single-peaked hydrograph (**Figure 7.6**). Peak Pb (5003 µg/l), Zn (1791 µg/l), Cd (8 µg/l) and Mn (68 µg/l) concentrations occurred prior to peak storm discharge. Lead concentrations were far in excess of the mean steady flow concentration (269 µg/l Pb) observed in routine baseline sampling (section 6.1.1), when Zn was the main contaminant. This would suggest that Pb, which is far more toxic than Zn, is highly mobile during flood events. Clockwise hysteresis (**Figure 7.4**) in the relationship between metal concentration and flow, with maximum concentrations reached before peak discharge, suggests that a surface or near-surface source of metals - in the mine spoil or river bed - was the primary origin for the spike of the contamination. The occurrence of peak Fe (85 µg/l) and Cu (23 µg/l) concentrations after peak discharge (**Figure 7.6**) and after the other metal peaks suggests a different source for these metals – a source possibly rich in chalcopyrite. Differences observed in the timing of metal peaks could be a result of different surface and/or subsurface flowpaths within the mine spoil dominating at different times during the event, e.g. peaks in Cu and Fe might represent a delayed throughflow component of runoff or, more likely, water arriving from the peaty areas upstream of Dylife. The arrival of mine water from the abandoned stope or Footway shaft is unlikely as this water should also have elevated Pb and

Zn concentrations (section 6.1.1). Another possibility is that Fe and Cu are associated with suspended sediments disturbed from the river bed at high flows, although the greatest turbulence and hence, metal levels, might be expected at peak discharge. In any case, rising Fe levels after peak discharge also coincided with decreasing levels of some of the toxic metals. It is difficult to establish strong relationships between metals during flood events due to variations in discharge, however, strong negative relationships existed between Fe and Pb ( $r = -0.910$ ,  $\alpha = <0.01$ ), Zn ( $r = -0.965$ ,  $\alpha = <0.01$ ) and Cd ( $r = -0.802$ ,  $\alpha = <0.05$ ) on the falling limb of the hydrograph in *Event 4*, possibly indicating that adsorption and/or co-precipitation with Fe acts as an attenuation mechanism in some flood events.

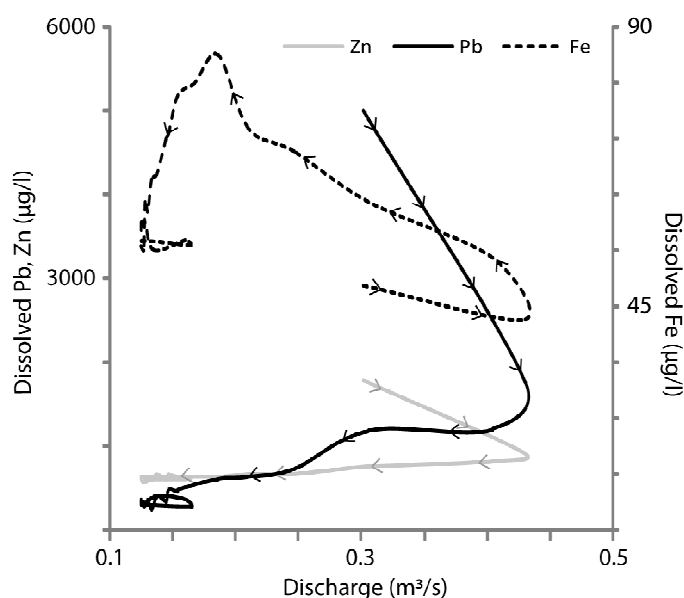
*Event 5* (13/08/08) was similarly characterised by significant metal flushing before peak discharge (6147  $\mu\text{g/l}$  Pb, 918  $\mu\text{g/l}$  Zn, 210  $\mu\text{g/l}$  Cu, 5  $\mu\text{g/l}$  Cd, 763  $\mu\text{g/l}$  Fe, 184  $\mu\text{g/l}$  Mn) (**Figure 7.7**). However, Zn and Cd concentrations did not reach levels recorded in *Event 4*. This may be related to the magnitude of the event which was significantly smaller than *Event 4*. However, this event still recorded the maximum Pb concentration in the study period. The similar peaks in Pb between events might be related to its concentration in the mine spoil which is likely to be significantly greater than Zn. The greater solubility of Zn also means that a higher proportion of available (oxidised) Zn (than available Pb) will likely be flushed from the spoil in any single flood event. Available Zn in any subsequent flood event will be lower than available Pb.

*Event 6* (03/09/08) exhibited the largest flood peak (0.465  $\text{m}^3/\text{s}$ ) of the sampled events (**Figure 7.8**). Despite this, metal concentrations during flushing were considerably lower (maximum 1277  $\mu\text{g/l}$  Pb, 692  $\mu\text{g/l}$  Zn, 26  $\mu\text{g/l}$  Cu) than in *Event 4*, probably reflecting the gradual exhaustion of oxidised material throughout the summer. The lack of response of metal concentrations to a second flood peak in both *Event 5* and *Event 6* suggest that metal exhaustion by successive flood events is an important mechanism controlling metal availability.

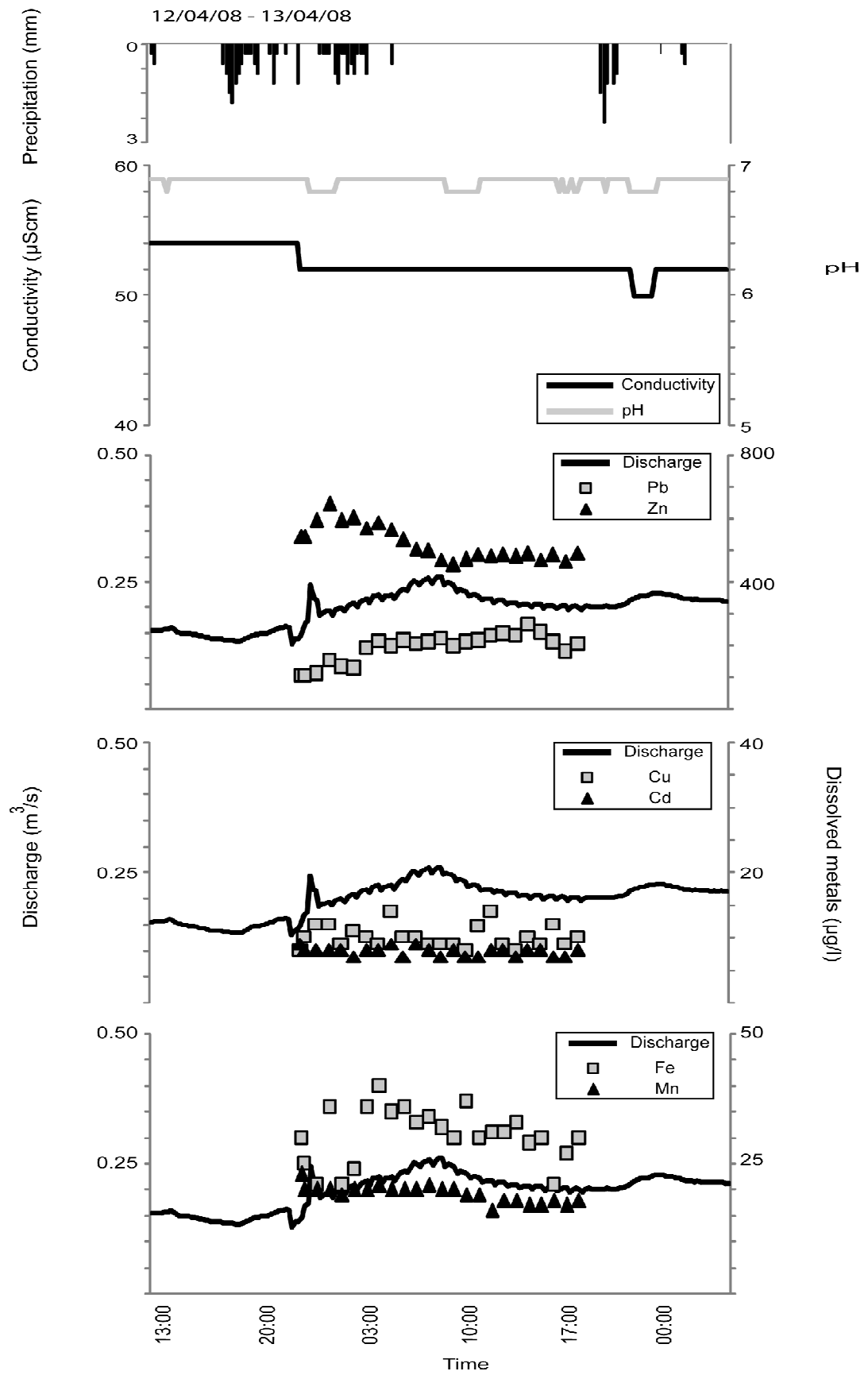
*Event 7* (30/09/08) was initiated by an intense period of rainfall lasting more than 24 hours (50.2mm) (**Figure 7.9**). However, there was little rainfall in the previous

three weeks (40mm) which resulted in the lowest discharge during the study period prior to this event. Due to the decline to annual low discharge, the sampler was not activated until about 7 hours after the start of the flood event. As a result, much of the rising limb of the hydrograph, when metal flushing might be expected, was not sampled. However, elevated metals (maximum 840  $\mu\text{g/l}$  Pb, 881  $\mu\text{g/l}$  Zn, 32  $\mu\text{g/l}$  Cu, 8  $\mu\text{g/l}$  Cd) were still recorded in the initial water samples, possibly reflecting the falling limb of the metal chemograph for the event.

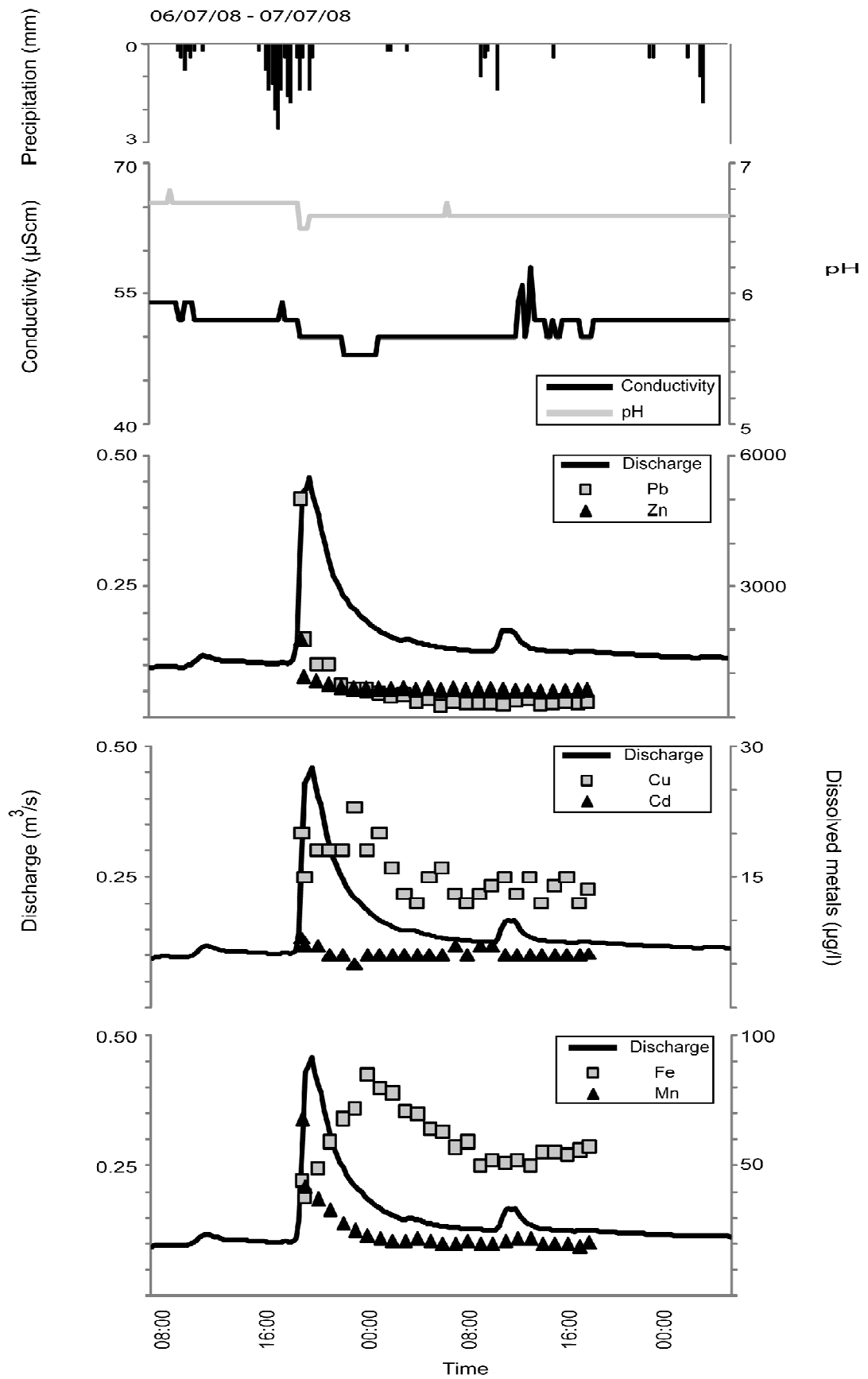
The storm hydrograph in *Event 8* (08/11/08) (**Figure 7.10**) was characterised by a rapid rise in discharge followed by a relatively attenuated fall to baseflow over the course of 12 hours. The event was characterised by metal flushing, however, peak metal concentrations were similar to (279  $\mu\text{g/l}$  Pb) or less than (534  $\mu\text{g/l}$  Zn) steady flow values. Similar to previous flood events, there was some variability in Fe and Cu concentrations throughout. There was very little rainfall in the week preceding this event (5.2mm), however, a large flood flow (26/11/08;  $Q_p = 0.548$ ) prior to the dry period combined with the gradual exhaustion of oxidised metals over the summer and autumn months, perhaps explain the relatively low metal concentrations.



**Figure 7.4:** Clockwise (Pb, Zn) and anti-clockwise (Fe) hysteresis in the relationship between metal concentration and discharge in Event 4 (06/07/08)

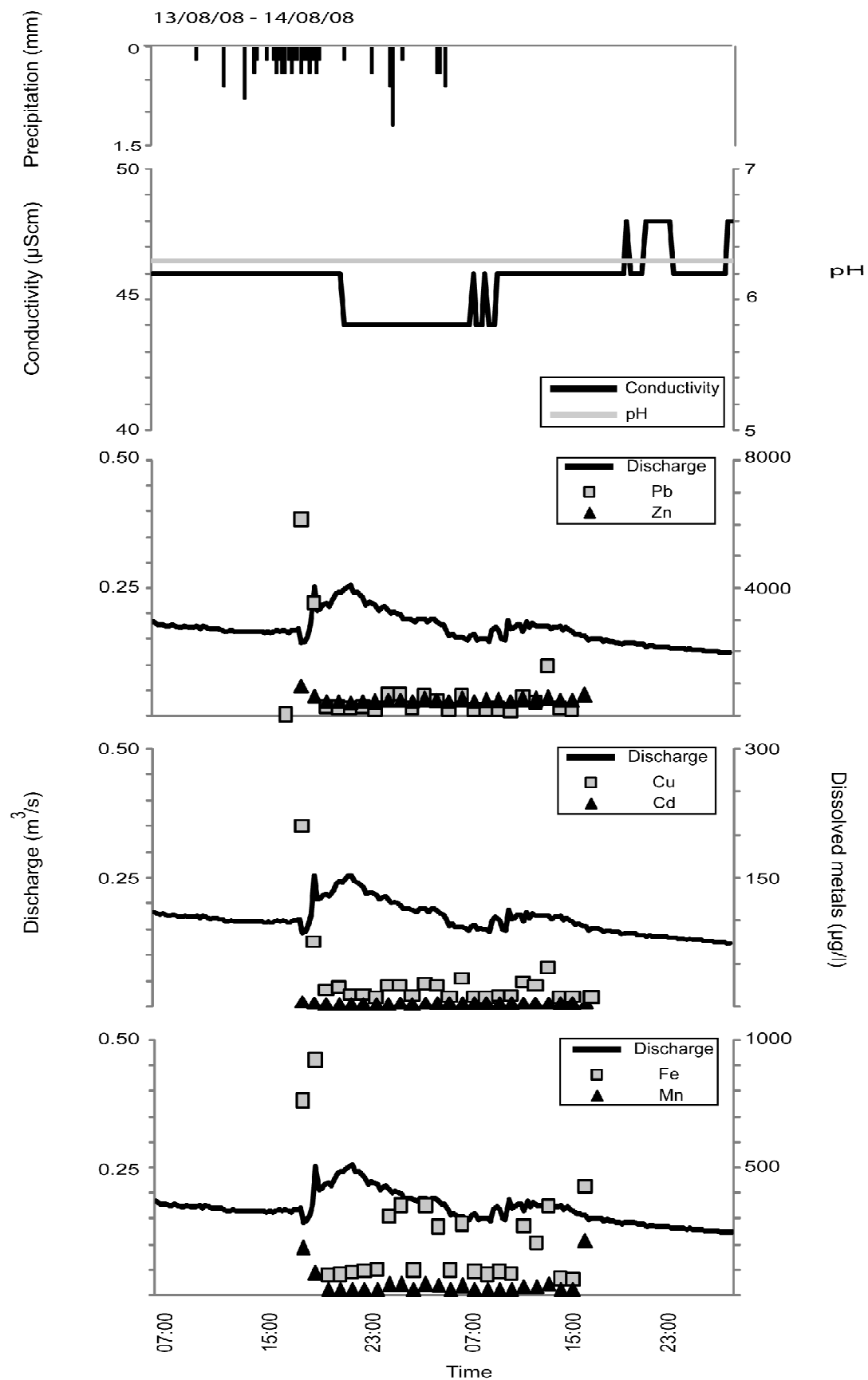


**Figure 7.5:** Mine station flood event 12/04/08

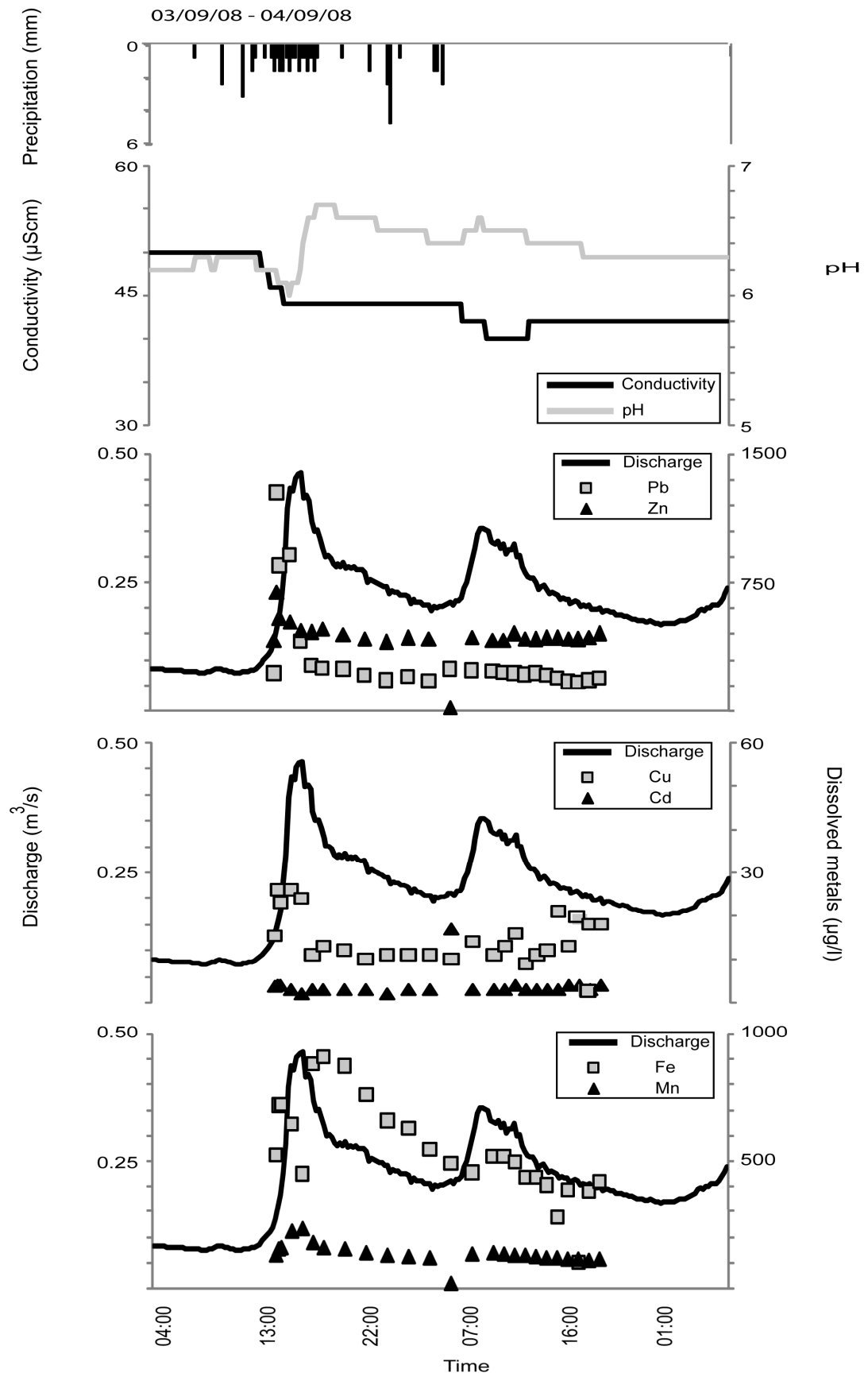


**Figure 7.6:** Mine station flood event 06/07/08

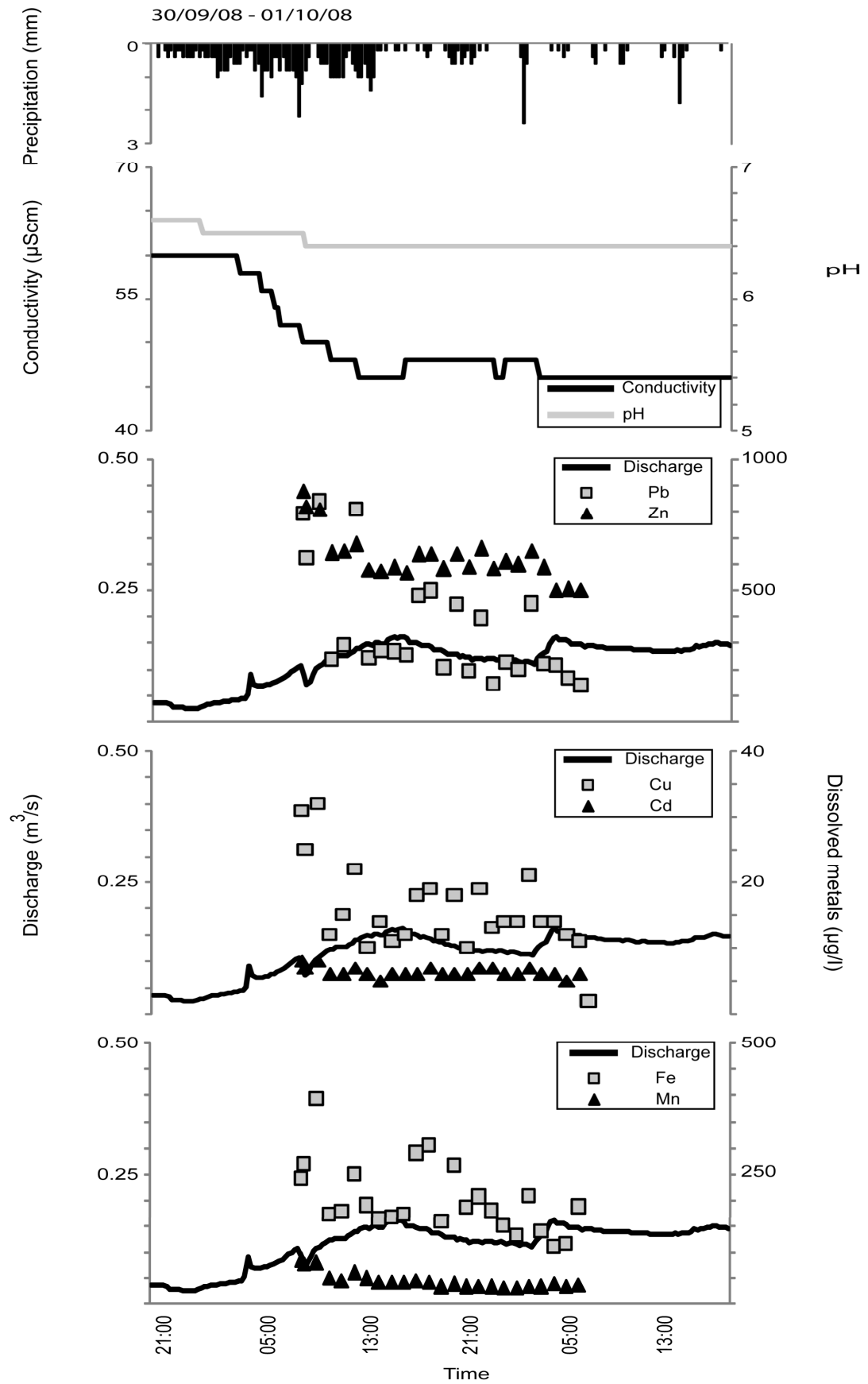




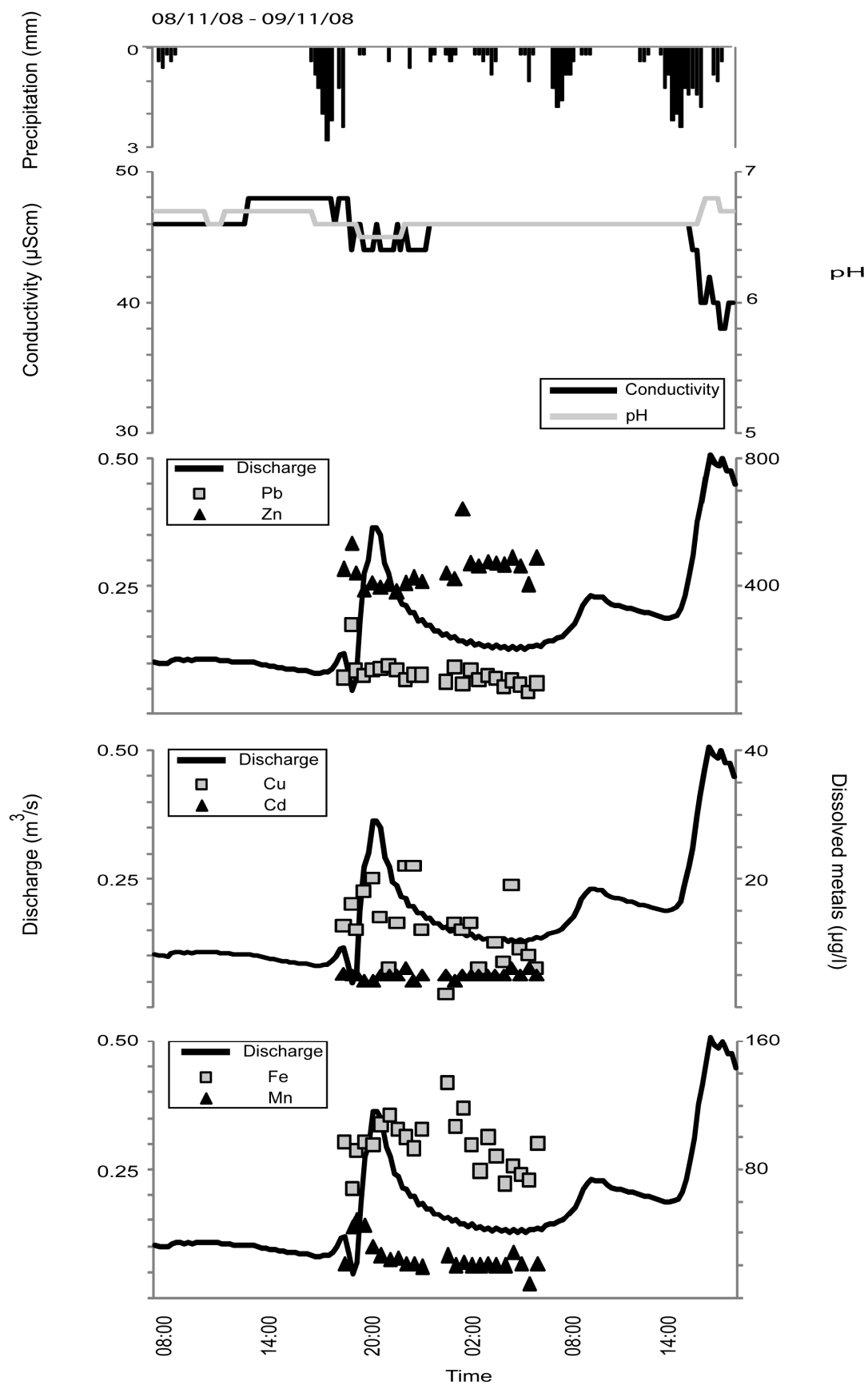
**Figure 7.7:** Mine station flood event 13/08/08



**Figure 7.8:** Mine station flood event 03/09/08



**Figure 7.9: Mine station flood event 30/09/08**



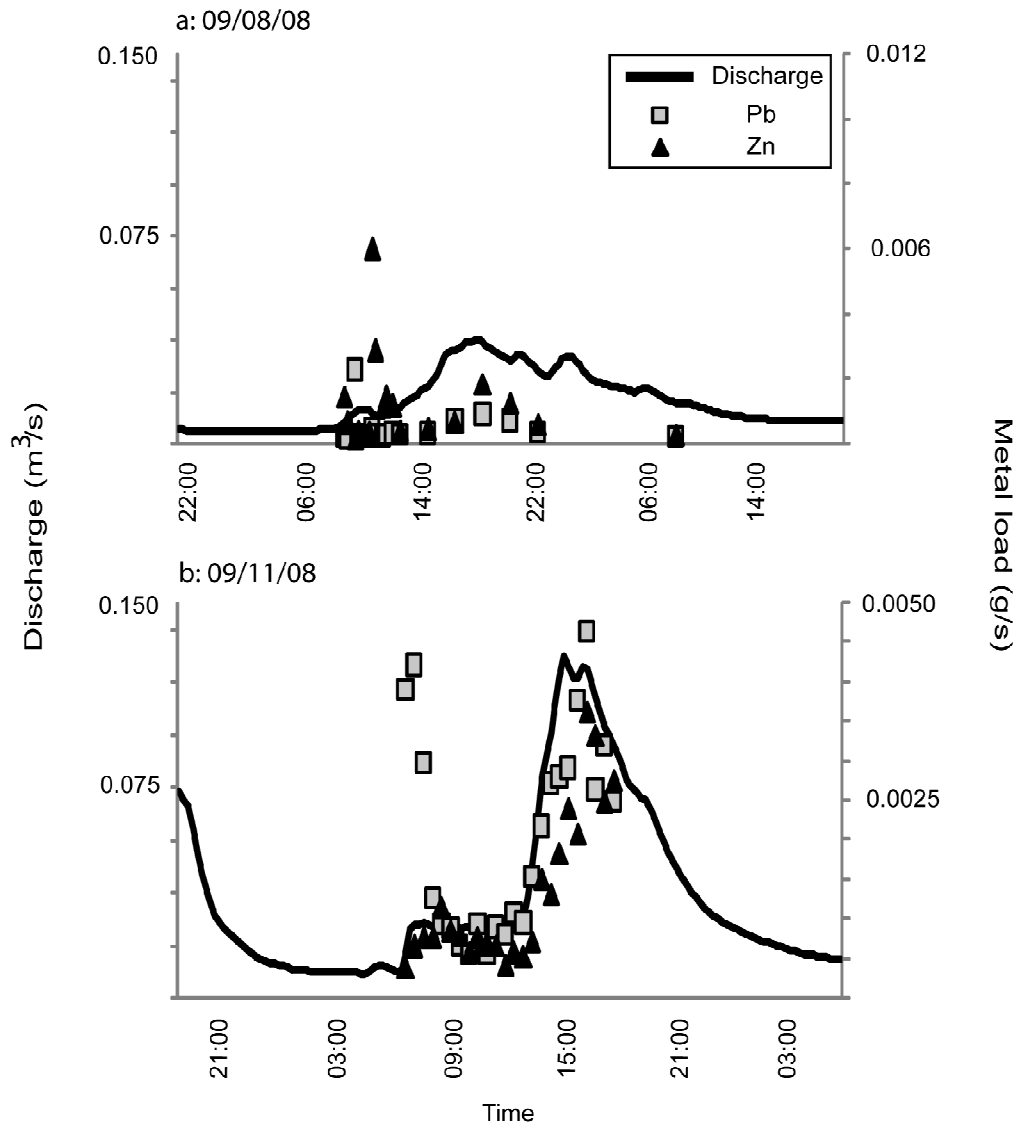
**Figure 7.10:** Mine station flood event 08/11/08

### 7.1.3 Estimating heavy metal fluxes and loads during flood events

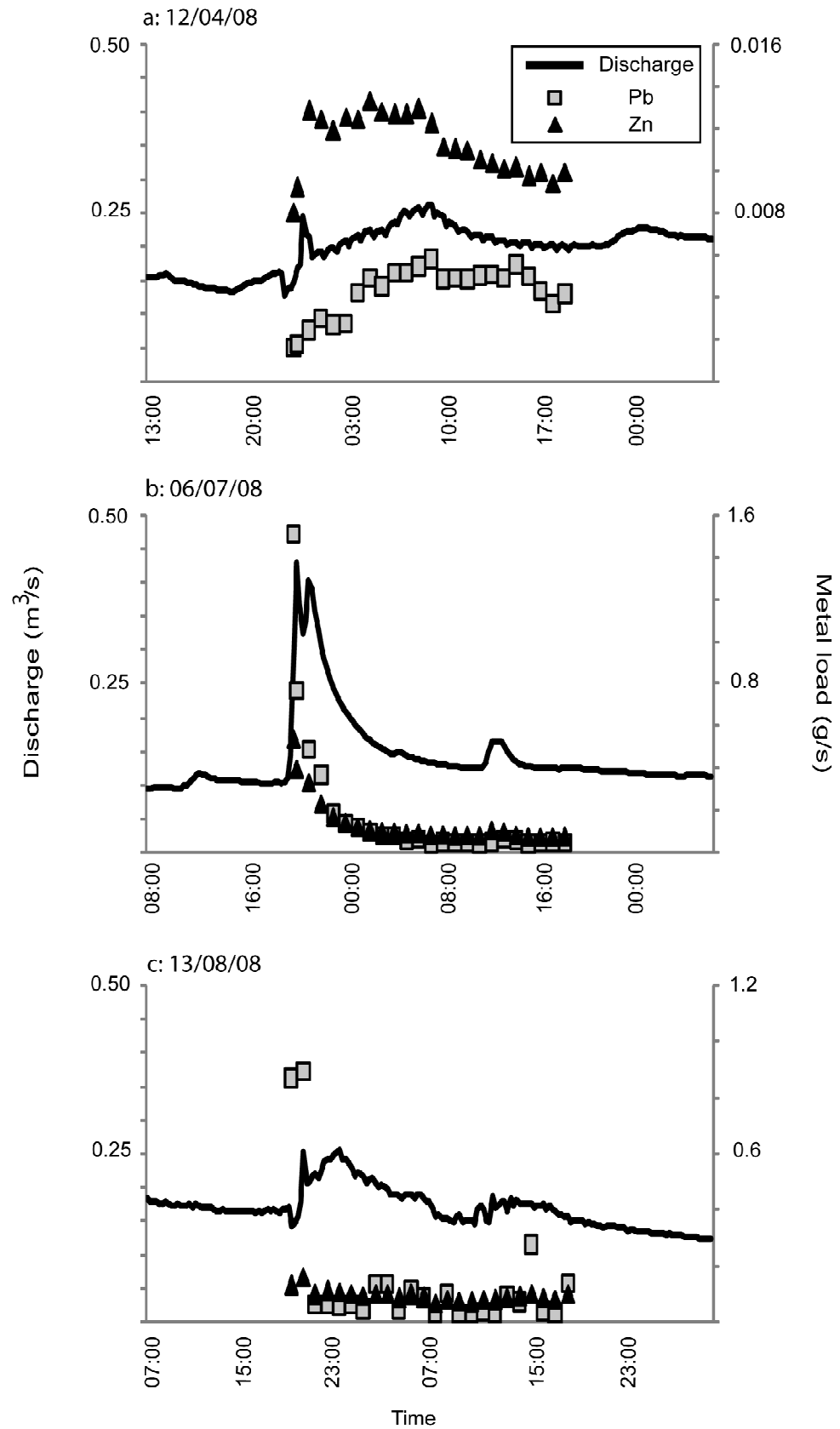
Elemental concentrations have been combined with river discharge to calculate metal fluxes and loads during flood events. Minimum and maximum metal fluxes (g/hr) and total flood metal loads (kg) at both monitoring stations and for all four chalcophile metals are shown in **Table 7.5**. There is considerable variation between the minimum and maximum metal fluxes, as a result of the flushing of metals during the initial stages of runoff, and the sharp decline to baseline values which occurs soon after the peak metal flux. The total metal load for each flood event was low at the control station compared to values for the mine station (**Figures 7.11**). At the mine station, total Zn loads for flood events (c. 24 hrs) were similar to daily loads of between 8 and 16 kg (depending on season) established in section 6.1.3 under steady flow conditions (**Figures 7.12 and 7.13**). This suggests that flood flows have no greater significance than steady flows for the transport of Zn. However, during flood events, total Pb loads of up to 16 kg were estimated. Calculations in section 6.1.3 estimated Pb fluxes between 2 and 5 kg/day under steady flow conditions. This suggests that Pb transport in flood flows has some significance in the annual metal load. The reason behind the different behaviour of the two metals could be related to their solution chemistry. Zinc is more soluble than Pb and a greater proportion of this metal can be leached by slowly moving subsurface waters during baseflow. However, the greater stability of Pb means high loads might be restricted to high flow conditions which disturb and oxidise Pb-enriched sediment. A general trend of decreasing peak metal fluxes in flood events occurred through the summer and autumn months from July to November, most likely a result of the gradual exhaustion of oxidised and available metals (**Figure 7.14**).

**Table 7.5:** Maximum and minimum metals fluxes (g/hr) and total storm metal loads (kg) for flood events at both monitoring stations

Storm Events	Pb			Zn			Cu			Cd		
	Min (g/hr)	Max (g/hr)	Total storm (kg)	Min (g/hr)	Max (g/hr)	Total storm (kg)	Min (g/hr)	Max (g/hr)	Total storm (kg)	Min (g/hr)	Max (g/hr)	Total storm (kg)
<i>Control station</i>												
09/08/08	0.51	8.12	0.03	0.40	22	0.07	0.55	3.50	0.02	0.09	0.89	<0.01
09/11/08	1.95	17	0.18	1.38	13	0.11	0.52	12	0.07	0.09	2.06	0.01
<i>Downstream station</i>												
12/04/08	56	209	3.65	289	481	9.71	4.24	27	0.21	4.77	8.14	0.14
06/07/08	125	5441	16	269	1948	12	5.43	26	0.26	2.70	11	0.10
13/08/08	90	4042	16	241	577	8.04	5.39	153	0.59	1.35	3.65	0.04
03/09/08	127	1429	9.02	11	821	13	7.58	42	0.47	1.74	13	0.11
30/09/08	63	407	3.86	213	341	6.97	4.46	12	0.18	1.82	3.59	0.07
08/11/08	31	179	1.77	88	537	6.34	1.12	26	0.20	0.83	6.29	0.07

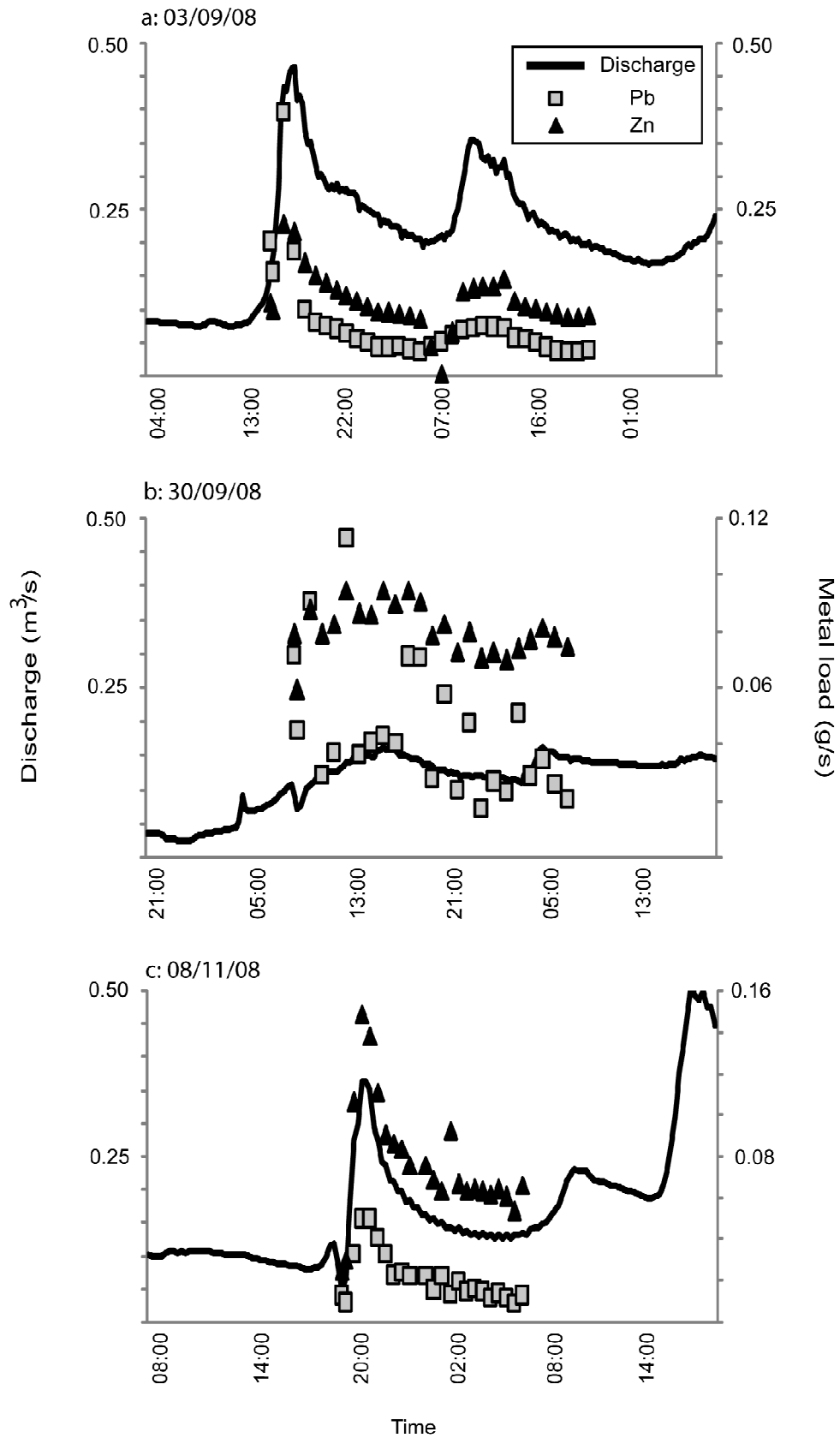


**Figure 7.11:** Metal loads during control station flood events

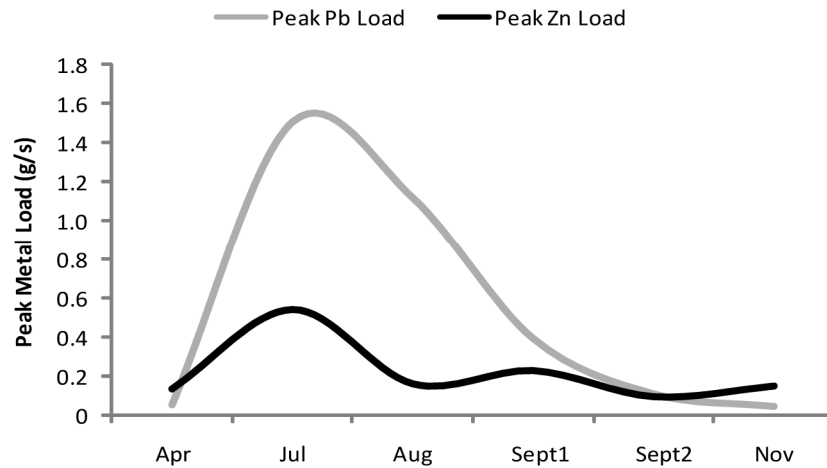


**Figure 7.12:** Metal loads during downstream station flood events – a) Event 3, b) Event 4 and c) Event 5





**Figure 7.13:** Metal loads during downstream station flood events – a) Event 6, b) Event 7 and c) Event 8



**Figure 7.14:** Flood event peak Pb and Zn fluxes at the mine station from spring to autumn

#### 7.1.4 The importance of antecedent soil moisture

In the absence of measured soil moisture, peak storm metal loads were correlated against three separate indices acting as surrogates of antecedent soil moisture in the Afon Twymyn catchment. The antecedent precipitation index (API) provides a representation of the state of wetness of a catchment (Shaw, 2004). It is calculated on a daily basis and assumes soil moisture declines exponentially when there is no rainfall. It assumes that, the further back in time, the less important rainfall is in determining catchment wetness. Thus:

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

where  $API_t$  is the index  $t$  days after the first days  $API_0$ .  $K$  is a recession constant. If there is rainfall then this is added to the index. Two other indices of catchment wetness were utilised – pre-flood event discharge and the number of hours with rainfall in the 10 days prior to the flood event.

Correlations between flood event peak metal loads and pre-event  $Q$  and hours with rainfall were not significant and generally weak (**Table 7.6**). API at 5 and 10 days performed better with strong and significant negative correlations for Pb,

suggesting that the level of flushing of Pb during flood events is strongly linked to catchment wetness. Non-significant correlations for Zn are possibly a function of the greater relative increase in Pb concentrations during flood events. The reasons for the poor performance of the other two indices might be related to variation in the intensity of rainfall (for Hours with rainfall index) and the natural variation which occurs in baseflow throughout the year (for pre-event Q index).

The effect of dry antecedent soil moisture conditions would have been to increase metal oxidation and availability on the surface of the mine spoil and increase the soil moisture deficit. The increased soil moisture deficit will have minimised both throughflow and deeper seated flows that might otherwise be expected to cause, in wetter months, both lateral sub-surface flows from contaminated soil or spoil and groundwater efflux from the abandoned stope.

**Table 7.6:** *Pearson correlation coefficients between flood event peak metal concentrations and catchment wetness indices*

<b>Metal</b>	<b>API (5 days)</b>	<b>API (10 days)</b>	<b>Pre-event Q</b>	<b>Hours with rainfall (10 days)</b>
<b>Pb</b>	-0.827*	-0.904*	0.560	-0.767
<b>Zn</b>	-0.606	-0.780	0.206	-0.151

\* Correlation significant at 0.05

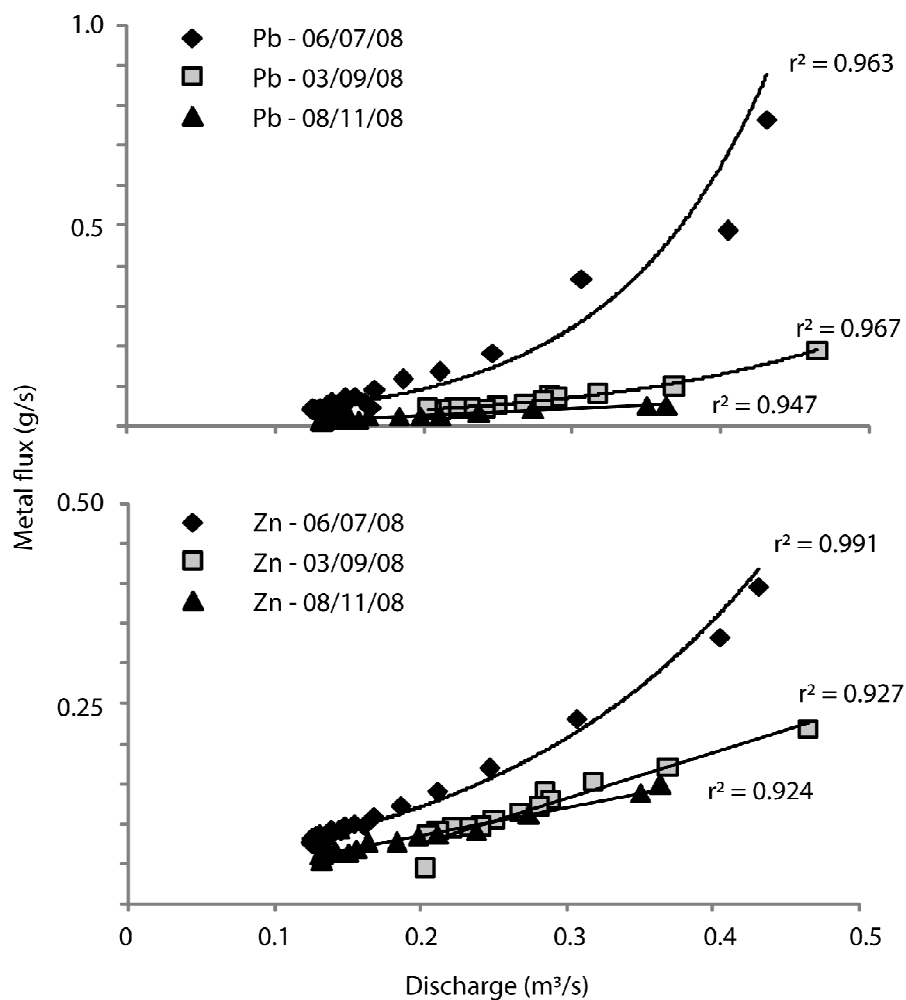
#### 7.1.5 Towards a predictive model of metal flushing at abandoned metal mines

This study has collected much hydrological and chemical information which could be applied in a semi-quantitative predictive model of metal flushing at Dylife mine. In particular, it is possible to generate equations describing two important processes:

1. Attenuation of metals on the falling limb of single-peaked flood hydrographs.
2. Recession limb of single-peaked flood hydrographs.

### *Attenuation of metals on the falling limb of single-peaked flood hydrographs*

Rating curves of discharge and metal load are used widely in remediation and scientific investigations of abandoned mine sites in order to establish parameters and design criteria for treatment technologies and water quality models (Younger *et al.*, 2002). Such rating curves rarely encompass measurements during flood events. As a result, there is a risk of the design metal loads of remediation technologies being frequently exceeded. Given that a large part of the annual metal flux takes place during flood events (Canovas *et al.*, 2008), and many remediation technologies are fine-tuned to treat a narrow range of metal load (Nuttall and Younger, 2000), this can result in significant volumes of contaminated water not receiving treatment during flood events. In this section, rating curves of metals flux and discharge have been applied to three single-peaked hydrographs – *Event 4*, *Event 6* and *Event 8*. Hysteresis limits the predictive powers of simple rating equations for entire flood events. Therefore, regression models were applied to the recession limbs of the flood hydrographs only. Strong and significant regression relationships are evident for both Pb and Zn for all three flood events (**Table 7.7**), illustrating how the rate of fall of metals flux during flood events could potentially be modelled with some degree of confidence. It must be noted, however, that this study has applied regression relationships to simple, single-peaked hydrographs only with no significant complications. Multi-peaked hydrographs might introduce significant uncertainty in the modelled relationship. The relationship between metals flux and discharge changed significantly from July to November, most likely reflecting the gradual exhaustion of metals through the summer and autumn months (**Figure 7.15**). The difference in the relationship between the three rating curves demonstrates the temporal variability in the load/discharge relationship that can occur in flood events between months/seasons. Exponential relationships might be generally more appropriate for Pb and during the summer months when a greater level of flushing is expected. Linear relationships might be best suited for Zn and during the autumn months. As a consequence, it may be appropriate to define multiple regression relationships for flood events in each month or season rather than a single relationship for floods at all times of the year.



**Figure 7.15:** Relationship between metals flux and discharge on the recession limbs of Event 4, Event 6 and Event 8

**Table 7.7:** Regression model summaries for metals flux and discharge on the recession limbs of Event 4, Event 6 and Event 8 (best-fit models in bold)

Regression model		Pb			Zn		
		Event 4 (n = 23)	Event 6 (n = 14)	Event 8 (n = 20)	Event 4 (n = 23)	Event 6 (n = 14)	Event 8 (n = 20)
Linear	$r^2$	0.936	0.934	<b>0.947</b>	0.982	<b>0.927</b>	<b>0.924</b>
Power	$r^2$	0.936	0.957	0.876	0.984	0.804	0.888
Exponential	$r^2$	<b>0.963</b>	<b>0.967</b>	0.834	<b>0.991</b>	0.746	0.891

Note: All model results significant at  $\alpha = <0.01$

**Table 7.8:** Regression equations of best-fit models for metals flux and discharge on the recession limbs of Event 4, Event 6 and Event 8

Storm	Regression model	Regression equation	r <sup>2</sup> value
Event 4 (Pb)	Exponential	$y = 0.013^{9.754x}$	0.963
Event 6 (Pb)	Exponential	$y = 0.011^{6.122x}$	0.967
Event 8 (Pb)	Linear	$y = 0.165x - 0.008$	0.947
Event 4 (Zn)	Exponential	$y = 0.041^{5.356x}$	0.991
Event 6 (Zn)	Linear	$y = 0.566x - 0.036$	0.927
Event 8 (Zn)	Linear	$y = 0.347x + 0.016$	0.924

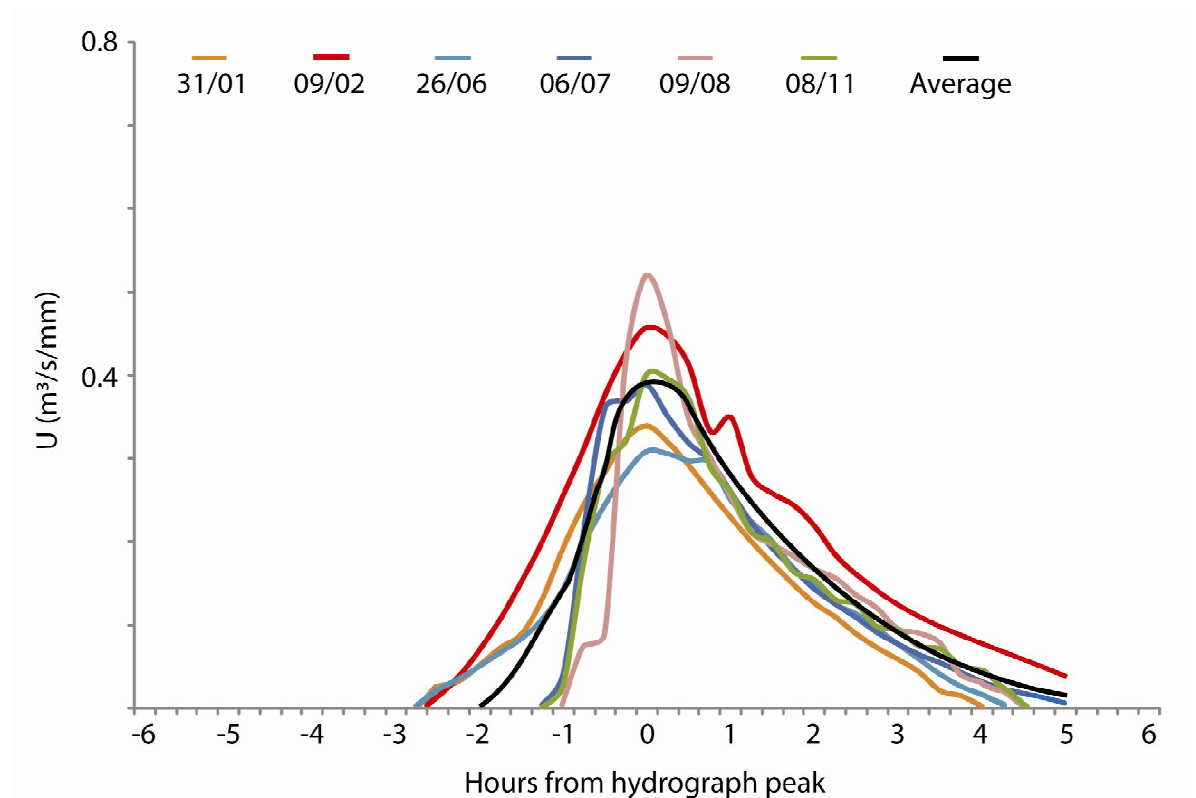
#### *Recession limb of single-peaked flood hydrographs*

Using the unit hydrograph method (Sherman, 1932) (assuming a unit of rainfall over the catchment always produces the same catchment response), it is possible to create a relationship describing the general form of the hydrograph response to rainfall events. Particularly useful from a modelling perspective is an equation describing the rate of fall of the recession curve during flood events. A master or average recession curve could be re-scaled to fit any (single-peaked) hydrograph of the future.

Six single-peaked runoff events of similar magnitude were selected from the mine station discharge record. Storms were selected to cover the range of the discharge record. Stormflow was separated from baseflow using the constant slope method (Shaw, 2004). The resultant hydrographs of direct storm runoff were scaled to become measures of the relative proportion of total direct runoff occurring at each point in time (**Figure 7.16**). Variations in the unit hydrographs are most likely a result of variations in antecedent soil moisture and in the spatial characteristics of rainfall and in the hyetographs of excess rainfall (Chapman, 1996). The relatively short time span of the unit hydrographs (c. 7-8 hours) indicates relatively little storage in the catchment due, principally, to the underlying (generally) impermeable geology, the small size of the catchment and the saturated peaty soils, particularly above Dylife. There is some variability in the time to peak discharge (c. 1-3 hours) suggesting the varying importance of

overland flow and throughflow between events, depending on precipitation characteristics and antecedent moisture conditions.

A single unit hydrograph was obtained using the method of Pilgrim (1987) by averaging the peak discharges and the times to peak and sketching a unit hydrograph that conforms in general shape to the individual samples (**Figure 7.16**). The effective rainfall for the average unit hydrograph was determined by averaging  $T$  hours effective rainfall for the six individual unit hydrographs. The ordinates of this average 3 hour unit hydrograph are given in **Table 7.9**. Through the principles of superposition and proportionality, the unit hydrograph can be used to predict runoff from other precipitation events.

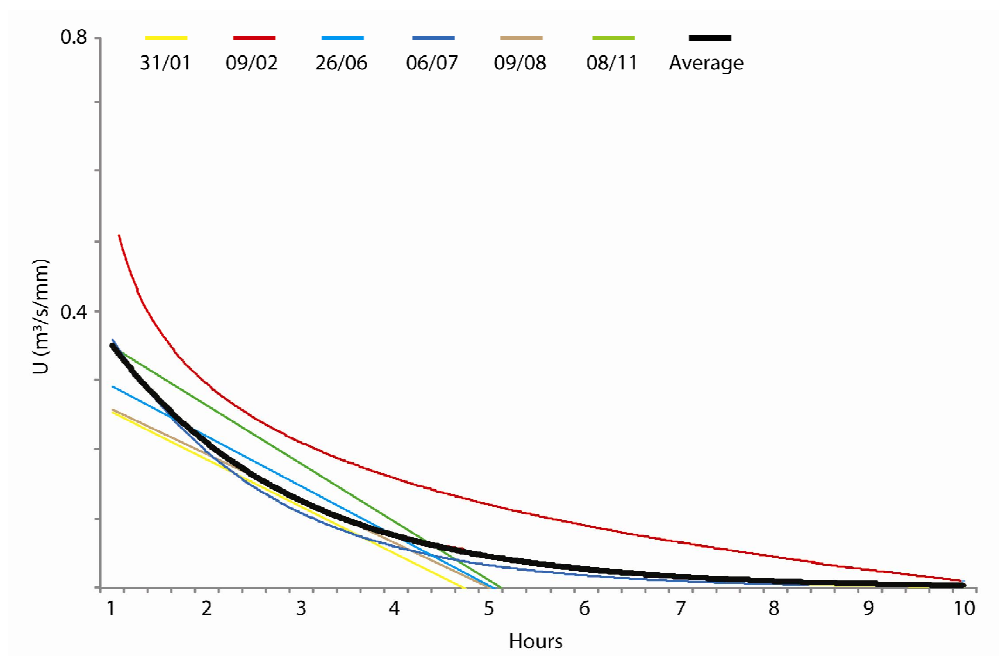


**Figure 7.16:** Unit hydrographs for selected storm events at mine station in 2008 (average unit hydrograph represents 3 hrs effective rainfall)

**Table 7.9:** Ordinates of 3 hr unit hydrograph

Time (hrs) from beginning of UH	0	1	2	3	4	5	6	7
Unit Hydrograph ordinates ( $\text{m}^3/\text{s}/\text{mm}$ )	0	0.15	0.39	0.28	0.17	0.1	0.049	0.02

The best-fit regression lines for each of the unit hydrograph recession curves are illustrated in **Figure 7.17**. The results from a variety of models and the regression equations for each of the best-fit models are presented in **Table 7.10** and **Table 7.11**, respectively. Although there is some variation in which model produces the best-fit to the data, there is also a great deal of commonality with linear, exponential and log-linear models all yielding strong and significant regression relationships. This gives confidence in the predictability of the rate of fall of the recession limb of single-peaked flood events in the Afon Twymyn at Dylife mine. The average recession curve, calculated by averaging data from all of the recession limbs, is best approximated by an exponential model.



**Figure 7.17:** Best-fit and average regression lines for recession limbs of unit hydrographs



**Table 7.10:** Regression model summaries for recession limbs of unit hydrographs (best-fit models in bold)

Regression model / Storm date		31/01	09/02	26/06	06/07	09/08	08/11	Average
Linear	$r^2$	<b>0.979</b>	<b>0.982</b>	<b>0.984</b>	0.959	0.883	0.926	0.966
Power	$r^2$	0.606	0.652	0.661	0.804	0.920	0.845	0.807
Exponential	$r^2$	0.851	0.876	0.914	<b>0.987</b>	0.972	0.911	<b>0.984</b>
Log	$r^2$	0.935	0.924	0.862	0.954	<b>0.986</b>	<b>0.951</b>	0.954

Note: All model results significant at  $\alpha = <0.01$

**Table 7.11:** Regression equations of best-fit models for recession limbs of unit hydrographs

Storm	Regression model	Regression equation	$r^2$ value
<b>31/01</b>	Linear	$y = -0.021x + 0.341$	0.979
<b>09/02</b>	Linear	$y = -0.026x + 0.465$	0.982
<b>26/06</b>	Linear	$y = -0.020x + 0.345$	0.984
<b>06/07</b>	Exponential	$y = 0.524^{-0.15x}$	0.987
<b>09/08</b>	Log	$y = -0.17\log(x) + 0.643$	0.986
<b>08/11</b>	Log	$y = -0.14\log(x) + 0.474$	0.951
<b>Average</b>	Exponential	$y = 0.502^{-0.12x}$	0.984

## 7.2 Discussion

### 7.2.1 The impact of short-term flood events on heavy metal concentrations

This study has identified significant flushing of heavy metals during flood events in the Afon Twymyn at Dylife mine. During flushing events, peak metal concentrations were many times greater than those observed under steady flow conditions. Notably, peak Pb concentrations were far greater than peak Zn concentrations suggesting that, during flood events, Pb is the primary contaminant from an ecological perspective. This highlights the importance of including flood sampling during water quality monitoring programmes. Standard water quality monitoring would present an incomplete picture where Zn is the main contaminant

and remediation might be focussed primarily on treating this metal. Several other authors have noted similar flushing of metals during flood events at metal mines (Grimshaw *et al.*, 1976; Canovas *et al.*, 2008). However, as far as is known, this is the only study to investigate hydrochemical variation in multiple flood events over the course of a year and to identify variability in metal flushing and the shape of the metal chemograph throughout seasons.

During all of the sampled flood events and for most metals, hysteretic effects were evident in the relationship between metal concentrations and discharge. For most metals (e.g. Pb, Zn), the relationship proceeded in a clockwise fashion with dissolved concentrations increasing on the rising limb of the hydrograph and decreasing on the falling limb. However, anti-clockwise hysteresis also occurred for some metals, most notably Fe. The phenomenon of hysteresis during flood events is well-established for general water chemistry (Webb *et al.*, 1987) and for heavy metals at mine sites (Lambing *et al.*, 1999; Canovas *et al.*, 2008). In the present study, the hysteresis effect and the variation in the concentration of different metals between and during flood events probably reflected a number of factors, including: flood hydrograph characteristics, antecedent soil moisture, the concentration of different minerals at the mine (e.g. galena is likely to be more abundant than sphalerite or chalcopyrite), the different origins of material within the mine spoil and catchment, the different solution chemistry of minerals, and different flowpaths (particularly in the mine spoil) operating at different times.

Hysteresis in relatively small river catchments, such as the Afon Twymyn, is generally a function of vertically distributed and differentiated sources of runoff, rather than areally aggregated runoff (Webb *et al.*, 1987). The immediacy of the initial metal peaks and the lack of significant fluctuations thereafter might suggest surface and/or river bed materials were the immediate contamination sources during flood events at Dylife mine. Point source contributions from mine workings (e.g. adits and shafts) do not seem to be important. Indeed, observations during stormflow identified only one mine opening (a collapsed stope) to discharge into the river (section 6.1.1). Sampling of mine water emanating from this portal revealed relatively low heavy metal concentrations and circum-neutral pH (section

6.1.1). Some researchers (Hammarstrom *et al.*, 2005; Canovas *et al.*, 2008; Gilchrist *et al.*, 2009) have suggested that dissolution and flushing of efflorescent metal salts, which have accumulated on the surface of mine spoil, is a primary contamination mechanism at mine sites. Keith *et al.* (2001) found efflorescent salts to occur as thin crusts in intermittent streams and pools on the surface of mine spoil. Evaporation of these water bodies acted to concentrate metals and acidity and eventually lead to the accumulation of surface crusts which could be dissolved and flushed into rivers during storms. At Dylife mine, water with elevated dissolved metal concentrations collects in pools between the main spoil tips area and the main river channel (section 6.1.1). Several small ephemeral streams also drain the mine spoil, most notably the southern channel (MineT) to the east of the mine. During flood events, 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 probably important mechanisms leading to high dissolved metal concentrations on the rising limb of hydrographs. In some flood 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 (pore) waters.

In addition to overland flow and the dissolution of surface evaporative salts, it is possible that translatory flows (Hewlett and Hibbert, 1967) played a role in generating the observed metal peaks. 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 the storm runoff of a flood event. Genereax and Hooper (1998) calculated, from a range of catchment sizes and land covers, that  $70 \pm 20\%$  of storm flow at peak discharge was composed of pre-event water. The relative contribution of translatory flow to the flood 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 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). Due to the unconsolidated nature of most mine spoils, there often exist preferential flow paths (e.g. macropores) within the spoil capable of storing and transferring large

quantities of water (Hawkins, 2004). In general, mine spoil exhibits a hydraulic conductivity two orders of magnitude greater than the adjacent unmined strata (Hawkins, 1998). The predominant rainfall pattern (low intensity, high frequency) in the upper Twymyn catchment (section 5.1) likely ensures that the Dylife mine spoil remains partially saturated throughout the year. The greater residence (and leaching) time of pre-event water in the mine spoil means this water is likely to contain high levels of dissolved heavy metals (Cidu and Mereu, 2007), possibly higher levels than that leached by overland flow at the beginning of a flood event. As a result, it is probable that both overland flow and translatory flow are important both in the generation of contaminants and in their routing to the river channel. Complicating factors leading to variation in the relative importance of each of these flow processes between flood events include precipitation characteristics and antecedent moisture conditions (Renshaw *et al.*, 2003). The possible importance of translatory flows in mine spoil during flood events has not been mentioned in other studies of metal flushing at mine sites (e.g. Sanden *et al.*, 1997; Canovas *et al.*, 2008). Perhaps this is because these studies have taken place in semi-arid regions and considered only flood events at the transition from dry to wet season, when the saturation levels and residence times of water in mine spoils are low. In such circumstances, peak metal concentrations at or before peak discharge would most likely be related to quick return flow, with throughflow only contributing on the falling limb of the flood hydrograph (Canovas *et al.*, 2008).

After the initial flushing of metals, the majority of flood events were characterised by rapid decreases in metal concentrations to values similar to or lower than pre-event values, providing strong evidence for the mine spoil and river bed as the only sources of contamination. Considerable variation in heavy metal concentrations can occur in rivers draining catchments with multiple mining areas or where there are several sources of contamination (mine spoil/tailings and mine portals) (Mighanetera *et al.*, 2009). In the present study, the rapid decrease in metal concentrations was most likely due to rain-water dilution and the fact that available contaminant had been scavenged in the first flush. However, several other processes could also account for the attenuation in metal concentrations.

Changes might be related to fluctuations in stream pH and in the oxidation-reduction potential of the river water. It is difficult in this study to establish relationships between pH and metal concentrations during flood events due to variations in discharge, however, the general inverse relationship between dissolved heavy metals and pH is well known (Younger *et al.*, 2002), and it is highly likely that fluctuations in stream pH (acidity) on the falling limb of flood hydrographs (e.g. *Event 6*) influenced metal concentrations. Changes in pH might have resulted in metals being released or scavenged by hosts (e.g. Fe/Mn). The majority of flood events were characterised by decreases in pH during the initial stages of runoff or at peak discharge, indicating inputs of acidity. Increased acidity was likely to have its provenance in dissolution of oxidised metals accumulated in the mine spoil and/or the river bed or its margins. Carbonic acid from decomposing plant and animal matter will also have been a factor (Neal, 1997). Decreases in pH might also be related to precipitation of ferric iron hydroxides (Johnson, 2003). Iron hydroxide precipitate or 'ochre' is not common in the bed or banks of the Afon Twymyn. However, there are extensive deposits on the surface of the mine spoil and many small temporary channels with ochre deposits are evident during storm periods. Precipitation of Fe hydroxides and dissolution of metal sulphates in surface and sub-surface runoff would release acidity into this water before it reaches the river channel. During flood events, changes in pH were not dramatic and, in one case, i.e. *Event 5* (13/08/08), no change occurred. The maintenance of a steady pH throughout an event is still indicative of inputs of acidity since, without mine drainage, dilution with storm runoff would be expected to increase pH (Lambing *et al.*, 1999). Keith *et al.* (2001) found that water in Boulder Creek, California, maintained a pH of 3 even during a substantial flood event. In modelling experiments without mine drainage, the effect of dilution by rainfall was to raise the river pH to 5.1. Some flood events in this study exhibited increases in stream pH suggesting that river water composition was influenced by water from other parts of the catchment. For example, in *Event 6* (03/09/08), the increase in pH after peak storm discharge might have been the result of dilution and/or the delivery of non-mine sourced water after the initial storm runoff.

Several important studies have demonstrated that the solute content in overland flow and subsurface flow is related to the length of dry period before a flood event (e.g. Walling and Foster, 1975; Klein, 1981). Antecedent soil moisture conditions are thought to be an important mechanism controlling, not only the speed of response of a hydrograph to a rainfall event, but also the availability of solutes to be leached and flushed into a river. The importance of dry antecedent soil moisture conditions in the generation of larger metal concentrations and loads has also been suggested by several authors studying mining-impacted rivers (Bird, 1987; Braungardt *et al.*, 2003; Desbarats and Dirom, 2004). However, there has been little evidence in these studies linking increased metal loads to low catchment wetness. The strong relationship between high API (antecedent precipitation index) scores and low Pb levels in flood events in this study suggests that antecedent soil moisture conditions were important in determining the level of flushing of Pb. However, two other indices failed to identify a similar relationship. The failure of these indices could be related to the nature of precipitation and discharge in upland central Wales. Studies which have suggested 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 division between long, dry summers and subsequent large rainfalls in the autumn months. The unpredictable and short-lived nature of wet and dry periods in upland central Wales most likely made the assessment of antecedent soil moisture influence more difficult. The climate of Wales prohibits the extent of oxidation that occurs during the long dry summers of south-west Spain for example. The atypical rains in the summer of 2008 might also have clouded the picture. A further complicating factor could be the importance of translatory flows which might be responsible for elevated metals during wetter periods.

#### 7.2.2 The importance of metal loads

Calculation of metal loads is important as they provide an indication of metals flux at different temporal scales. Metal loads transported by the Afon Twymyn during flood events are small compared to some other metal mining regions (**Table 7.12**). Differences reflect the size of the river system, the extent of mining and mineralisation, the buffering capacity of local rocks and the length of mine

abandonment. In the studies below, a large proportion of the annual metal load was flushed during storm events.

**Table 7.12:** Comparison of metal loads during flood events in mining-affected river catchments (modified from Canovas *et al.*, 2008)

Variable / River system	Afon Twymyn Event 4 (06/07/08)	Rio Tinto Canovas <i>et al.</i> (2008)	Boulder Creek Keith <i>et al.</i> (2001)	Contrary Creek Dagenhart (1980)
Q <sub>max</sub> (m <sup>3</sup> /s)	0.430	127	17	0.58
pH (min/max)	6.0 / 6.7	2.3 / 3.6	3.0	2.9 / 4.0
Pb <sub>max</sub>	<b>5.00</b> (1.51)	-	-	-
Zn <sub>max</sub>	<b>1.79</b> (0.54)	<b>145</b> (820)	<b>5.5</b> (2.7)	<b>70</b> (21)
Cu <sub>max</sub>	<b>0.018</b> (<0.01)	<b>148</b> (830)	<b>3.7</b> (1.8)	<b>17</b> (3.7)
Cd <sub>max</sub>	<b>0.017</b> (<0.01)	-	-	-

Metal loads in brackets (g/s)

**Metal concentrations in bold (mg/l)**

In the Afon Twymyn, it appears that flood events lasting approximately 24 hrs transport a similar Zn load as would be transported in a day under steady flow conditions. It seems that, for Zn, the processes of flushing and dilution in flood events cancel each other out. However, transportation of Pb during flood flows is far greater than during steady flows. Given the more toxic nature of Pb, such high Pb loads will likely have serious deleterious impacts on aquatic ecology and would pose serious concerns over the efficiency of potential remediation strategies. Although water samples were not collected further downstream of Dylife during flood events, depending on the dilution capacity of the river and the magnitude of metal loads, it can be inferred that significant breaches of Environmental Quality Standards (EQSs) for Pb, Zn and possibly Cu occurred beyond the mine, in stretches of the Afon Twymyn that would normally pass EQSs. This poses a concern, not only for aquatic ecology, but also for the recovery of trout populations which have so far not managed to penetrate the Afon Twymyn upstream of Pennant (Parsons Brinckerhoff Ltd., 2005).

Due to the experimental setup, in many cases it was difficult to sample the initial stages of storm runoff. In addition, the technical problems encountered with the mine station sampler prevented a setup where more samples were taken at the beginning of an event. As a result, it is possible that higher metal fluxes were missed at the beginning of some sampling events. Therefore, the metal loads calculated in this study for flood flows are likely to be underestimates.

### **7.3 Chapter summary**

Most flood events substantially increased heavy metal concentrations and loads, and the potential toxicity of river water at Dylife mine. Measured metal concentrations during flood events were far greater than Environmental Quality Standards (EQSs) and it is possible that serious breaches of EQSs occurred for some distance downstream of Dylife mine. The immediacy of the metal flush on the rising limb and peak of each hydrograph suggests a surface source of metals as the primary source of contamination and overland flow as the principal component of runoff delivering metals to the river. The source of metals was most likely efflorescent metal sulphates on the surface of the mine spoil, and highly mobile and bioavailable metals adsorbed to the sediment of the river bed/margins. However, metal-rich, translatory flows may become increasingly important during wetter periods.

The lack of variation of metal concentrations after the initial peaks suggest there were no variations in mine water contributions throughout events and that mine spoil and river bed material were the only contaminant sources. Dry antecedent soil moisture conditions appear to have been important in creating sporadically higher Pb availability and in dispersing it during the first, but not necessarily the largest, pulse of subsequent runoff. The main mechanisms accounting for dilution of metals after peak discharge were likely a combination of dilution by rainwater, adsorption and co-precipitation of metals with Fe solids, and the gradual exhaustion of available metals throughout the event.

Estimates of heavy metal loads (in particular Pb) during flood events highlight the importance of flood flows in the annual metal load of mining-impacted rivers.



Furthermore, the discrepancies recorded in Pb loads between steady and flood flows highlight the importance of including high-resolution temporal sampling of river water chemistry under all flow conditions when investigating contaminant/ecosystem relations and developing remediation strategies. The relationships established between flood event metals flux and discharge and the equations describing the rate of fall of hydrograph recession limbs demonstrate the potential for modelling metal flushing at abandoned mine sites like Dylife where the pattern of metal flushing during flood events is relatively simple and not confounded by multiple sources of contamination.

Although many of the results of this study may not quantitatively relate to other mining-impacted rivers, the patterns of variation observed provide evidence of the key factors to consider more generally when characterising mining-impacted rivers and/or investigating possible remediation strategies.

## 8. The Impact of Metal Mine Contamination on Macroinvertebrate Communities

### 8.0 Introduction

Benthic macroinvertebrate communities can be severely impacted by metal mine drainage (Stoertz *et al.*, 2002; Knott *et al.*, 2009). The key position of macroinvertebrates in aquatic ecosystems means that negative impacts on them can have widespread consequences for the entire aquatic ecosystem. The most frequent contaminants in metal mining-impacted rivers are dissolved heavy metals, sulphates, acidity and metal precipitates (Braungardt *et al.*, 2003). Different concentrations and combinations of these contaminants, as well as variations in local lithology and background water chemistry, can lead to great variability between regions in the response of aquatic systems to mine pollution. Furthermore, a number of biotic factors, including feeding mechanism and size, can strongly influence the toxicity of metal mine contamination to macroinvertebrates (Krantzberg, 1989). Classification of aquatic ecosystem status for the EU Water Framework Directive will be achieved using macroinvertebrate communities as diagnostic tools. Yet, variation in the character of metal mine pollution and in the response of macroinvertebrate communities poses questions over the reliability of these organisms as a biodiagnostic tool in metal mining-impacted rivers.

The aim of this chapter is to investigate the relationship between metal mine contaminants and the macroinvertebrate community of the Afon Twymyn, addressing research questions 5 and 6 in section 1.1. The following objectives have been formulated to achieve this goal:

1. Investigate macroinvertebrate community structure in the Afon Twymyn.
2. Assess the health of the macroinvertebrate community using a variety of biotic and diversity indices.
3. Examine the environmental factors influencing macroinvertebrate community structure in the Afon Twymyn.

#### 4. Investigate metal bioaccumulation in macroinvertebrates.

### 8.1 Macroinvertebrate community health

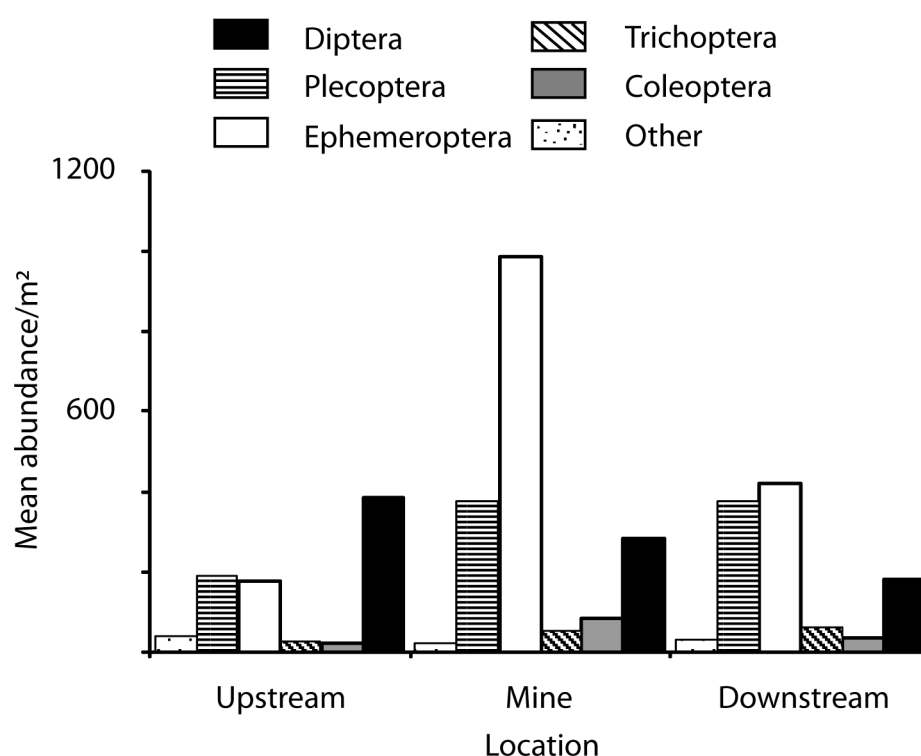
Investigations of river water chemistry and sediment geochemistry in Chapter 6 identified the Afon Twymyn to be seriously contaminated by drainage from Dylife mine. In Chapter 7, flood events were observed to significantly increase the potential toxicity of the river water, if only for a short time period. Due to the extent of water and sediment contamination, it is hypothesized that the macroinvertebrate community of the Afon Twymyn is severely impacted, reflecting a wider classification of the river ecological status as 'poor' (section 2.6). Based on field and laboratory investigations (Armitage, 1980; Winner *et al.*, 1980), the most impacted macroinvertebrates are expected to include species of Ephemeroptera (mayfly) and Trichoptera (caddisfly).

#### 8.1.1 Linear variation in macroinvertebrate community structure

A total of 89 macroinvertebrate samples were collected from the Afon Twymyn and 39 taxa were recorded in these samples (**Appendix 8.1**). The total number of macroinvertebrates sampled was 11,209 (March, 1,981; June, 5,022; October, 4,206). The estimated total invertebrate density at all sites varied over the study period from 10 – 4,220 individuals/m<sup>2</sup>.

The mean number of individuals in the major macroinvertebrate orders found at control, mine and downstream sites are illustrated in **Figure 8.1**. At control sites (22-29), the major macroinvertebrate orders recorded were Diptera (true fly larvae) (46%), Plecoptera (stonefly) (23%) and Ephemeroptera (mayfly) (21%) (**Table 8.1**). At mine sites (7-21), there was a shift in community structure and the assemblage was dominated by Ephemeroptera (55%), with decreases in the percentage of Plecoptera (21%) and Diptera (16%). Downstream of the mine (1-6), macroinvertebrate communities were characterized by Ephemeroptera (38%) and Plecoptera (34%). The percentage of Diptera (16%) remained fairly constant. The distribution of the other major macroinvertebrate orders was relatively stable throughout the Afon Twymyn, with the exception of Trichoptera (caddisfly), which increased from 2.9%, at both control and mine sites, to 5.7% at downstream sites.

Macroinvertebrate taxa recorded under 'Other' included Oligochaeta, Gammaridae, Sphaeriidae, Zygoptera, Anisoptera, Lymnaeidae, Planariidae and Ostracoda. Overall, Ephemeroptera made up 42% of the macroinvertebrate community, with Plecoptera (24%) and Diptera (23%) being the next most abundant orders.



**Figure 8.1:** Mean abundance of major macroinvertebrate orders for all three macroinvertebrate surveys

**Table 8.1:** Percentage of macroinvertebrates in the major orders at each site group

Macroinvertebrate Order	Control sites	Mine sites	Downstream sites	Afon Twymyn
Diptera	46.3	15.8	16.3	22.6
Coleoptera	2.6	4.7	3.3	5.1
Trichoptera	2.9	2.9	5.7	2.4
Ephemeroptera	21.2	54.7	38.1	42.4
Plecoptera	22.4	20.8	34.1	25.1
Other	4.6	1.1	2.5	2.4
Total	100	100	100	100

Closer examination of the macroinvertebrate assemblage reveals that one or two families dominated each order (**Table 8.2**). Simuliidae and Chironomidae were the most abundant Diptera, reaching maximum densities of 2,920/m<sup>2</sup> and 760/m<sup>2</sup>, respectively. Chironomidae were more abundant at control and downstream sites, whereas Simuliidae were more evenly distributed. The low relative abundance of Chironomidae at mine sites is a little surprising as this family has been studied extensively (e.g. Janssens De Bisthoven *et al.*, 2004) due to its apparent high tolerance of metal mine contamination and dominance of the most polluted stretches of rivers (Armitage *et al.*, 2007). The use of Chironomidae as a single diagnostic measure of metal mine contamination has been suggested by Winner *et al.* (1980). Coleoptera were represented principally by Scirtidae and Elmidae. *Elmis aenea* and *Limnius volckmari* comprised the Elmidae taxa, and reached densities of 300/m<sup>2</sup> and 110/m<sup>2</sup>, respectively, primarily at mine sites. Trichoptera species were distributed relatively evenly throughout the system. *Hydropsyche siltalai* was the most abundant Trichoptera species recorded at a density of 360/m<sup>2</sup>, while other less abundant species included *Polycentropus flavomaculatus* (50/m<sup>2</sup>), *Rhyacophila dorsalis* (110/m<sup>2</sup>) and *Limnephilidae* sp. (40/m<sup>2</sup>). Ephemeroptera were dominated by *Baetis rhodani* at densities of up to 2,840/m<sup>2</sup> at mine and downstream sites. Baetidae are considered to be the most metal tolerant Ephemeroptera family (Beasley and Kneale, 2002) and *B. rhodani* was by far the most numerous species (of any macroinvertebrate) collected in this study. A similar spatial pattern was observed for Heptageniidae, another Ephemeroptera family, which reached densities up to 56/m<sup>2</sup>. In terms of abundance and number of taxa, Plecoptera were the most widespread macroinvertebrates in the Afon Twymyn. Plecoptera are generally considered to be more tolerant of metal pollution than many of the other macroinvertebrate orders (Beasley and Kneale, 2003). Four principal families were identified: Leuctridae, Chloroperlidae, Nemouridae and Perlodidae. The most commonly occurring species were *Chloroperla* sp. (300/m<sup>2</sup>), *Isoperla grammatica* (130/m<sup>2</sup>), *Leuctra hippopus* (1740/m<sup>2</sup>), *Amphinemura sulcicollis* (270/m<sup>2</sup>) and *Protonemura praecox* (180/m<sup>2</sup>). *Chloroperla* sp., *L. hippopus* and *I. grammatica* were evenly distributed throughout the catchment, however, *A. sulcicollis* and *P. praecox* were found predominantly at mine sites. Oligochaeta (420/m<sup>2</sup>) were the most frequently occurring of the remaining taxa, being recorded throughout the catchment. However, they were

notably absent from the most heavily polluted river stretch adjacent to the main spoil tips area. This is surprising as, much like Chironomidae, Oligochaeta are generally considered to be most abundant in heavily contaminated stretches of river (Gerhardt, 2007) due to the elimination of more sensitive macroinvertebrate species. Gammaridae and Mollusca were almost completely absent from the river, which was not unexpected given the low calcium and slightly acidic conditions observed in the river (section 6.1.1).

**Table 8.2:** Macroinvertebrate families making up the major orders (%)

Order	Macroinvertebrate Families (%)	
Diptera	Chironomidae (35%)	Simuliidae (57%)
Coleoptera	Elmidae (46%)	Scirtidae (39%)
Trichoptera	Hydropsychidae (50%)	
Ephemeroptera	Baetidae (84%)	
Plecoptera	Chloroperlidae (22%)	Leuctridae (65%)
Other	Oligochaeta (90%)	

#### 8.1.2 Linear and seasonal variation in biological index scores

In this section, a range of biotic and diversity indices are used in an attempt to measure the impact of metal mine contamination on the macroinvertebrate community. An introduction to these indices and a discussion of the rationale behind their use has been presented in section 4.5.4.

Very few significant differences were noted in the measured biological indices between locations and seasons (**Appendix 8.2**). In general, diversity (Shannon-Weiner) and dominance (Berger-Parker) scores were not significantly different between locations (**Figures 8.2 and 8.3**). However, mean scores for the entire study period did increase (dominance) and decrease (diversity) slightly at mine sites (**Table 8.3**). This is, possibly, a result of the impact of metal mine contamination, the effect being the elimination of sensitive species at the expense of more tolerant species (e.g. *L. hippopus* and *B. rhodani*). However, the lack of significant changes in diversity and dominance indices makes it difficult to infer this process with any confidence. Seasonal differences in diversity and

dominance were equally unclear. A general pattern of increasing dominance scores was observed from March to October, although this pattern was only significant between October and March (**Appendix 8.2**). Decreased diversity scores were noted in June and October. The observed seasonal pattern in diversity and dominance scores may reflect increased dissolved metal concentrations in June and October relative to March (section 6.1.2).

The number of macroinvertebrate taxa present in the Afon Twymyn remained relatively constant for much of the year, except in October, when numbers increased with distance downstream (**Figures 8.4**). Macroinvertebrate abundance remained relatively constant in March; however, increased abundances were recorded at mine and downstream sites in June and October (**Figure 8.5**). The highest mean macroinvertebrate abundances were recorded in June and the lowest in March (**Figure 8.5**). This pattern represents a gradual increase in macroinvertebrate fauna in the river from March to June prior to emergence of aquatic insects sometime after this. The overall pattern appears to be one of maintained or increased abundance and number of taxa with distance downstream in the Afon Twymyn. Generally, these metrics would be expected to increase with distance downstream in a catchment due to greater habitat area and increased nutrients (Clements *et al.*, 1992). Values are also greater in June and October reflecting the increased number of individuals following reproduction through the summer months and early autumn. The absence of depressed scores at mine sites or during the months of June and October (when metal concentrations and loads were greatest) suggests relatively little negative impact on macroinvertebrate abundance and number of taxa.

No significant differences were recorded in BMWP or ASPT values between locations or seasons (**Appendix 8.2**), reflecting the inadequacy of these indices in discerning the impacts of metal pollution (**Figures 8.6 and 8.7**). As discussed previously (section 4.5.4), these indices have been developed primarily for detecting organic pollution. However, these indices are used widely in England and Wales to measure biological status in all watercourses, regardless of the suspected pollution source/type. Percent EPT taxa generally increased at mine sites (**Figure 8.8**), where values were significantly different to control site values

(**Appendix 8.2**). This is surprising given EPT taxa are generally considered to be the most pollution sensitive macroinvertebrate taxa (Lenat, 1988). The increase at mine sites is probably a result of the large number of Plecoptera families present at these sites, which could indicate metal contamination (due to the apparent metal tolerance of this order) or, paradoxically, a healthy river ecosystem (aside from metal pollution, they are generally intolerant of pollution). The removal of Plecoptera taxa from this metric and the measurement of percent ET taxa instead resulted in less difference between locations. This is because Ephemeroptera and Trichoptera taxa were more even in their distribution in the Afon Twymyn than Plecoptera taxa.

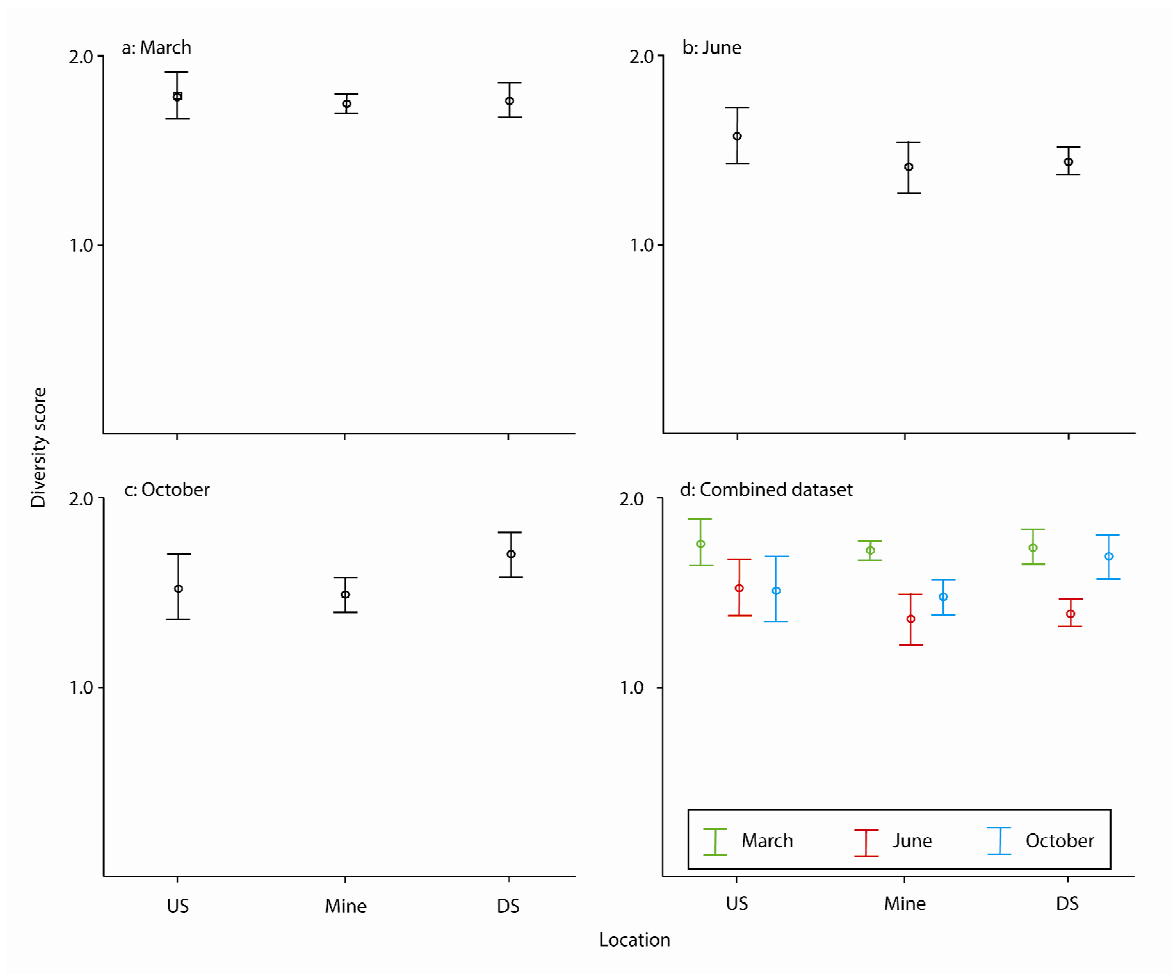
From a total of 51 possible AWIC scoring taxa, only 28 occurred at study sites. The missing taxa were principally from the most acid sensitive AWIC groups. Differences in values between locations and seasons were generally significant (**Appendix 8.2**). Much like other indices, improved AMIC scores were apparent in June and October probably related to increased numbers of offspring in these months. A general pattern of increasing scores occurred with increasing distance downstream (**Figure 8.9**). This pattern most likely reflects increases in pH with distance downstream. Mean scores did not decrease at mine sites, reflecting the lack of significantly acidic drainage from the mine. As a result, this index was not successful in identifying the impact of metal mine contamination.

From the examination of community structure and biological indices, the macroinvertebrate fauna of the Afon Twymyn appears to be in a relatively healthy state, with most of the major orders of macroinvertebrate present. This result conflicts with the water and sediment data (Chapter 6 and Chapter 7), which would suggest that the macroinvertebrate community should exhibit a measurable impact. Far from being severely impacted, Ephemeroptera and Trichoptera taxa were found throughout the Afon Twymyn, although, one mayfly taxa was found to dominate the order. The greater abundance of Plecoptera taxa and Baetidae, particularly at mine sites, might reflect a superior tolerance of metal pollution compared to other macroinvertebrate taxa. However, these taxa are also expected to be abundant in unpolluted river systems (Biological Monitoring Working Party, 1978).

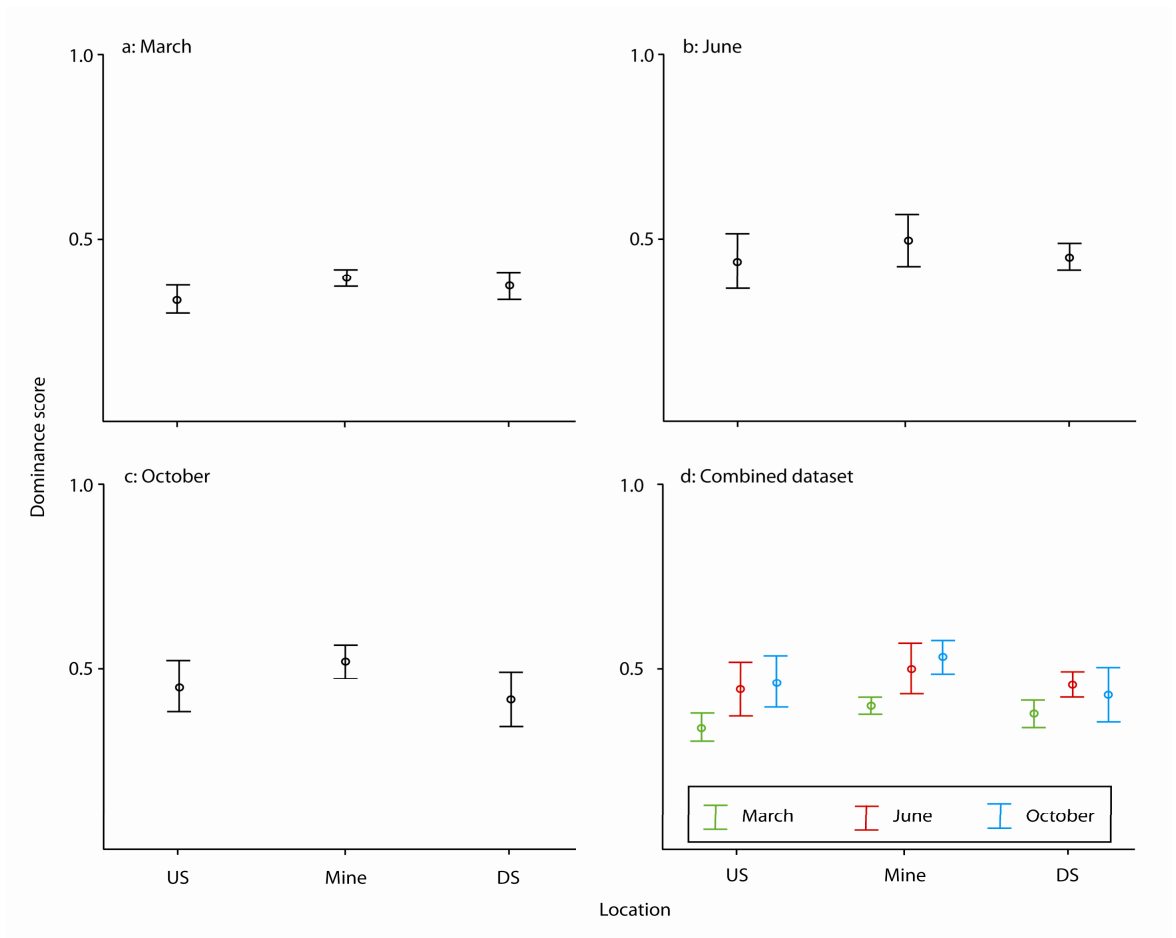


**Table 8.3:** Mean and range (in parenthesis) of calculated biotic and diversity indices at each site group

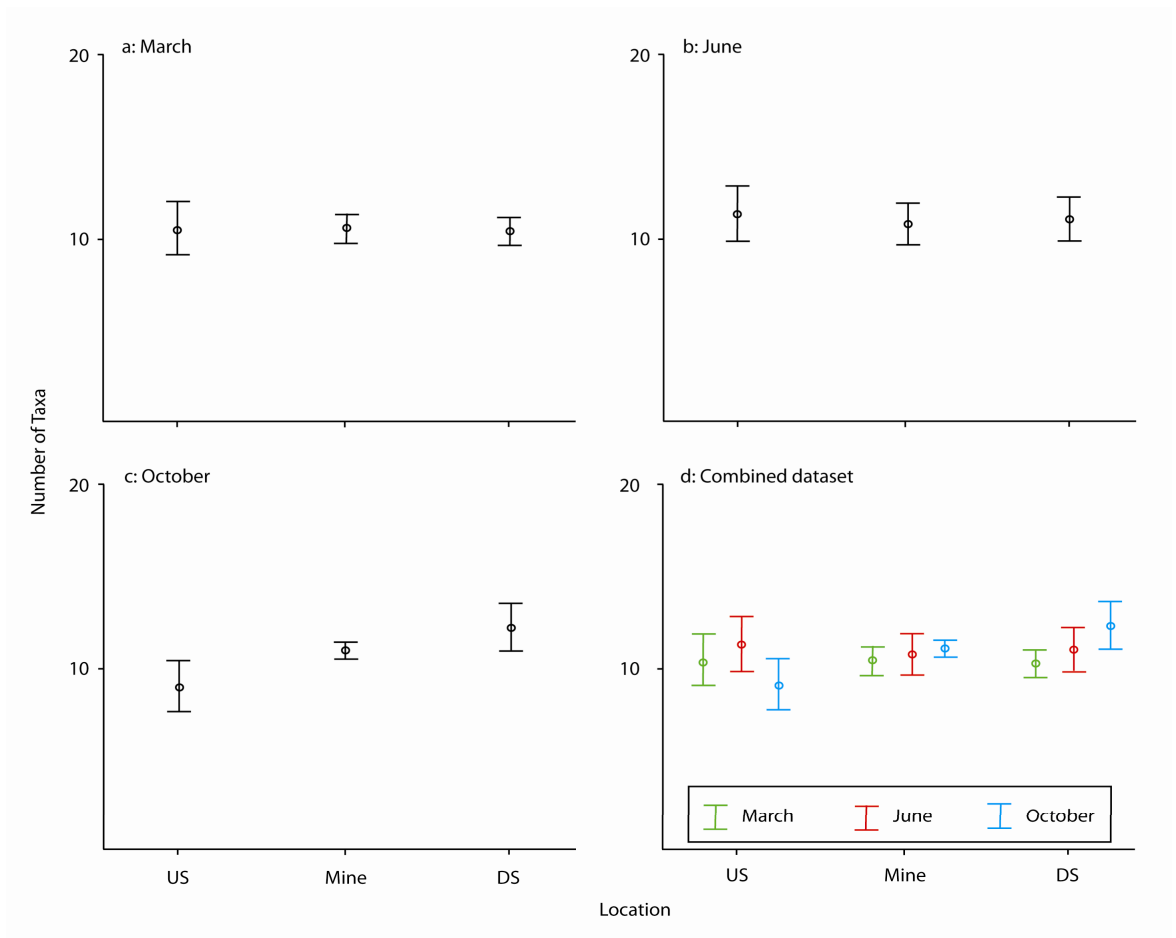
Indices	Mean		
	Control sites	Mine sites	Downstream sites
Diversity	1.65 (1.18	1.56 (0.98 –	1.65
(range)	– 2.1)	1.94)	(1.4 – 1.79)
Dominance	0.41 (0.24 –	0.47 (0.33 –	0.41 (0.36 –
(range)	0.68)	0.72)	0.54)
No. Taxa	10.2	10.8	11.3 (7.5
(range)	(7 – 15)	(6 – 13.7)	– 14)
Abundance	102.5 (42	166.2	198.7 (139.3 –
(range)	– 249)	(26 – 225.7)	396.5)
% EPT Taxa	52.8 (11.6 –	78.6 (46.4 –	73.7 (43.6
(range)	100)	97.1)	– 92)
ASPT	7.2	7.0	6.8
(range)	(5.4 – 8.1)	(5.1 – 8.0)	(6.1 – 7.6)
BMWP	98.8	95.2	91.1
(range)	(38.5 – 122)	(38 – 125)	(42.5 – 119)
AWIC	3.6	3.7	4.1
(range)	(1.0 – 6.0)	(2.8 – 4.6)	(3.5 – 4.6)



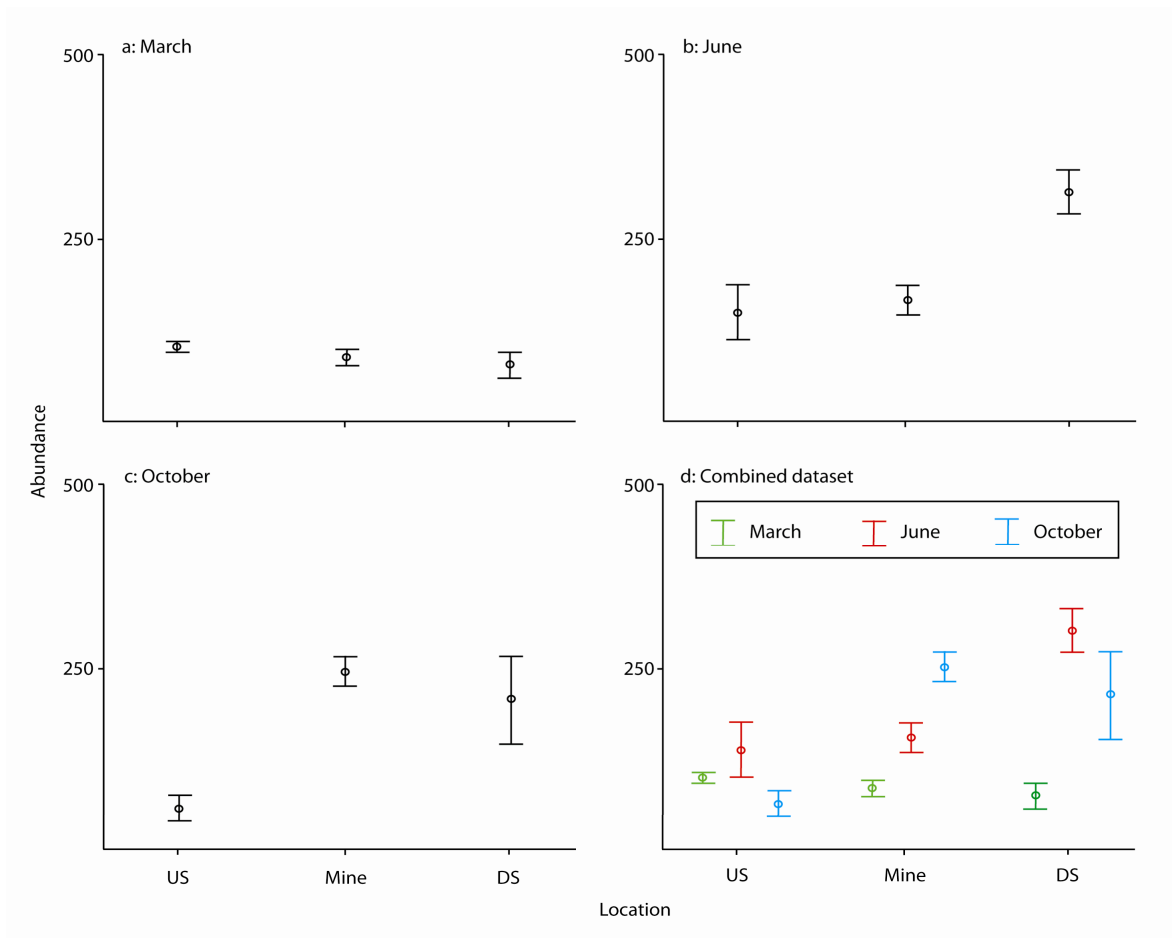
**Figure 8.2:** Linear and temporal variation in mean scores (with 1 standard error) for Shannon-Wiener diversity index. a) March, b) June, c) October, d) Combined dataset



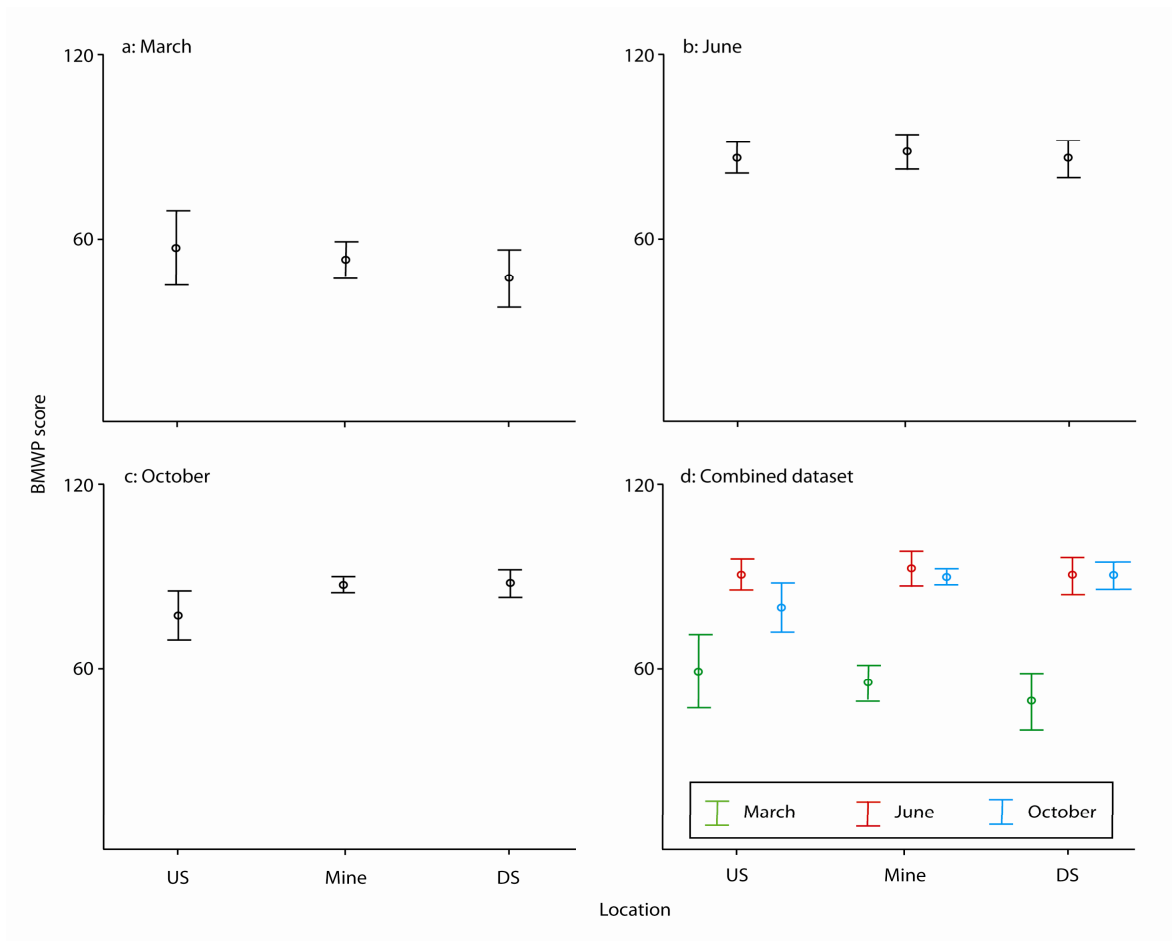
**Figure 8.3:** Linear and temporal variation in mean scores (with 1 standard error) for Berger-Parker dominance index. a) March, b) June, c) October, d) Combined dataset



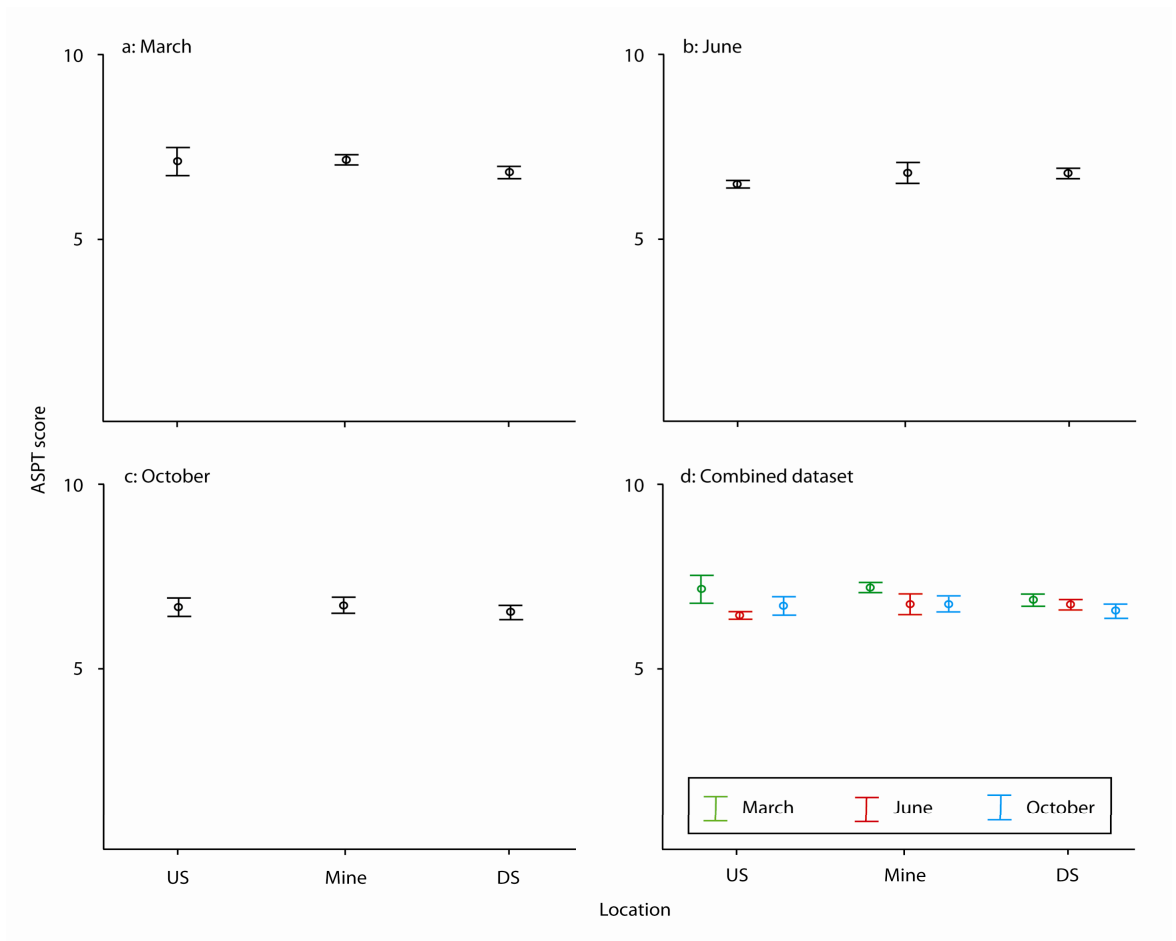
**Figure 8.4:** Linear and temporal variation in mean scores (with 1 standard error) for number of macroinvertebrate taxa. a) March, b) June, c) October, d) Combined dataset



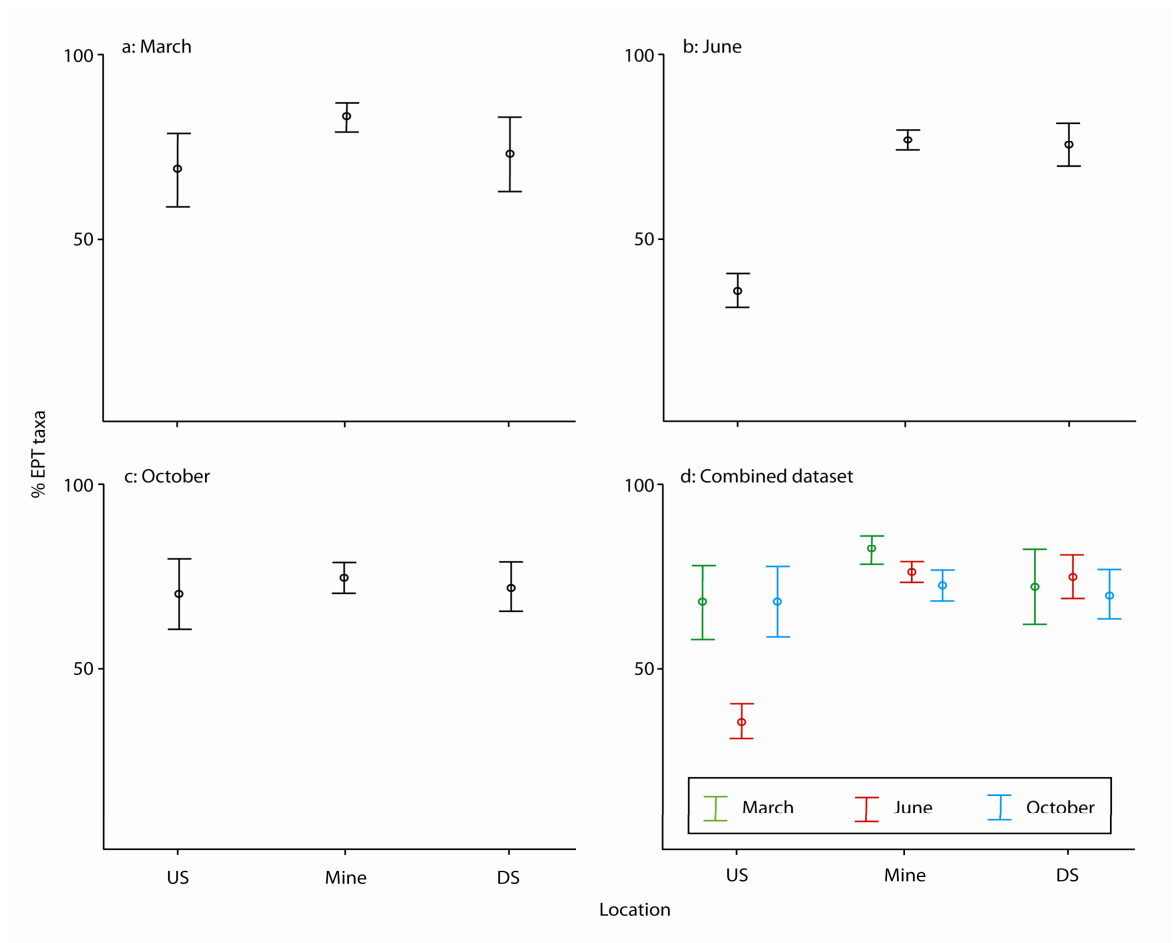
**Figure 8.5:** Linear and temporal variation in mean scores (with 1 standard error) for macroinvertebrate abundance. a) March, b) June, c) October, d) Combined dataset



**Figure 8.6:** Linear and temporal variation in mean scores (with 1 standard error) for BMWP index. a) March, b) June, c) October, d) Combined dataset

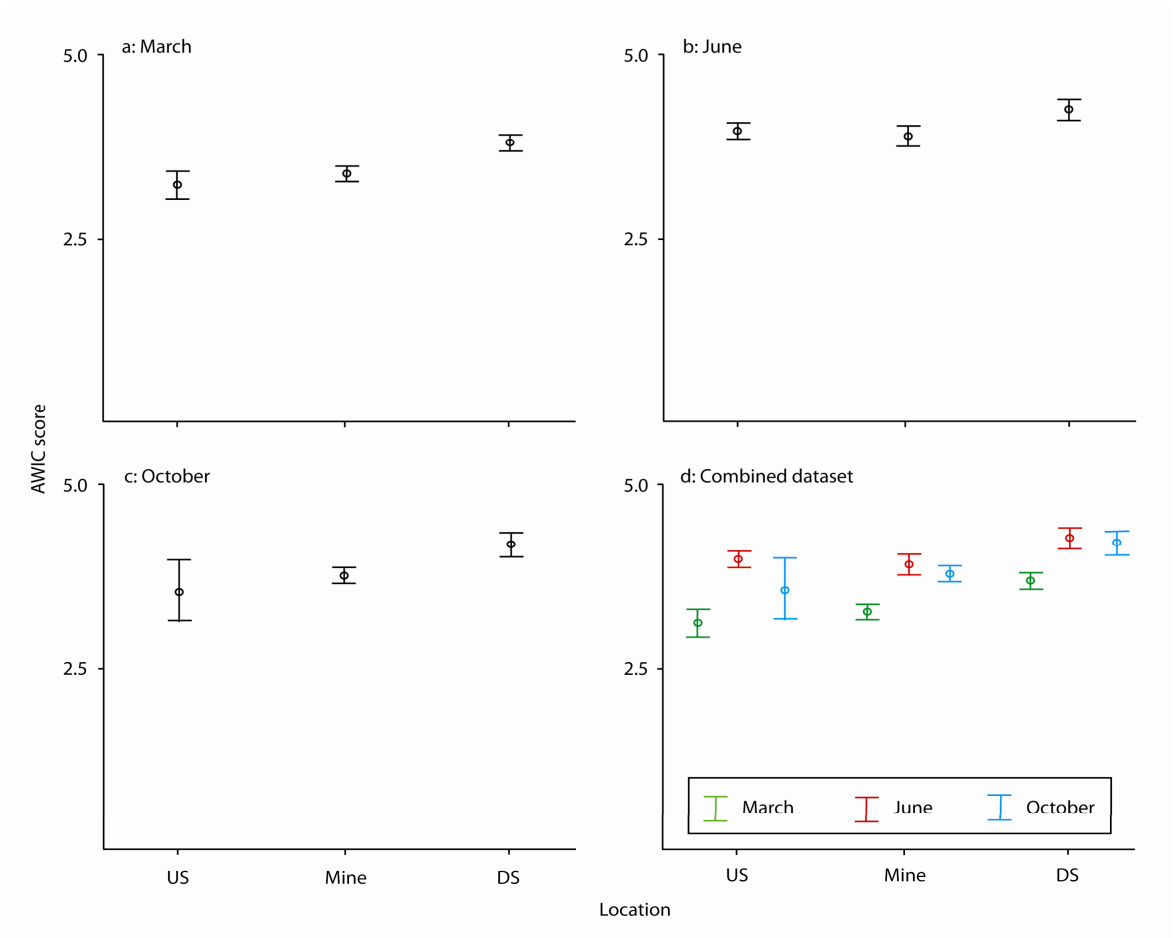


**Figure 8.7:** Linear and temporal variation in mean scores (with 1 standard error) for ASPT index. a) March, b) June, c) October, d) Combined dataset



**Figure 8.8:** Linear and temporal variation in mean scores (with 1 standard error) for % EPT index. a) March, b) June, c) October, d) Combined dataset





**Figure 8.9:** Linear and temporal variation in mean scores (with 1 standard error) for AWIC index. a) March, b) June, c) October, d) Combined dataset

## 8.2 Ordination analysis

The previous analyses did not identify any significant negative impact on the macroinvertebrate community as a result of metal mine pollution. Whereas the previous sections have focussed on changes in community structure without reference to the particular environmental stressors, this section seeks to understand how specific pollutants (e.g. heavy metals, acidity) might affect community composition.

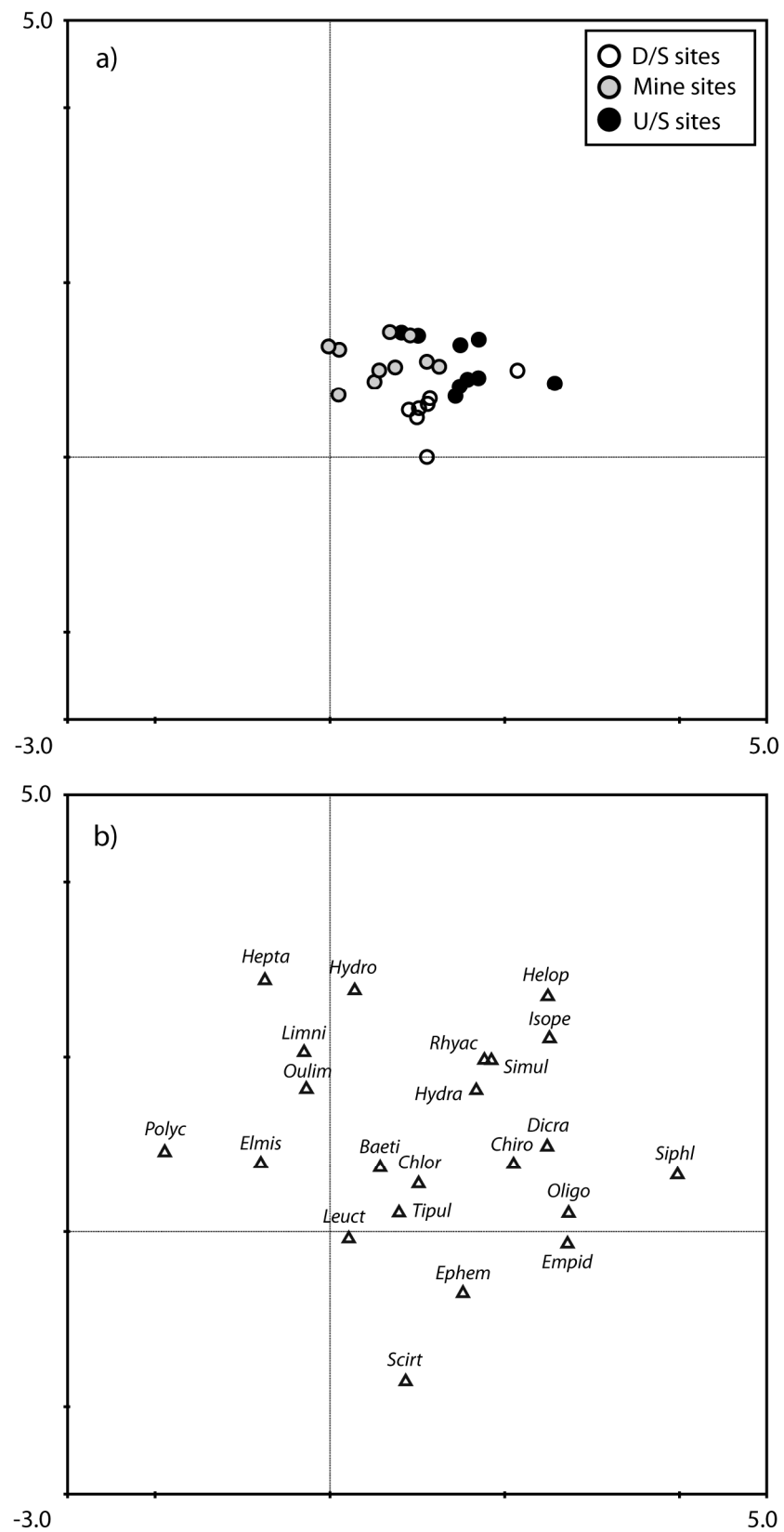
### 8.2.1 Site – species relationships

The purpose of this sub-section is to confirm the observations in section 8.1.1 that certain macroinvertebrate taxa display a preference for different locations/habitats in the Afon Twymyn. Macroinvertebrate data were first examined using Correspondence Analysis (CA) and Detrended Correspondence Analysis (DCA) in the programme CANOCO 4.5 (ter Braak and Smilauer, 2002). CA explained more of the species variance in all cases. However, there was a strong arch effect evident in the CA analyses due to the unimodal distribution of the species (section 4.7.2). DCA detrends this artefact and was, therefore, chosen for analysis of site-species relationships (Randerson, 1993). In the DCA biplots, taxa names have been shortened to the first five letters for ease of display and interpretation (**Table 8.4**).

Four DCA runs were conducted incorporating macroinvertebrate abundances for March, June, October, and a combined dataset. All four DCA runs showed clear groupings of sites along both ordination axes in relation to whether they were control, mine or downstream sites (**Figure 8.10 and 8.11; Appendix 8.3 and Appendix 8.4**). Some overlap occurred between site groups reflecting similarities in some of the sites that border each site group. The association appeared to be strongest in June, most likely due to the impact of increased flow in March and October (resulting in increased hydrological disturbance and greater mobility of organisms), and, possibly, the stronger dissolved metal gradient in June. Sample location explained 40.3% of the variation in community composition in June (**Table 8.5**). However, only 33.1% of the variation was explained by sample location when data for the three months was combined in Run 4 (**Table 8.6**),

reflecting the impact of season on macroinvertebrate community composition. The greatest variation in community composition was explained in October (40.8%) (**Appendix 8.4**).

Some taxa were consistently found at the same group of sites (upstream, mine and downstream) throughout the sampling period. Scirtidae were strongly linked to downstream sites (**Figure 8.10**). *L. hippopus*, *B. rhodani* and *Chloroperla* sp. were strongly linked to mines sites (**Figure 8.11**). Weaker associations with mine sites were also evident for *P. praecox*, *A. sulcicollis*, *E. aenea*, *R. dorsalis*, *H. siltalai*, Polycentropididae and Heptageniidae. At control sites, the strongest associations were with *S. lacustris*, *I. grammatica* and Limnephilidae (Trichoptera) (**Figure 8.11**). This analysis confirms the association between mine sites and certain Ephemeroptera (*B. rhodani*) and Plecoptera (*L. hippopus*, *Chloroperla* sp., *P. Praecox*, *A. sulcicollis*) taxa.



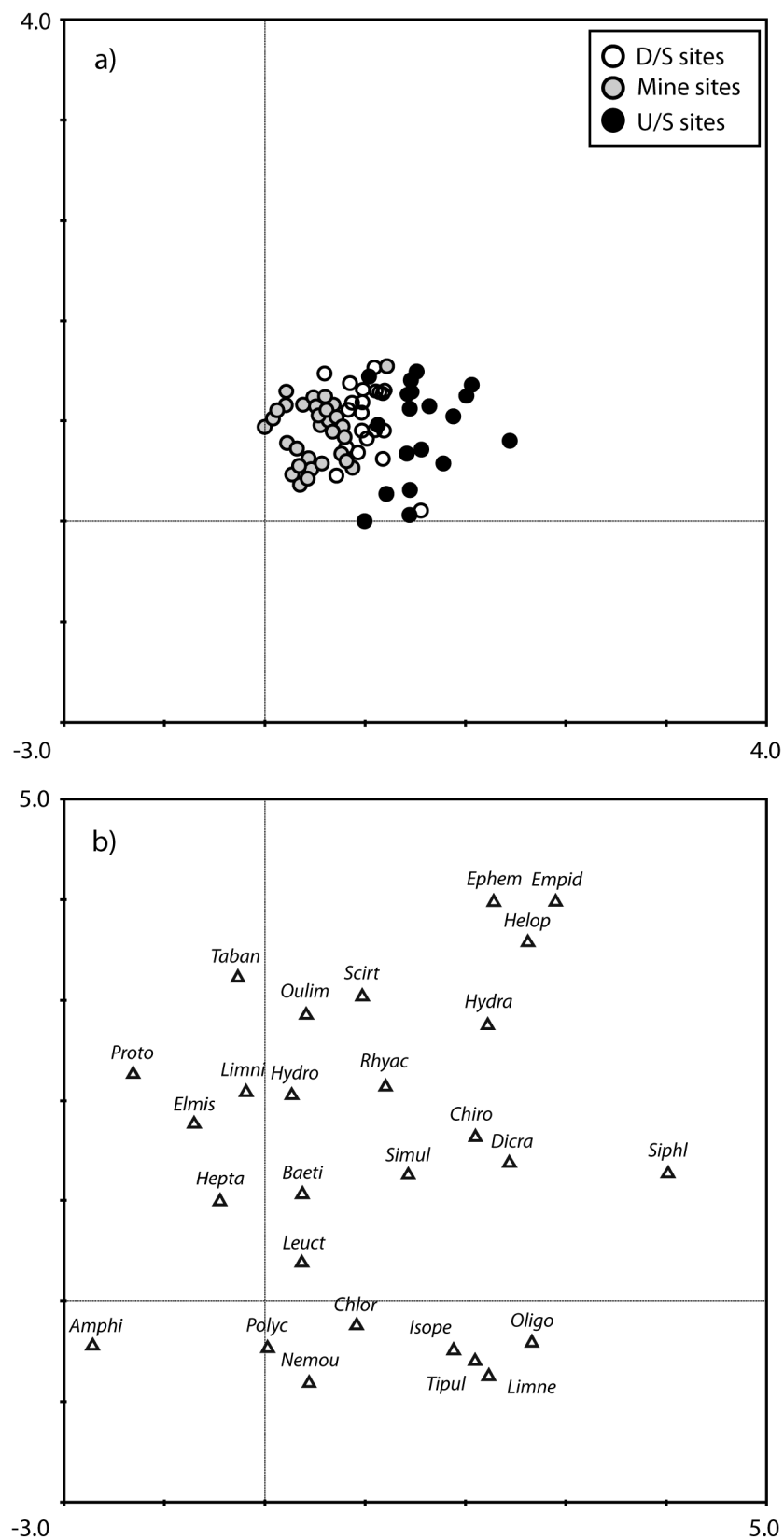
**Figure 8.10:** DCA biplots for Run 2 (June): a) sites and b) species

**Table 8.4:** Key to abbreviated taxa names in DCA and CCA biplots

Taxa	Abbreviation
Chironomidae	Chiro
Simuliidae	Simul
Tipulidae	Tipul
Tabanidae	Taban
Dicranota	Dicra
Empididae	Empid
Helophoridae	Helop
Hydraenidae	Hydra
Limnius volckmari	Limni
Elmis aenea	Elmis
Oulimnius	Oulim
Scirtidae	Scirt
Hydropsyche siltalai	Hydro
Rhyacophila dorsalis	Rhyac
Polycentropus flavomaculatus	Polyc
Limnephilidae	Limne
Ephemerella ignita	Ephem
Heptaenidae	Hepta
Baetis rhodani	Baeti
Siphonurus lacustris	Siphl
Chloroperlidae	Chlor
Leuctra hippopus	Leuct
Amphinemura sulcicollis	Amphi
Isoperla grammatica	Isope
Protonemura praecox	Proto
Oligochaeta	Oligo

**Table 8.5:** Summary of key findings from June DCA analysis (Run 2)

Axis	1	2	3	4
Eigenvalues	0.288	0.092	0.052	0.036
Lengths of gradient	2.585	1.441	1.485	1.079
Cumulative % variance of species data	24.8	32.7	37.1	40.3



**Figure 8.11:** DCA biplots for Run 4 (Combined dataset): a) sites and b) species

**Table 8.6:** Summary of key findings from combined dataset DCA analysis (Run 4)

Axis	1	2	3	4
Eigenvalues	0.245	0.1420	0.095	0.070
Lengths of gradient	2.439	1.539	1.806	1.430
Cumulative % variance of species data	14.7	23.2	28.9	33.1

### 8.2.2 Species – environment relationships

Detrended Correspondence Analysis (DCA) identified that some taxa were associated with the major site groups within the Afon Twymyn. However, DCA is unable to determine why the observed patterns occur. In this section, Canonical Correspondence Analysis (CCA) is used to investigate the relationship between macroinvertebrate abundance and hydrological and sedimentological variables (from Chapter 6). It is hypothesized that metal mine contaminants (e.g. dissolved metals, sediment-bound metals, acidity) significantly influence macroinvertebrate community composition in the Afon Twymyn. Six CCA runs were conducted incorporating macroinvertebrate abundance, water quality and sediment quality data (**Table 8.7**). These data are first plotted using ordination diagrams, graphically representing the community structure and the community response to the environmental variables. The significance of individual environmental variables was then tested. In the CCA biplots, taxa names have been shortened to the first five letters for ease of display (**Table 8.4**).

**Table 8.7:** Details of each CCA model run

CCA runs	Constituents
Run 1	Macroinvertebrate abundance and water quality data (March)
Run 2	Macroinvertebrate abundance and water quality data (June)
Run 3	Macroinvertebrate abundance and sediment quality data (June)
Run 4	Macroinvertebrate abundance, water and sediment quality data (June)
Run 5	Macroinvertebrate abundance and water quality data (October)
Run 6	Macroinvertebrate abundances and water quality data (March, June, October)

In the ordination biplots, species and sites are represented by points and environmental variables by vectors. Environmental variables with long vectors are more strongly associated with community composition than those with short vectors. Species located close to the vectors on the ordination can be said to be strongly associated with that environmental variable. Species located close to the vector tips are largely restricted to locations with those characteristics and vice versa for species endpoints projected near or beyond the origin of the vector. The species points are projected onto each environmental variable (axis) with the order of projection points corresponding to the ranking of the weighted averages of the species with respect to the concentration/value of an individual variable. The projection point of a species onto an environmental variable indicates the optimum conditions (within the dataset) at which that species thrives.

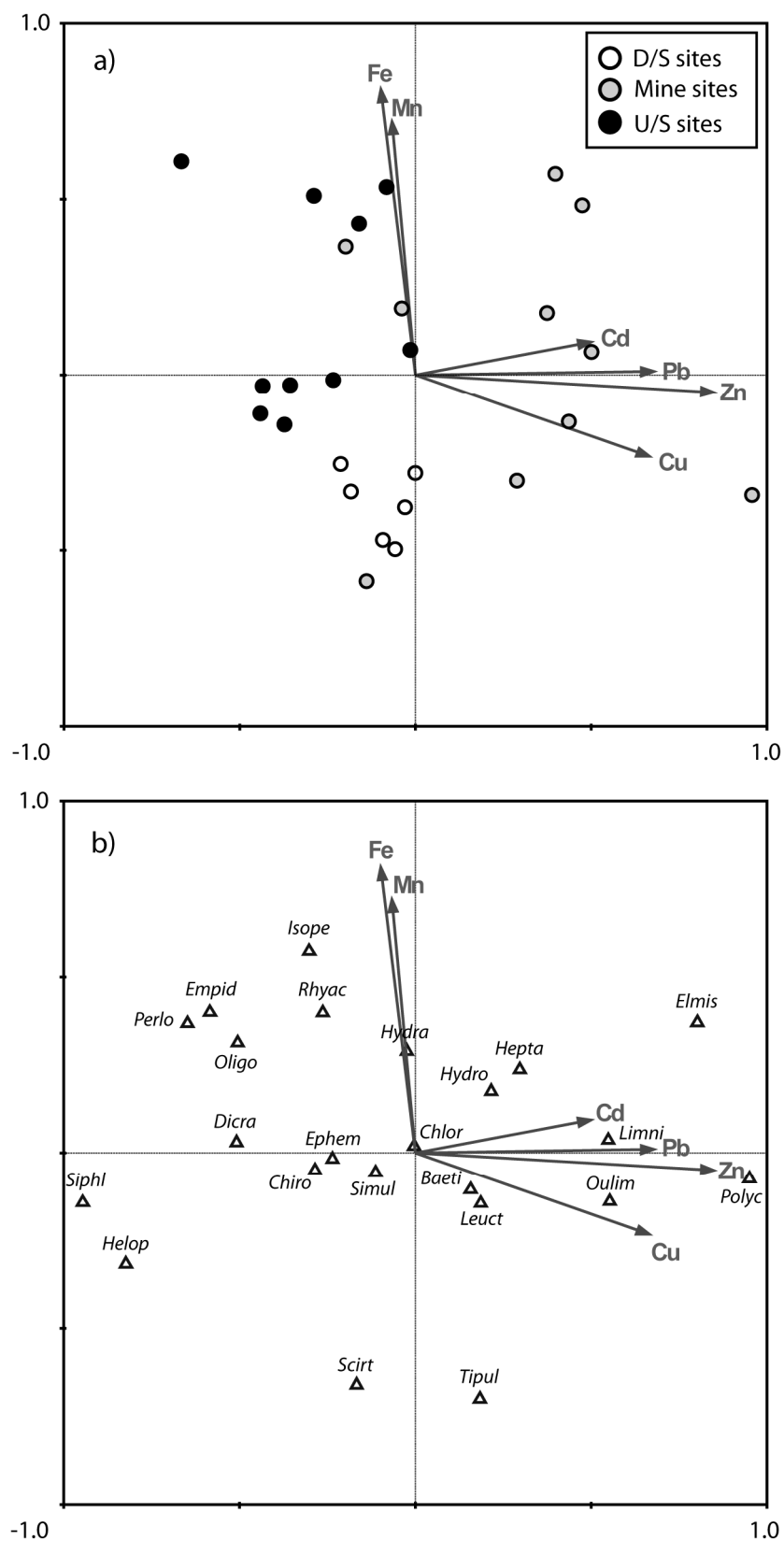
Each CCA run produced slightly different patterns within the ordination diagrams (**Figures 8.12 and 8.13; Appendices 8.5, 8.6, 8.7 and 8.8**), reflecting seasonal variations in species composition and environmental conditions at individual sites. However, CCA runs (except March) generally distinguished between three groups of environmental variables, namely chalcophile metals (Zn, Pb, Cu and Cd), common metals (Fe and Mn) and physico-chemical measurements (pH, conductivity and temperature), demonstrating the distinctiveness of these contaminants/measurements. Examination of the distribution of taxa on the first two canonical axes identified a general pattern of species-environment relationships. Species which appeared to be associated with chalcophile metals were *Amphinemura sulcicollis*, *Protonemura praecox*, *Elmis aenea*, and *Polycentropus flavomaculatus* (**Figure 8.12**). Taxa associated with Fe and Mn were *Oligochaeta*, *Isoperla grammatica*, *Helophorus* sp., Hydraenidae, Empididae, *Siphonurus lacustris*, and Limnephilidae (**Figure 8.13**). These were also the taxa which showed most sensitivity to the chalcophile metals. Taxa which displayed no particular sensitivity or association with any of the variables included *Chloroperla* sp., *B. rhodani*, Heptageniidae, Simuliidae, *Rhyacophila dorsalis*, *Hydropsyche siltalai*, and *Leuctra hippopus* (**Appendices 8.5, 8.6, 8.7 and 8.8**).

In all six CCA runs, except Run 4, a test of significance of the first canonical axis confirmed the presence of a significant environmental gradient within the data ( $\alpha =$



< 0.05) (**Table 7.9 and Table 7.11; Appendices 8.5, 8.6, 8.7 and 8.8**). In Run 1 (March, water data only) and Run 2 (June, water data only), dissolved Pb and Fe were the most significant variables explaining macroinvertebrate community composition (**Appendices 8.5 and 8.6**). Temperature was also significant in Run 1, as was conductivity in Run 2. In Run 3 (June, sediment only), only Zn was significant (**Table 8.8**). When sediment and water quality data for June were combined in Run 4, conductivity, sediment-bound Zn, sediment-bound Cu and dissolved Fe appeared to significantly influence the macroinvertebrate community (**Appendix 8.7**). Dissolved Pb and Zn were significant in Run 5 (October, water only) (**Appendix 8.8**). When the water quality data was combined in Run 6, all of the environmental variables (except Cu and Mn) were significant in explaining macroinvertebrate composition (**Table 8.9**).

The results of the DCA and CCA analyses suggest significant differences in the structure of the macroinvertebrate communities between impacted and unimpacted sample sites and that metal mine contaminants are significantly influencing the observed community structure. Some macroinvertebrate taxa occur more frequently at mine sites, however, this does not appear to be a result of a preference for polluted sites. Rather, these taxa (e.g. *L. hippopus*, *B. rhodani*) display an apparent indifference to metal pollution and exist in greater numbers at mine sites due to the sensitivity and elimination of other taxa (e.g. *Limnephilidae* sp., *I. Grammatica*, *S. lacustris*). Other taxa (e.g. *P. flavomaculatus*, *A. sulcicollis*) displayed a very strong association with chalcophile metals and were found almost exclusively at mine sites. The variation in community composition explained by the four canonical axes is quite high. Sediment-bound metals in Run 3 explained the greatest amount of species-environment relationship (91.2%) (**Table 8.10**). The addition of water quality variables in Run 4 did not improve the explained variance (**Appendix 8.7**). For the combined water quality data set (Run 6), the cumulative amount of species-environment relationship explained was 80.4% (**Table 8.11**).



**Figure 8.12:** CCA biplots for Run 3 (June, sediment only): a) site-environment and b) species-environment

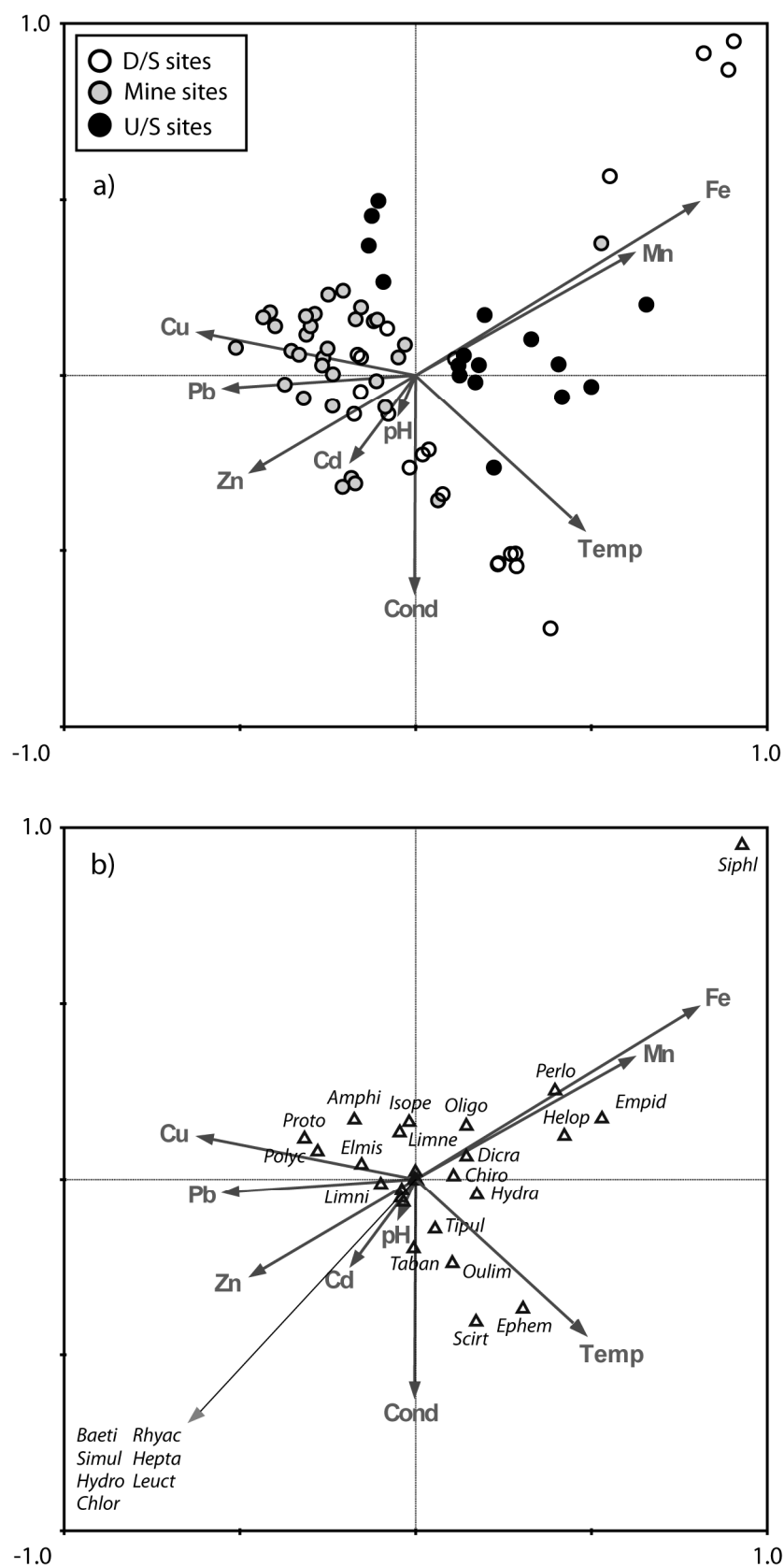
**Table 8.8:** Rankings for weighted sediment variables in June using unrestricted Monte Carlo significance test (Run 3)

Rank	Variable	Lambda-A	p	F
1	Zn	0.132	<b>0.004</b>	3.06
2	Cu	0.101	0.118	1.51
3	Pb	0.094	0.323	1.11
4	Fe	0.069	0.089	1.63
5	Cd	0.058	0.643	0.73
6	Mn	0.054	0.739	0.67

Significant (p = <0.05) in bold

**Table 8.9:** Summary of key findings from June sediment dataset CCA analysis (Run 3)

Axis	1	2	3	4
Eigenvalues	0.171	0.081	0.048	0.033
Species-environment correlations	0.822	0.744	0.824	0.616
Cumulative % variance				
a. Species data	14.7	21.6	25.8	28.6
b. Species-environment data	46.9	68.9	82.1	91.2
Significance of first canonical axis			F ratio	P value
			3.277	0.026



**Figure 8.13:** CCA biplots for Run 6 (combined water dataset): a) site-environment and b) species-environment

**Table 8.10:** Rankings and for weighted combined water quality variables using unrestricted Monte Carlo significance test (Run 6)

Rank	Variable	Lambda-A	p	F
1	Fe	0.130	<b>0.001</b>	5.76
2	Temp	0.094	<b>0.001</b>	4.55
3	Pb	0.092	<b>0.001</b>	3.66
4	Zn	0.087	<b>0.004</b>	2.61
5	Mn	0.080	0.176	1.32
6	Cu	0.078	0.395	1.04
7	Cond	0.069	<b>0.017</b>	1.92
8	Cd	0.064	<b>0.001</b>	2.38
9	pH	0.026	<b>0.016</b>	2.40

Significant (p = <0.05) in bold

**Table 8.11:** Summary of key findings from combined water quality dataset CCA analysis (Run 6)

Axis	1	2	3	4
Eigenvalues	0.146	0.125	0.103	0.052
Species-environment correlations	0.814	0.834	0.862	0.800
Cumulative % variance				
a. Species data	8.8	16.3	22.5	25.6
b. Species-environment data	27.5	51.1	70.5	80.4
Significance of first canonical axis			F ratio 5.766	P value <0.001

### 8.3 Metal bioaccumulation in macroinvertebrates

Results from the CCA analyses indicate metal mine contaminants are a major factor structuring the macroinvertebrate community of the Afon Twymyn, even if the standard biological indices indicate that the community is relatively healthy. Contaminants may be affecting specific biological processes in taxa resulting in the elimination of certain taxa at mine sites (e.g. *I. grammatica*) and the favouring of others (e.g. *B. rhodani*). The nature of these biological processes remains unclear, however, examination of metal bioaccumulation in different taxa from different feeding guilds may help in the inference of these biological processes. The following section investigates metal bioaccumulation in three macroinvertebrate species – *Hydropsyche siltalai* (Trichoptera – caddisfly), *Baetis rhodani* (Ephemeroptera – mayfly) and *Leuctra hippopus* (Plecoptera – stonefly). These species were selected for analysis to represent different contaminant exposure routes (section 4.5.4). The previous section found sediment-bound contaminants explained a greater amount of variance in community structure than water column contaminants. Therefore, it is hypothesized that metal bioaccumulation in the algal scrapers (*B. rhodani* and *L. hippopus*), which feed on detritus and living matter in the sediment, will be greater than in the omnivorous filter feeder (*H. siltalai*), which filters organic matter and detritus from the water column.

The sites chosen for sampling were 3, 8, 12, 16, 18 and 21 (**Figure 4.1**). Following analyses of water and sediment chemistry in Chapter 6, sites were divided into control/recovery (3, 16, 21) and impacted (8, 12, 18) sites. Macroinvertebrate samples were collected, processed, digested and analysed in line with the method outlined in section 4.5.4. Water samples were collected concurrently with macroinvertebrate samples and analysed for dissolved heavy metals (Zn, Pb).

#### 8.3.1 Metals in the water column

As expected, metal concentrations were highest at impacted sites and lowest at control/recovery sites (**Table 8.12**). Higher values were found in October probably

due to the effects of greater dilution in March and the flushing of oxidized metals accumulated over the summer (section 6.1.2).

### 8.3.2 Metals in macroinvertebrates

In general, metal concentrations were greater in macroinvertebrates from impacted sites (**Figure 8.14; Table 8.13**). However, differences between site groups were not large and generally not significant (**Appendix 8.9**). Significant differences were only found between site groups for Pb in *L. hippopus* and *B. rhodani*. Non-significant differences were recorded for Zn, possibly due to the relatively small sample sizes and the fact that this metal is an essential element and, therefore, well regulated by organisms. The pattern of accumulation for Zn was *H. siltalai* > *B. rhodani* > *L. hippopus*. For Pb, the pattern was *B. rhodani* > *L. hippopus* > *H. siltalai*. These patterns may reflect the different feeding strategies/mechanisms of the species. As a filter feeder, *H. siltalai* feeds mainly from the water column where dissolved Zn is the main contaminant (under steady flow conditions) and most likely exists in the most bioavailable free ion state (section 6.1.1). The algal scrapers feed principally on the sediment where Pb is the main contaminant and exists in a highly bioavailable geochemical phase (section 6.2.4). Correlations between metal concentrations in macroinvertebrate tissues and the environment were generally weak (**Appendix 8.10**), however, correlations between Zn in the tissue of *H. siltalai* and in the water column were strong and significant. A general pattern of increased metal concentrations was observed in all three macroinvertebrate species in October. This could be related to higher dissolved metal concentrations during this month and increased metal uptake by organisms. However, only Zn concentrations in all three species were significantly different between seasons (**Appendix 8.9**). It appears that metal bioaccumulation is occurring to a greater extent at mine sites than at control/recovery sites. However, the level of metal bioaccumulation in *H. siltalai* appears not to be as severe as in another mining-impacted river. The only other comparable study (which could be found in the literature) of metal bioaccumulation in *Hydropsyche* sp. observed individuals to accumulate a mean of 117 µg/g Pb and 3207 µg/g Zn (Sola *et al.*, 2004). Zinc bioaccumulation is far greater in the study of Sola *et al.* (2004) than in the present study, however, it

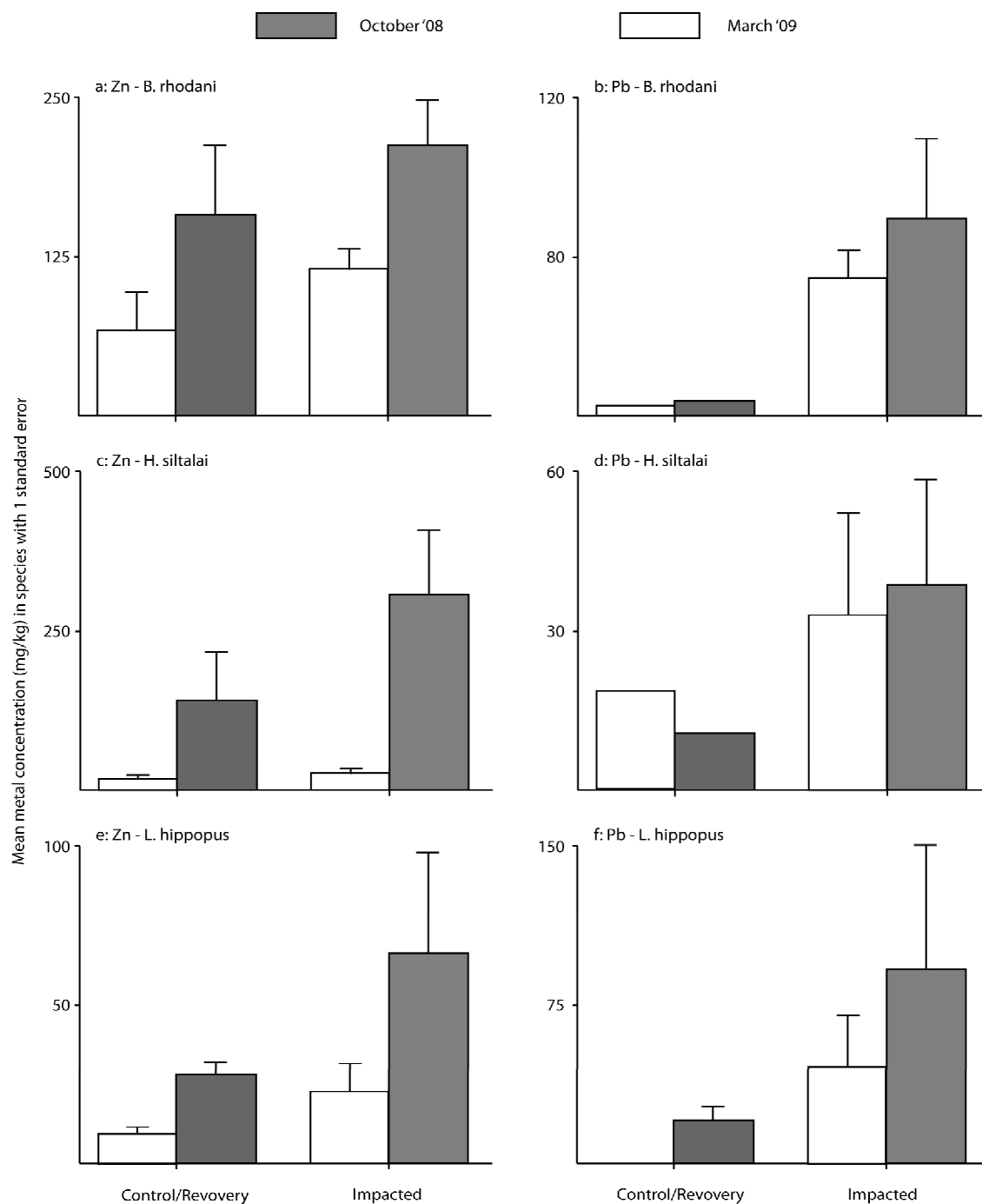
must be stressed that dissolved Zn concentrations in the comparison study were far greater than the levels observed (under steady flow conditions) in this study. It may be that the species investigated in this study have developed biological processes to prevent metal accumulation to toxic levels. These species were found to show no particular sensitivity to metal mine contaminants (section 8.2.2). Rather than metal concentrations in macroinvertebrates reflecting where the organisms live (i.e. river bed sediment), it appears that organism feeding type may have a stronger influence on metal bioaccumulation.

**Table 8.12:** Mean metal concentrations and standard error (in parenthesis) in water column samples ( $\mu\text{g/l}$ )

Site	Pb		Zn	
	October '08	March '09	October '08	March '09
3	77 (4.5)	66 (5.6)	234 (11.6)	221 (5)
16	98 (4.9)	83 (6.4)	56 (2.1)	36 (2.1)
21	56 (4.5)	52 (4.4)	18 (1.5)	14 (1.3)
8	201 (10.1)	173 (14.2)	589 (12.5)	442 (22.6)
12	187 (5.7)	169 (8.3)	298 (8.2)	233 (8.2)
18	77 (4.6)	78 (4.5)	77 (4.6)	70 (4.7)

ND = not detectable





**Figure 8.14:** Mean metal concentrations in macroinvertebrate tissue at control/recovery and impacted sites ( $\mu\text{g/g}$ )

**Table 8.13:** Mean metal concentrations in macroinvertebrate tissues ( $\mu\text{g/g}$ )

Sample	Pb		Zn	
	October '08	March '09	October '08	March '09
<b><i>H. siltalai</i></b>				
3	11	19	219	24
16	ND	ND	60	12
21	0.35	NS	138	NS
8	70	52	410	33
12	13	NS	204	NS
18	7.50	14	202	21
<b><i>B. rhodani</i></b>				
3	ND	ND	105	99
16	5.81	3.71	211	37
21	5.38	NS	129	NS
8	101	67	284	143
12	109	32	183	117
18	13	59	169	89
<b><i>L. hippopus</i></b>				
3	26	ND	24	12
16	14	ND	32	8.05
21	14	NS	37	NS
8	33	70	35	32
12	150	21	98	14
18	86	NS	40	NS

ND = not detectable

NS = no species found

## 8.4 Discussion

### 8.4.1 The macroinvertebrate community of a metal mining-impacted stream

In this study, Ephemeroptera were found to be the dominant macroinvertebrate order. Ephemeroptera are generally found in a variety of habitats including lakes,

wetlands, streams and rivers (Bouchard, 2004). Results from CCA analyses showed that Ephemeroptera were generally associated with metal pollution, in marked contrast to the results of many other studies (Clements *et al.*, 1992; Kiffney and Clements, 1994; Gower *et al.*, 1994; Schultheis *et al.*, 1997; Malmqvist and Hoffsten, 1999; Clements *et al.*, 2002). However, this may be due to the dominance of *B. rhodani* in the Ephemeroptera taxa. Rather than showing a preference for polluted sites, the relative metal tolerance of *B. rhodani* combined with the particular sensitivity of other taxa might have allowed *B. rhodani* to dominate at mine sites. Other mayfly herbivores (e.g. *Siphonurus lacustris*) display metal sensitivity and are limited to control or downstream sites. The overwhelming dominance of *B. rhodani* may also be related to its large number of brooding cycles per year. *B. rhodani* is multi-voltine – it may have more than two broods per year (Jop, 1991). Many other mayfly species are uni- or bi-voltine. The widespread distribution of *B. rhodani* and its position near the origin of the species-environment ordination biplots supports the findings of some others in that it has moderate to high metal tolerance (Roline, 1988; Beltman *et al.*, 1999; Gower *et al.*, 1994; Beasley and Kneale, 2002).

In this study, the macroinvertebrate fauna was dominated by stoneflies, which is not surprising given their reputation for metal and acid tolerance (Beasley and Kneale, 2002). Plecoptera are also usually found in abundance in rivers like the Afon Twymyn where fast-running waters, high dissolved oxygen levels, cold water and coarse substrates predominate (Bouchard, 2004). However, there was considerable variation in associations between Plecoptera taxa and environmental variables. *Leuctra hippopus* (herbivore) and *Chloroperla* sp. (predator) showed moderate associations with heavy metals with consistent positions near the origin of the species-environment biplots. These species probably exhibit the same behaviour as *B. rhodani*, taking advantage of the absence of sensitive taxa. *Protonemura praecox* and *Amphinemura sulcicollis* (herbivores) were strongly associated with the chalcophile metals while *Isoperla grammatica* (predator) appeared more sensitive and confined mainly to control sites with an association with Fe and Mn. Similar patterns were reported by Beasley and Kneale (2002) for West Yorkshire rivers, and by Armitage *et al.* (2007) in the River Nent, Cumbria.

Much like Plecoptera, Trichoptera (caddisflies) prefer running lotic waters (Bouchard, 2004). In this study, caddisflies also showed varying response to metal pollution between families. The cased caddisfly, Limnephilidae (herbivore), was particularly sensitive to metal pollution (Beasley and Kneale, 2002). However, caseless caddisflies showed greater tolerance. *Rhyacophila dorsalis* (predator) and *Hydropsyche siltalai* (omnivore) showed moderate metal tolerance, and *Polycentropus flavomaculatus* (omnivore) appeared to be the most tolerant Trichoptera taxa. Other authors have found similar metal tolerances in caseless caddisflies, especially Hydropsychidae (Winner *et al.*, 1980; Gray, 1998; Hickey and Clements, 1998; Sola *et al.*, 2004).

#### 8.4.2 The performance of biological indices

All of the biological indices used in this study failed to detect any substantial negative impacts on macroinvertebrate assemblages that could be associated with metal mine contaminants. BMWP and ASPT were not significantly different between locations or seasons. Despite some success in detecting the effects of acid mine drainage (Armitage, 1980; Nelson and Roline, 1996; Garcia-Criado *et al.*, 1999; Gray and Delaney, 2008), these biotic indices have been developed primarily to detect organic pollution. It is possible that, in mining-affected rivers like the Afon Twymyn which are not significantly acidic, BMWP and ASPT scores may be less successful. It may be the case where BMWP/ASPT have successfully discerned the impact of metal mine pollution, that these scores identified the additional toxic stress caused by acidic pollution. Similar patterns to that of BMWP/ASPT scores were recorded for percent EPT taxa. Measurements of EPT taxa have been reported to elucidate the effects of AMD in other river systems (Garcia-Criado *et al.*, 1999; Malmqvist and Hoffsen, 1999). In this study, slightly higher EPT scores at mine sites point to an improvement in ecosystem health. However, the result was strongly influenced by the presence of large numbers of Plecoptera taxa at mine sites. It is difficult to say whether the increase at mine sites reflects an increase in metal pollution or an increase in ecosystem health as both situations have been suggested to account for the observed pattern (Biological Monitoring Working Party, 1978; Beasley and Kneale, 2002). In general, Shannon-Weiner diversity and Berger-Parker dominance indices were not significantly different between locations and seasons. However, mean scores

did decrease and increase, respectively, at mine sites, an effect which has been observed in other mining-impacted rivers (Hirst *et al.*, 2002; Marques *et al.*, 2003; Smolders *et al.*, 2003; Doi *et al.*, 2007; Van Damme *et al.*, 2008). However, other studies (Chadwick and Canton, 1983; Willis, 1985; Chadwick *et al.*, 1986) have also noted the inadequacy of diversity indices in general to discern the impacts of metal pollution. Inconsistency between seasons in the Shannon-Weiner index has also been noted by Chadwick *et al.* (1986) and Garcia-Criado *et al.* (1999). The AWIC index performed as expected, that is, scores generally improved with distance downstream, corresponding to the gradual increase in stream pH. Therefore, this pressure-specific index (measuring impact caused by a specific contaminant) successfully identified changes in acidity and its impact on macroinvertebrate communities. However, the index was unable to detect the impact of mine drainage at Dylife, most likely because mine drainage did not reduce the pH of mine sites below that of control sites. Even if severe acid drainage was occurring at Dylife, it is not clear whether the AWIC index would be able to discern its impact. One of the principal limitations of this index is bias in the calibration data towards circum-neutral and alkaline sites (Ormerod *et al.*, 2006). During the development of the AWIC index, only 4% of test sites had a pH less than 6.5 (Ormerod *et al.*, 2006). Yet, it has been shown that several species of Diptera, Coleoptera, Ephemeroptera, Plecoptera and Trichoptera can survive in even the most acidic (pH  $\leq 3$ ) habitats (Goncalves-Rodrigues and Scharf, 2001). In addition, metal mine drainage will result, in most rivers, in a pH  $< 6.5$ . Therefore, this index may not prove useful for biomonitoring purposes in rivers suffering from mine drainage. Furthermore, a number of taxa found ubiquitously in this study (e.g. *B. rhodani*, Heptageniidae, Oligochaeta), are assigned to the most acid sensitive group in the AWIC index. Their occurrence throughout the Afon Twymyn, in moderately acidic to circum-neutral waters might warrant reinvestigation of their classification in the AWIC index among the most acid-sensitive macroinvertebrates.

There are many biological indices available for the measurement of specific pollution types, e.g. organic contaminants (Biological Monitoring Working Party, 1978), acid conditions (Davy-Bowker *et al.*, 2005) and heavy metal (Cu) pollution (Clements *et al.*, 1992). However, it is the multi-factor nature of many mine water

discharges (i.e. acidity, dissolved metals, sulphates and metal precipitates) which makes it difficult to diagnose problems clearly. Organic pollution generally causes a decrease in diversity as sensitive organisms are lost, and an increase in the abundance of tolerant organisms due to nutrient enrichment (Gray, 2003). Metal mine contamination is generally believed to be non-selective, i.e. it favours no one taxa (Metcalf-Smith, 1996). However, it appears in this study that contamination was selective, as some taxa (e.g. *B. rhodani*, *L. hippopus*) appeared to thrive in the polluted environment and in the absence of sensitive species. It may be that metal mine contamination is non-selective when there is the added stress of chronic acidity.

#### 8.4.3 The relationship between metal mine contaminants and macroinvertebrate communities

Based on CCA analyses, the most significant environmental parameters influencing macroinvertebrate community composition were dissolved Fe, Pb, Zn, sediment-bound Zn and conductivity. This supports the findings of other authors who found dissolved Pb (Armitage *et al.*, 2007), and particularly dissolved Zn (Armitage, 1980; Malmqvist and Hoffsten, 1999; Armitage *et al.*, 2007), strongly influenced macroinvertebrate community composition in metal mining-impacted rivers. In the CCA analyses, metal mine contaminants (water column and sediment-bound) accounted for between 68 and 91% of the variation in macroinvertebrate community composition. The number of factors influencing species composition in any river is potentially very large. However, the number of important factors is typically few. That is, a few factors can explain the majority of the explainable variation (Randerson, 1993). In this study, the variation in community composition explained by metal mine contaminants is large, therefore, one can be relatively confident that these environmental variables are the major influence on community structure. However, this contradicts with the results of the biological indices which suggest no measureable impact of mine contaminants on community health. The reason for this is that traditional metrics of community health consider only a single community change/impact (e.g. diversity) whereas multi-variate analyses such as CCA theoretically combine all of the possible changes/impacts that might occur in community health as a result of an environmental stressor. In the present study, CCA is not detecting the exact

change/impact which is occurring in community health, however, it is identifying something which unimetric indices cannot, that is, a strong and significant difference in community structure between impacted and unimpacted stretches of river.

In addition to metal mine contaminants, several other biotic and abiotic factors are likely to have an impact on community composition. Other significant water quality variables will include pH (Allen *et al.*, 1996) and sulphate concentrations (Garcia-Criado *et al.*, 1999). Reduced pH and increased sulphate concentrations are characteristic of acid mine drainage which is not present at Dylife mine. Additional variance will undoubtedly be explained by instream habitat type, availability and quality (Wood, 1997; Beasley, 2002; McCullough *et al.*, 2009). For example, this study identified some taxa such as Leuctridae, Chloroperlidae, Baetidae, Heptageniidae, Rhyacophilidae and Hydropsychidae to be associated with metal contamination, as they were found in large numbers at mine and downstream sites. However, these taxa also show a preference for slow to fast moving stony and riffle-dominated habitats found, in this study, at mine and downstream sites. Conversely, species of Siphonuridae, Ephemerellidae, Perlodidae and Limnephilidae, found mainly at control sites, prefer environments where lake edge habitats and small ponds predominate. Therefore, habitat availability and quality, and the specific habitat preferences of species, may also play a crucial role in structuring macroinvertebrate communities.

Many biotic factors will also influence community abundance. Organisms exposed to chronic heavy metal contamination may accumulate metals in their tissue (Yi *et al.*, 2008). Metal accumulation can vary between species depending on a number of physiological factors which dictate the pollution tolerance or sensitivity of an organism (Kiffney and Clements, 2003). However, the principal factor determining metal accumulation will be the exposure route. Metal uptake or intake takes place through active ingestion or by passive uptake on external body surfaces (Sola *et al.*, 2004), depending on whether the metal came from the water column or was ingested with food. In this study, correlations between metal concentrations in macroinvertebrate tissues and the environment were generally weak (**Appendix 8.10**). Other authors have noted similar weak relationships (Sola *et al.*, 2004;

Battaglia *et al.*, 2005; Sola and Prat, 2006). This is due to the numerous biotic and abiotic factors which can influence metal bioaccumulation. However, some significant correlations were found between metals in organisms and dissolved Zn. Correlations were particularly strong for *H. siltalai*, reflecting the feeding group (filter-feeder) of this caddisfly and the high concentrations of dissolved Zn in the water column. These results suggest that *H. siltalai* incorporates metals from the water column. The mode of metal accumulation is, however, unclear. Dissolved metal species in the water column can adsorb to the surface of organisms, pass through cell membranes and accumulate in organisms (Novotny, 1995). Low concentrations of major ions in the Afon Twymyn (section 6.1.1) suggest much of the heavy metal load in the river exists as free ion species, allowing metals to accumulate easily in organisms. Metal accumulation from food sources is another possibility. Although Pb accumulation was higher in the algal grazers than in the filter feeder (suggesting metal accumulation from sediment was important for these organisms), correlations between sediment-bound metals and tissue metal concentrations were weak (**Appendix 7.10**). Given the high concentrations of bioavailable metals in the sediment of the Afon Twymyn, metals would be expected to accumulate to a high degree in primary producers, which, in turn, should be reflected in algal scrapers (Farag *et al.*, 1998; Yi *et al.*, 2008). It may be the case that organisms whose primary metal exposure route is through food (e.g. *B. rhodani* and *L. hippopus*), have mechanisms to prevent adsorption of metals into tissue from the gut. If this is the case, it would appear that the water column is the primary metal exposure route, and that metal accumulation via adsorption of dissolved metal species is the primary metal accumulation mechanism. Therefore, organisms that spend the majority of their time exposed to the water column (e.g. filter feeders such as *H. siltalai*) may be most at risk and the best indicators of the level of impact of mine drainage on the macroinvertebrate community.

Another biotic process possibly contributing to macroinvertebrate community composition is natural tolerances to certain metal pollutants (Spehar *et al.*, 1978; Gower and Darlington, 1990; Bahrndorff *et al.*, 2006). The Afon Twymyn has been severely polluted by mine drainage for several centuries. Natural mineralisation in the region suggests that the river has always had relatively high levels of metal contamination. As a result, it is possible that certain macroinvertebrate species



have developed unique genetic tolerances of certain metals or mixtures of metals (Morgan *et al.*, 2007). Perhaps, *B. rhodani* and *L. hippopus* have developed a physiological and/or behavioural adaptation to moderate metal concentrations in their tissues. Mechanisms of tolerance might be increased metal excretion and/or decreased metallothionein production. Metallothionein is a metal-binding protein with the principal function of accumulating essential metals for normal metabolic processes (Howard, 1998). However, its presence leads to the accumulation of toxic metals also. Decreased production of this protein may allow certain organisms to accumulate lower amounts of toxic metals.

## 8.5 Chapter summary

This chapter has investigated the relationship between metal mine contaminants and macroinvertebrate community composition in the Afon Twymyn. Several common biological indices and a study of metal bioaccumulation in macroinvertebrates present a picture where there is no apparent measureable negative impact on biota of metal mine contaminants, despite the severe level of contamination in the river. However, CCA analyses reveal that metal mine contaminants are significantly influencing macroinvertebrate community structure in the Afon Twymyn, suggesting an impact on community health is occurring and that biological indices, in their current form, cannot detect this impact. In general, the Afon Twymyn supports a healthy and varied macroinvertebrate community, however, there are significant differences in community structure upstream and downstream of the mine as a function of the metal gradient. It could be that both the biological indices and the CCA analyses are yielding the correct answer. The polluted and unpolluted stretches of the river have different communities because of the metal pollution. However, due to the length of time the mine has been abandoned and the naturally high levels of metals which likely occurred pre-mining activity, some species in the polluted stretch have developed physiological and behavioural adaptations which allow them to maintain a relatively healthy community in the polluted conditions. As a result, biological indices indicate little difference in community health between impacted and unimpacted stretches of river. This is certainly a possibility, however, it is thought to be more likely that the biological indices are generally not capable of discerning the impact of a multi-factor pollutant like mine drainage, particularly in the absence of significant acidity.

Although biological indices have not been developed specifically to identify metal mine pollution impacts, they are used frequently in ecological assessments of mining-impacted rivers by both scientists and environmental regulators. Some of these indices are also being used to characterise water bodies for the Water Framework Directive. Some indices have proved useful in identifying metal pollution impacts, however, the multifactor nature of metal mine contamination, and variations in the concentrations of its constituents between regions, makes it difficult to identify any one index as effective in mining-impacted rivers. The success of the CCA analyses in identifying differences in community structure between mining and unmined stretches of the river pose questions over the suitability of existing biological indices for detecting metal mine pollution, particularly in moderately polluted and circum-neutral rivers. It is suggested that current biological indices may not be a suitable biodiagnostic tool in some mining-impacted rivers where contamination is moderate and where mining activity may have ceased for some time.

## **9. Conclusions**

### **9.0 Introduction**

The results of a series of laboratory and field-based studies have been presented and discussed with the principal aim of identifying the hydrological, sedimentological and ecological impacts of metal mine contamination in the Afon Twymyn. This chapter will summarise the principal findings of this research and discuss them in relation to some of the wider issues and challenges surrounding metal mine contamination and its management.

### **9.1 Summary of thesis aims**

Mine water pollution affects all components of the river environment. Therefore, this thesis has used a multidisciplinary approach to examine the impacts of historical metal mining on river systems with reference to hydrological, sedimentological and ecological systems. This research has been carried out in the context of the European Union Water Framework Directive (WFD) which seeks to improve aquatic environments using an ecosystem-centered approach and a focus on river basin planning and management. Therefore, the aims of the thesis were formulated in order to investigate physical, chemical and biological processes at mine sites which are, currently, poorly understood, and which pose concerns for the achievement of the aims of the WFD.

In Chapter 1, the principal aims of this thesis were set out (section 1.1). Chapter 6 focused on hydrological and sedimentological impacts of historic mining activity. Investigation of linear and temporal patterns of water (section 6.1) and sediment contamination (section 6.2) allowed the identification of contaminant sources (section 6.3.1), contaminant dispersal patterns below Dylife mine (section 6.3.3), and assessment of the mobility and potential bioavailability of sediment-bound heavy metals (section 6.3.4). Diffuse pollution from mine spoil was found to be the principal contamination source at Dylife mine. The importance of diffuse pollution at abandoned metal mines has been highlighted in other studies around the UK

(e.g. Mayes *et al.*, 2008; Mighanetara *et al.*, 2009). It was found that the majority of heavy metals in bed sediments of the Afon Twymyn exist in highly mobile geochemical phases, potentially posing serious threats to ecological integrity. Of particular concern was the high proportion of Pb found in highly mobile and bioavailable phases. This highlights the benefits of reporting the bioavailable metals as opposed to total metals. When sediment chemistry is investigated, most scientific studies (**Figure 2.3**) and regulatory agencies have historically focused on total sediment metals which will not provide accurate information on the potential mobility and bioavailability of contaminants.

Contaminant dynamics during flood events were explored in Chapter 7 through the use of automatic water samplers. Trends in river hydrochemistry during flood events were established, as were the primary contaminant sources and mechanisms controlling heavy metal concentrations and loads (section 7.1.2). Sampling as part of this study identified that flood events play a significant role in the transport of metal contaminants from Dylife mine. Similar findings have been reported elsewhere (e.g. Lambing *et al.*, 1999, Canovas *et al.*, 2008). This study further observed that the level of flushing of metals in flood events varies throughout the year, with antecedent soil moisture conditions and different flow processes within the mine spoil strongly influencing metal concentrations and loads (section 7.1.4 and section 7.1.5). The evidence presented in this thesis highlights the need for high-resolution temporal sampling of water quality during flood flows when investigating remediation strategies or conducting contaminant/ecosystem investigations.

Chapter 8 assessed the performance of biological indices in detecting the impact of metal mine contamination in the Afon Twymyn (section 8.1), investigated the relationship between metal mine contaminants and macroinvertebrates (section 8.2), and examined bioaccumulation of heavy metal contaminants in macroinvertebrates (section 8.3). A range of biological indices (BMWP, ASPT, Shannon-Wiener Diversity, Berger-Parker Dominance, percent EPT taxa, AWIC, macroinvertebrate abundance and number of taxa) widely employed in routine biomonitoring studies failed to identify any negative impacts on the macroinvertebrate community of the Afon Twymyn as a result of metal mine

contamination. However, multivariate analyses (DCA and CCA) identified that significant differences do exist in macroinvertebrate community composition from polluted and unpolluted stretches of the river and that metal mine contaminants were the principal environmental variables causing these differences. This raises questions over the suitability of a number of the most widely applied biological indices for the assessment of metal mine pollution impacts.

A final principal finding of this thesis is the benefit of tackling water quality problems (such as historical metal mining) with a multi-disciplinary, geographical approach. It is only by considering all components of a river system in a holistic manner that a more complete understanding can be gained of the environmental impact of contaminants. The information presented in this study has provided an understanding of the character of mine water pollution at Dylife, how it interacts with and moves through the river environment, and also its current and potential future impacts on the aquatic ecosystem.

## **9.2 Hydrological impacts**

Historical metal mining in the UK has left a significant legacy of contamination in river environments. This legacy can be seen most clearly in the central Wales mining district where most rivers in the region fail to meet water quality guidelines along significant stretches of water (Abdullah and Royle, 1972; Environment Agency, 2002). The main water quality contaminants of concern are the chalcophile metals – Zn, Pb, Cu and Cd – derived from the dissolution of metal sulphates. Comparison of metal concentrations observed in the present study with Environmental Quality Standards (EQSs) for the EU Freshwater Fish Directive and Dangerous Substances Directive (**Table 9.1**) reveals significant water quality failures in the Afon Twymyn and confirms Dylife mine as one of the most polluting metal mines in the UK. Dissolved Zn and Pb levels exceed guidelines by up to 60 and 100 times, respectively. The most serious water quality failures occur opposite the main spoil tips area. Exceedances of EQSs continue to occur for some considerable distance downstream of the mine although they are not as serious as those observed at Dylife.

**Table 9.1:** Percentage of sampling sites in this study failing to meet Environmental Quality Standards ( $\mu\text{g/l}$ ) for water quality (Environment Agency, 2008c)

Metal	EQS	Control sites	Mine sites	D/S sites
<i>Freshwater Fish Directive</i>				
<b>Zn</b>	30 <sup>1,3,4,6</sup>	0	87	100
<b>Cu</b>	5 <sup>2,3,5,6</sup>	0	67	83
<i>Dangerous Substances Directive</i>				
<b>Pb</b>	4 <sup>2,6</sup>	100	100	100
<b>Cd</b>	5 <sup>1,6</sup>	0	33	0

- 1 Total (annual average)
- 2 Dissolved (annual average)
- 3 Salmonid standard
- 4 Total (95 percentile), salmonid standard
- 5 Dissolved (95 percentile), salmonid standard
- 6 Hardness related

### 9.2.1 The importance of flood event chemistry

Mine water drainage can occur from multiple sources in a catchment, from mine portals or mine tailings/spoil. In the present study, diffuse drainage from mine spoil was found to be the major source of contamination (section 6.3.1). This would appear to be the most challenging aspect from a remediation perspective. Point sources of contamination can be relatively easily collected and routed to treatment areas. The chemistry, flow, and contaminant loads 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 around the UK (e.g. Whitehead *et al.*, 2005). Such systems have proved relatively efficient at treating these single, point and steady flow discharges. However, the transport of contaminants from mine sites is not as simple and continuous as it might seem. This study has shown that significant quantities of metal contaminants can be mobilised from mine sites during flood events (section 7.1.2). During these events, many small discharges draining mine spoil can combine to create a significant diffuse discharge which could completely

bypass or inundate a treatment system. In an effort to protect treatment systems from flooding, some remediation programmes have installed engineering works to divert river flows (within a certain magnitude) away from treatment systems (Connelly, 2009). In upland central Wales, where large flood events are frequent, this could mean significant quantities of mobilised mine waste not receiving treatment. Many remediation investigations do not appear to incorporate chemical measurements of river water under conditions of flood flow (e.g. Parsons Brinckerhoff Ltd., 2005). Without these measurements, long-term predictions of the contaminant removal capacity of treatment systems might be inaccurate, affecting 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 might be over-estimated (Lambing *et al.*, 1999). This study also identified acid flushes during the initial stages of storm runoff (section 7.1.2). Although the scale of the acid flush was not large, greater levels of acidity might be expected at mine sites with greater quantities of sulphide minerals. Large-scale acid flushes might compromise the functioning of alkalinity-based treatment systems, many of which are effective over only narrow pH ranges (Nuttall and Younger, 2000). The observations in this study emphasise the importance of including assessments of flood event chemistry in the data gathering phase of remediation projects. This is to establish more accurately the chemical variability of the water to be treated and the expected maximum contaminant loads.

#### 9.2.2 A predictive model of metal flushing for rivers passing through abandoned mine sites?

The flushing of metals at abandoned mine sites appears to be transient with rain-fed floods but flushing does not seem to be solely a function of the magnitude of a flood event. Antecedent conditions/catchment wetness appears to play an important role in regulating the availability of metals to be flushed into the river system (section 7.1.4). This obviously limits the potential for predicting contaminant loads during flood events. For example, the importance of antecedent soil moisture makes it difficult to assign metal loads to flood events of particular return periods. However, if an accurate representation of the

relationship between metal flushing and catchment wetness can be established, then there is the possibility of incorporating such a relationship into a predictive model of metal flushing for specific mine sites. Other important information as detailed in this study, describe the relationship between metals flux and discharge, and the general characteristics of the hydrograph response to rainfall events (section 7.1.5). Such a model might be appropriate for relatively simple systems such as the Afon Twymyn where multiple contaminant sources do not exist and stream pH is circum-neutral and relatively stable throughout flood events (a very variable stream pH might require geochemical modelling). However, establishing a robust relationship between metal flushing and catchment wetness might be the principal hurdle. Such a model might have greater success in semi-arid mining regions where dry and wet seasons are clearly defined and the vast majority of the annual metal load is transported during floods in the wet season. The absence of discernable wet and dry periods in the UK (and certainly in upland Wales) might make it difficult to establish such a relationship. The results of this study and others (e.g. Lambing *et al.*, 1999) show that metal flushing at mine sites during flood events is significant and needs to be considered during remediation planning. Growing concerns over environmental pollution in general have prompted the development of mathematical modelling techniques to simulate contaminant fluxes under different scenarios (Lane, 2003). The results presented in this study lend some mileage to the possibility and feasibility of a semi-quantitative predictive model of metal flushing for abandoned mine sites.

### 9.2.3 Principal environmental concerns

The large-scale movement of mine waste during flood events has significance for two principal aspects of environmental quality, especially when viewed in the context of climate change. In the first instance, this study identified that flood events significantly increase the potential toxicity of river water in the Afon Twymyn, if only for short periods of between 2-3 hrs (section 7.1.2). These conditions undoubtedly cause harm to the aquatic community and degrade biological quality (Wolz *et al.*, 2009). The long-term effects of these transient conditions can be established through investigations of aquatic ecosystem health. However, the added or individual impact of flood events is still largely unknown



due to the difficulty of measuring it. Predicted increases in the frequency and magnitude of floods across Europe due to climate change (Wilby *et al.*, 2006) have put an emphasis on bridging the knowledge gap between the physical remobilisation of contaminants during flood events and the potential toxicological impacts (Wolz *et al.*, 2009). Understanding the toxicological impacts of flood events will be important in the achievement of the aims of the Water Framework Directive for mining-affected river catchments. A second major concern facing environmental managers in river catchments affected by historical mining activity is the mobilisation and transport of mine wastes during floods and contamination of large areas of arable and pastoral land (Dennis *et al.*, 2009). This study has shown that flood events are a significant transport mechanism in the annual metal load of mining-impacted rivers, even in regions like the UK where the climate limits the availability of metals to be flushed (section 7.1.3). Concerns have been expressed in some regions over the safety of human food supplies, namely vegetables, fruit and livestock (Dennis *et al.*, 2003; Connelly, 2009). Increased flood frequency as a result of climate change has raised fears over the increased mobilisation and deposition of heavy metals in floodplains. Due to the importance of flood events in the mobilisation of mine wastes, it is suggested that measurements of flood chemistry become part of River Basin Management Plans (RBMPs) for river catchments affected by historical (and active) metal mining, in order to assess the potential for dispersal of contaminated waste to agricultural floodplains.

### **9.3 Sedimentological impacts**

#### **9.3.1 Sediment quality**

Many geochemical studies of the sediments of mining-impacted rivers reveal severe contamination with heavy metals which can extend for a considerable distance beyond the source of contamination. Similarly, this study has demonstrated that the bed sediment of the Afon Twymyn is grossly contaminated with heavy metals, in particular Pb (section 6.2.1). Work by Pyatt and Collin (1999) confirms elevated metals in the sediments of the Dyfi Estuary, approximately 45 km downstream of Dylife. Few scientific investigations, and, as far as is known, no regulatory assessments, measure the concentration of metals

in different geochemical phases. This study has found extremely high concentrations of sediment-bound metals in bioavailable geochemical phases, representing a serious potential risk to the health of aquatic ecology and a significant secondary source of diffuse pollution in the Afon Twymyn (section 6.2.4). Bioavailable metals can move relatively easily through the aquatic environment and interact with aquatic organisms through ion-exchange reactions (Farag *et al.*, 1998). Recently published Environment Agency draft Sediment Environmental Quality Standards (SEQSs) (Environment Agency, 2008b) are compared with sediment concentrations observed in this study (**Table 9.2**). The criteria suggest two effect levels. The threshold effect level (TEL) represents the value below which sediment-bound metals are not considered to be harmful to biota. The predicted effect level (PEL) represents values considered to exert an adverse impact on biota. Whereas Zn constitutes the principal metal contaminant in the water column, Pb is the primary sediment-bound contaminant. Overall, 62% of sites on the Afon Twymyn have Pb concentrations above the TEL limit with the majority of 'failures' occurring at Dylife mine (45%). At the mine, 41% of sites exceed the PEL limit indicating the severe level of Pb contamination in the Afon Twymyn at this point. As such, these sites are expected to have serious deleterious impacts on aquatic ecology. Downstream of the mine, 17% of sites have Pb concentrations above TEL levels. Significant failures of guidelines are noted for Zn, Cu and Cd at some sites; however, the extent of contamination is not as severe as for Pb.

The bed sediment of the Afon Twymyn is severely contaminated with heavy metals. However, analysis of total heavy metals, as is proposed in the Environment Agency draft guidelines, provides little information on the ecotoxicity of these metals and their potential mobility. Therein lies the justification for the analysis of bioavailable metals in this study. The discovery of high proportions of metals in bioavailable phases in the bed sediments of the Afon Twymyn highlight the risk posed to aquatic ecology and water quality and illustrate metal phase as a significant factor in the context of dispersal of mine waste downstream (section 6.2.2). Had residual metals also been considered in this study, more extensive draft guideline failures would have been expected due to the high concentration of metals usually found in this geochemical phase (Jain, 2004).

**Table 9.2:** Percentage of sites in this study failing to meet draft Environment Agency TEL and PEL (in parenthesis) values (total metals) for sediment quality (Environment Agency 2008b)

Metals	EA criteria (mg/kg)		Present study - % stations exceeding criteria			
	TEL	PEL	Control sites	Mine sites	Downstream sites	Total
Pb (PEL)	35	91.3	0 (0)	45 (41)	17 (0)	62 (41)
Zn (PEL)	123	315	0 (0)	17 (0)	0 (0)	17 (0)
Cu (PEL)	36.7	197	0 (0)	14 (0)	0 (0)	14 (0)
Cd (PEL)	0.596	3.53	0 (0)	21 (0)	0 (0)	21 (0)

### 9.3.2 Moving forward with sediment management

Currently, there are no agreed European or UK guidelines pertaining to pollution of river sediments. With more than 90% of contaminants in mining-affected river catchments associated with sediments (Macklin *et al.*, 2006), this represents a serious handicap to achieving the aims of the Water Framework Directive. The development of Sediment Environmental Quality Standards is called for by the Water Framework Directive. However, proposals to date have been considered technically controversial with substantial logistical problems (Crane, 2003). A major difficulty stems from the nature of heavy metal pollutants. Assessment of metal toxicity is confounded by natural background concentrations; the existence of a number of chemical species; the concentrations of certain physico-chemical parameters; variations in organism tolerance/sensitivity; and the fact that some heavy metals (e.g. Zn, Cu) are essential elements for organisms (Forstner, 2004; Owens *et al.*, 2005; Comber *et al.*, 2008). These facts mean that metal toxicity to organisms will vary considerably between regions. Therefore, in order to classify accurately the ecological status of rivers impacted by metal mining, sediment assessments may need to be unique to each river catchment and incorporate

background metal concentrations, an assessment of bioavailable fractions, and concurrent water quality measurements (including major ions) (Netzband *et al.*, 2007; Brils, 2008; Forstner, 2009). There is also a debate over the practicality of sediment quality measurements in routine river ecosystem monitoring, as collecting and analysing sediment samples is a costly and time consuming process (Crane, 2003). Another difficulty is the absence of uniformity in guidelines and in sampling and analytical methods throughout Europe, resulting in a lack of inter-comparability between studies (Macklin *et al.*, 2006; Brils, 2008).

Recently, the importance of sediment systems in River Basin Management Plans has been accepted following the activity of the European Sediment Network (SedNet) and an initial under-emphasis in the Water Framework Directive (Forstner, 2002; Forstner and Salomons, 2008; Forstner, 2009). An amendment to the Water Framework Directive, Directive 2008/105/EC states that it should be left to individual Member States to identify, monitor and manage sediments which may pose a risk to aquatic ecology. Currently, sediment quality is not a feature of the overall assessment of river ecosystem status in England and Wales, although draft sediment quality criteria have been published (Environment Agency, 2008b). Given the results of the present study and other such geochemical investigations, should contamination of sediments of mining regions be assessed for bioavailable rather than total metals? This would be a more time consuming process. However, it is argued that the trade-off would be more useful and accurate information regarding the ecotoxicity of metals and the potential for metals to move beyond the mine site and to interact with different components of the river environment.

#### **9.4 Ecological impacts**

With ecology at the centre of the Water Framework Directive, characterising the impact of mine drainage on aquatic ecology, and implementing steps to improve water and sediment quality, will be important components of River Basin Management Plans in mining-affected river catchments. Therefore, this study sought to identify whether metal mine contaminants were influencing the benthic macroinvertebrate community of metal mining-impacted rivers, and whether some

widely used biological indices were generally effective in detecting the impacts of contamination.

#### 9.4.1 Biological quality

Using the Environment Agency of England and Wales biological quality classification scheme (based on BMWP scores) (Biological Monitoring Working Party, 1978), the biological quality of the Afon Twymyn during the study period was classified as fair to good (**Table 9.3**). These scores were consistent between seasons. Single Environment Agency measurements at Dylife mine in 2004 also rated the river here as having good biological quality. Further downstream, Environment Agency monitoring between 1990 and 2006 showed the biological quality to be good to very good at Bont Dolgadfan, Llanbrynmair and Commins Coch.

**Table 9.3:** *Percentage of sites in this study in each Environment Agency BMWP grade (Environment Agency, 2004)*

Grade	BMWP score	Percentage sites in each grade (%)			
		Control	Mine	D/S	Overall
A. Very Good	150 – 180	0	0	0	0
B. Good	100 – 150	31	13	25	20
C. Fair	50 – 100	69	87	75	80
D. Poor	15 – 50	0	0	0	0
E. Very Poor	0 - 15	0	0	0	0

#### 9.4.2 Macroinvertebrates as biomonitors of metal mine contamination

The results described above for the Afon Twymyn are surprising given the severe level of contamination of the water and sediment in the river. Similar results are reported for the other biological indices which could not detect any significant negative impact on the macroinvertebrate community (section 8.1.2). It appears to be a general pattern in the literature of widely varying performance of macroinvertebrates as indicators of contamination in mining-impacted rivers. This

is undoubtedly related to the varying character of mine waters around the world which is confounded when they enter surface hydrological systems. The length of time the ecological community has been exposed to contamination is a further complicating factor. However, results from the CCA analyses show significant differences in community structure between polluted and unpolluted sites and demonstrates that some impact is occurring that the single biological indices cannot measure. In view of this, it must be considered whether biological indices alone are a useful biodiagnostic tool in moderately contaminated river systems with a long history of impact, such as the Afon Twymyn (and most mining-impacted rivers in the UK). The sole use of the BMWP scoring system in England and Wales to evaluate biological quality in mining-impacted rivers is not supported by this research, due to it being developed primarily to detect the impacts of organic pollution. Currently, a universal method for determining ecological health at mine sites is neither available nor feasible, due to the many biotic and abiotic factors influencing community structure. Using imprecise measurement tools, it must be considered whether classifications of ecological status at abandoned metal mines for the WFD will represent accurately the health of aquatic communities and the level of impact exerted on them by mining activity. This is something that would need to be explored further by collating data from river systems with similar levels of contamination and mining legacy. The wider consideration here is whether the ecological assessment procedure to be implemented under the WFD can be applied universally regardless of the type of (potential) contamination or human impact.

There is much evidence indicating both the success and failure of diversity indices to discern the effects of metal mine drainage. Variability in success is likely to be a function of the complicated interplay between the mine water components, as well as other water quality parameters (e.g. TOC, water hardness). Clearly, there is scope for a biological index designed specifically for detecting the impacts of mine water contamination on aquatic communities. Such an index would need to incorporate the effects on a community of multiple environmental stressors, the most important of which are probably dissolved metals and acidity. Gray and Delaney (2008) suggest a modification of the AWIC index to incorporate metal toxicity. However, such a revision would also need to address the pH bias in the

calibration data and the (possibly) inaccurate grouping of macroinvertebrates in sensitivity groups. A revision of the BMW P system, based on species' tolerance to acidity and metal contamination, has also been suggested (Gray and Delaney, 2008). A better approach may be the utilization of a number of biological indices together. Although it has been difficult in this study to unequivocally identify impaired communities, other authors have found success using combinations of standard biotic indices (e.g. Clews and Ormerod, 2009).

In developing a new index for mine water contaminants, two important issues would need to be considered. Firstly, the severity of the mine discharge may affect whether biological indices identify ecological impacts. It appears that biological indices have greater success identifying biological impacts in rivers receiving more severe mine discharges than that observed at Dylife (e.g. Gray and Delaney, 2008). The combination of acidity and dissolved heavy metals in acid mine drainage may cause more impoverished macroinvertebrate communities and allow biological indices to identify them better. Secondly, the longevity of the mining impact may be a factor. It is known that over many generations some macroinvertebrates can develop tolerances to specific metals or combinations of metals (Morgan *et al.*, 2007). Such a circumstance is possible in the Afon Twymyn, and in other rivers where mine water discharges have occurred for millennia.

## **9.5 Climate change implications for the management of mining-impacted watercourses**

By the 2020s, climate change models predict warmer and drier summers and heavier winter precipitation in the UK, with intensified storm activity in all seasons (Murphy *et al.*, 2009). There is evidence that more rapid warming (Holden and Adamson, 2002) and increased precipitation (Malby *et al.*, 2007) is already occurring in upland regions. Such a scenario clearly has implications for the management of river catchments and in particular mining-impacted watercourses (most of which occur in upland areas). However, the WFD does not clearly mention risks posed by climate change to the achievement of its environmental objectives (Wilby *et al.*, 2006).

Current predictions of greater frequency and magnitude of floods will likely result in increased flushing of metals from mine sites and also reduced dilution of waters during low flows (Whitehead *et al.*, 2009). Warmer summers with greater occurrences of droughts will increase mineralisation and oxidations rates of heavy metals, thereby increasing the general availability of heavy metals. In peaty catchments, lower water tables and anaerobic conditions will enhance sulphur oxidation and nitrification processes (Whitehead *et al.*, 2009). At Dylife mine, this might result in more acidic conditions during storm flushing events. This has consequences for the mobilisation and toxicity of heavy metals during flood events.

Increased flood frequency in the latter part of the 20<sup>th</sup> century has lead to contaminated sediment loads in rivers draining former mining areas of north-east England comparable to levels at the height of mining activity in the late 19<sup>th</sup> century (Longfield and Macklin, 1999). The highest magnitude flood events and, consequently, the highest sediment fluxes seem to be linked to the frequency of cyclonic atmospheric circulations (Wilby *et al.*, 1997). Predicted increases in flood magnitude and frequency in the UK due to climate change could result in higher occurrence of extreme floods and consequently increased sediment fluxes and mobilisation of heavy metals (Longfield and Macklin, 1999). However, some regions might also benefit through dilution of contaminated sediments by cleaner sediments from hillslopes unaffected by mining activity (Coulthard and Macklin, 2003).

Monitoring of important parameters which classify ecological status (e.g. instream biology, physico-chemistry and hydromorphology) will need to take account of natural spatial and temporal variability in these parameters and the variability that is likely to occur as a result of climate change (Wilby *et al.*, 2006). Effects of climate change have already been found in the abundance and community composition of invertebrate populations (Durance and Ormerod, 2007). Increases in water temperature will affect the behaviour of aquatic organisms, in particular the timing and emergence of invertebrate populations (Durance and Ormerod, 2007). The WFD needs to take account of future changes that might occur in reference parameters.



## 9.6 Mine site remediation

In general, water quality is improving in England and Wales, as is the health of aquatic ecosystems (Durance and Ormerod, 2009). Even so, approximately 20% of river water quality objective failures in England and Wales are attributable to metal mine pollution (Environment Agency, 2002). The prevention of contaminated discharge from mine sites by mining companies is now required by law in most countries (Younger *et al.*, 2002). In Europe, the advent of the WFD has necessitated the development of inventories of contaminant impacts at active and also long abandoned mine sites (Environment Agency, 2008a). These new pieces of legislation, based on a greater understanding of the water and ecological quality issues arising from mine discharges, have prompted research into remediation technologies aimed at reducing the environmental impact of mines (PIRAMID, 2003). Active treatment technologies are well established and involve the use of energy and mechanised procedures (Jarvis *et al.*, 2006), and are dependent on continuous monitoring and maintenance (Robb and Robinson, 1995). In response to the high cost and energy/resource hungry active technologies, passive remediation utilising natural physical, chemical and biological processes and materials have found favour over the past 25 years (Younger *et al.*, 2002). Such systems use naturally available energy (e.g. topographical gradient, metabolic energy, photosynthesis) to drive remediation processes and have the principal advantages over active remediation of reduced cost and requiring only infrequent maintenance (Pulles and Heath, 2009). Passive systems do generally require more land area than for active treatment, and this is proving to be an obstacle to treatment at some mine sites in the UK where land area is limited (Geroni *et al.*, 2009).

Significant progress was made with passive technologies for the treatment of coal mine discharges in the 1990s in the USA (Hedin *et al.*, 1994), and a number of these technologies (e.g. wetlands) have been implemented in the UK to treat net-alkaline and net-acidic coal mine drainages (Batty and Younger, 2004). However, the adoption and implementation of passive remediation technologies specifically for metal mine discharges has been slow in the UK, mainly due to a lack of understanding of biogeochemical processes in metal mine discharges (Younger *et*

*al.*, 2002). Considerable success was achieved at the Wheal Jane Mine Passive Treatment Plant in Cornwall, UK, where a system of wetlands and rock filters treated acid mine drainage from Wheal Jane Tin Mine by encouraging precipitation and sulphidisation of metals in the wetlands (Whitehead *et al.*, 2005). This trial facility was decommissioned in 2008 after the collection of valuable data and knowledge for the future design of passive sustainable systems (Whitehead and Prior, 2005). Prior to its closure, this facility was the only fully operational and full scale passive system for the treatment of metal mine discharge in the UK.

Wetland systems have proved useful in removing zinc from some net-acidic mine waters (Whitehead *et al.*, 2005). However, a significant problem surrounds metal mine discharges, such as occurs at Dylife, where the mine drainage is circum-neutral and the principal contaminant is dissolved zinc. Such waters are not readily amenable to sulphidisation in traditional wetland systems (Younger, 2000). The principal issue is how to raise the pH of the mine water to a high enough level to encourage and maintain metal precipitation and/or adsorption. There have been numerous laboratory and field investigations of treatment systems utilising a variety of high surface area media to encourage adsorption and precipitation of metals. Tested sorbents have included de-alginated seaweed (Perkins *et al.*, 2006), ochre (Mayes *et al.*, 2009), caustic magnesia (Rotting *et al.*, 2008) and coal fly ash (Koukoulzas *et al.*, in press). Some success has been achieved by using a closed-system limestone reactor (Nuttal and Younger, 2000), which encourages zinc to precipitate as a carbonate (smithsonite) over a narrow pH range (pH 7.5 – 8.0). However, most of these technologies are still at the trial stage, and the principal hurdles to overcome include the blocking of filtering media with metal precipitates and the rapid consumption of reactive surfaces. These problems limit the high efficiency of these systems to very short time scales (hours to days in many cases) (Younger *et al.*, 2002). Further testing is required to achieve consistency of metal removal on medium to long-term timescales.

Before identifying a suitable remediation system for Dylife mine, a number of other challenges would need to be considered. To reduce costs, construction materials would be preferably locally sourced (Johnson and Hallberg, 2005). However, if limestone were to be used, it would need to be imported, incurring substantial

transport costs. If a closed-system limestone reactor of the type tested by Nuttall and Younger (2000) were to be used, accumulated smithsonite would need to be removed periodically from the limestone surface to maintain the systems efficiency. The removal and storage/disposal of accumulated smithsonite would need consideration and might incur additional costs. Clearly, the potential benefits of any remediation scheme would need to be weighed against the capital and maintenance costs.

A facility could be constructed at Dylife mine to capture and route diffuse runoff from the main spoil tips area to a treatment system constructed between the spoil and the main river channel. There is considerable space here for an extensive system, perhaps a combination of wetlands (to remove Pb) and limestone drains (to remove Zn). This would treat the majority of the heavy metal load. However, the diffuse nature of the mine waters would make it difficult to collect and route all of the contaminants to the treatment area (Mayes *et al.*, 2008). Wetlands and limestone drains would have to be designed to accommodate flood flows delivering large contaminant loads. There is also the problem of diffuse contaminant sources through mobile metal fractions in the river bed, which might bypass any treatment system.

Due to the great variability in the chemistry of metal mine discharges, it is likely that individual laboratory trials with different systems and substrates would be necessary to identify which is the most suitable to treat mine waters at Dylife. Such an approach has been taken at the Cwm Rheidol metal mines complex near Aberystwyth (Edwards and Potter, 2007). For individual mines, the investment in laboratory trials will have to be weighed against the severity of the mine discharge and its impact on the aquatic environment. Any monetary benefit arising from water quality improvements in the Afon Twymyn (e.g. re-establishment of salmonid fishery, tourism) by a treatment system, may not be sufficient to warrant investment in remediation at Dylife.

Even with mine water treatment, the legacy of contamination in the sediments of the Afon Twymyn will represent a significant secondary diffuse source of pollution long after other water quality parameters have improved to acceptable levels.

Therefore, contaminated sediments of mining-affected rivers will continue to pose a serious threat to ecological integrity and the achievement of 'good' chemical and ecological status under the Water Framework Directive. The traditional method of dealing with contaminated sediment is removal by dredging. This is an expensive and destructive process which could potentially mobilise vast reservoirs of bioavailable metals (Nayar *et al.*, 2004; Knott *et al.*, 2009). Furthermore, the removed sediment still needs to be treated and disposed of safely. Recently, geochemical engineering approaches involving in-situ and ex-situ biological and chemical treatment of contaminated soil/sediment have gained attention as an alternative (Forstner, 2004), and some success has been achieved in the stabilisation and removal of heavy metals (Guangwei *et al.*, 2009; Luoping *et al.*, 2009; Scanferla *et al.*, 2009). However, the principal necessity for the protection of sediment and aquatic systems is seen as the development of sediment quality guidelines.

A final consideration surrounds environmental quality standards for river systems, such as the Afon Twymyn, which have suffered millennia of heavy metal contamination. The target of 'good' ecological status means that only a slight diversion in water and ecological quality will be permitted from what could be expected in unmodified natural waters. In the case of most English and Welsh metal mines, which have been abandoned for over a century, the issue is whether the river systems which drain them have in fact returned to an unmodified state, given they would experience naturally elevated heavy metal concentrations due to local mineralisation. Clearly, as is the case with the Afon Twymyn, these river systems are grossly polluted; however, many of these sites have archaeological and sociological significance. Dylife mine is protected for its rare lichen species and is a Regionally Important Geodiversity Site (RIGS) for mineralogy (Brown, 2006). This makes the implementation of remediation strategies/technologies potentially difficult and controversial. Therefore, flexibility of environmental quality guidelines with respect to river systems with a substantial industrial legacy will be another important consideration in River Basin Management Plans (Netzband *et al.*, 2007).

## **9.7 Recommendations for future research**

Several opportunities for further research which could advance our understanding of mine water pollution impacts on river systems can be identified from this study. A knowledge gap still exists in our understanding of the movement of water in mine spoil and the process of metal leaching. Whilst the results of this study suggest the primary sources of contamination during runoff events are near-surface spoil materials, little is known about the movement of deeper seated flows and how they might influence metal leaching and contaminant movement. More specifically at Dylife mine, further research needs to be conducted in order to understand the movement of mine water underground, to identify underground sources of contamination and to assess the relative contribution of underground sources to the total metal load. It would be useful to test the hypothesis developed in this thesis that rivers receiving moderate contamination from metal mine sites appear to have relatively healthy macroinvertebrate communities when standard biological indices are used. This would require further data collection from multiple catchments with abandoned mine sites. Such an investigation might allow the development of a biological index specifically for detecting the impacts of moderate metal mine contamination as occurs at the majority of metal mine sites throughout the UK.

## **9.8 Chapter summary**

This thesis has investigated the hydrological, sedimentological and ecological impacts of metal mine contamination in river systems, with particular reference to a mining-impacted river in central Wales. It has also highlighted how a contamination episode (i.e. 18<sup>th</sup>/19<sup>th</sup> century mining), long forgotten and far removed from most industrial centres, continues to cause significant environmental concern. A multi-disciplinary approach incorporating aspects of hydrology, hydrochemistry, geochemistry and freshwater ecology, in a set of field and laboratory studies, has demonstrated: a) the significance of contaminated sediments in mining-impacted river channels as potential diffuse sources of contamination, and their potential to interact with, and accumulate in, organisms; b) the role of flood events in dispersing contaminants from mine sites and increasing the potential toxicity of river water; and c) the relationship between

metal mine contaminants and macroinvertebrate communities, and the difficulties inherent in assessing this relationship.

One of the principal tasks facing environmental monitoring agencies in the UK is the classification of rivers according to the criteria set out in the Water Framework Directive. The major challenge is then to maintain and improve the ecological and chemical status of rivers which fail to meet these criteria. The findings of this study demonstrate the benefits of using a multi-disciplinary approach to detect the impacts of metal mine contamination in river systems. The findings also highlight some of the principal issues which need to be considered in River Basin Management Plans in order to maintain and/or improve the health of rivers impacted by historical metal mining in the UK. Furthermore, the findings of this study pose questions over the validity of the current UK and EU approach to the assessment of sediment and ecological quality.

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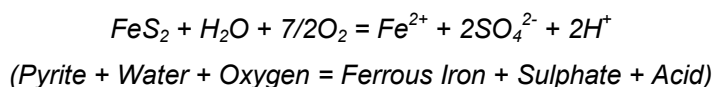
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## Appendix 2.1: The chemistry of pyrite weathering

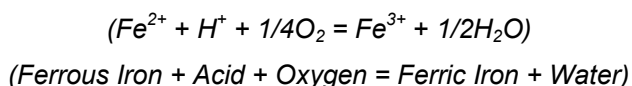
The process of sulphide weathering transfers electrons from the mineral phases of sulphur and metals to dissolved oxygen, forming soluble sulphur and metal oxides. Iron sulphides such as pyrite, marcasite and pyrrhotite are the most common sources of AMD production as they are ubiquitous in metal sulphide ores (Wilkin, 2008). The process of pyrite weathering is used here as an example. Four general equations describe the chemistry of pyrite weathering and the production of AMD (Robb, 1994).

### Reaction (1)



The first reaction in the weathering of pyrite involves the oxidation of pyrite by dissolved oxygen in moist or flooded conditions, although this process can also take place in dry conditions. Pyrite is oxidised to generate sulphate and ferrous iron. Acidity is produced in the form of sulphuric acid. Two moles of acidity are produced for each mole of pyrite oxidized. The acid conditions can dissolve oxidised metals (e.g. Zn, Pb, Cu, Cd).

### Reaction (2)

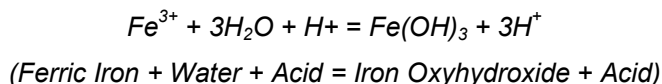


The second reaction involves the oxidation of dissolved ferrous iron to ferric iron which consumes one mole of acidity for each mole of ferrous iron. As pH and the amount of dissolved oxygen decrease, the rate of iron oxidation begins to slow and reactions **(1)** and **(2)** become less important. A sufficient supply of dissolved oxygen might be maintained through contact with the atmosphere but we will assume here that dissolved oxygen levels are falling.

In acidic and deoxygenated conditions the reaction rate can be catalyzed by a factor of  $10^6$  by acidophilic micro-organisms (Atkins and Pooley, 1982; Rawat and Singh, 1982; Johnson, 2003) who harness electrons as an energy source to grow and maintain cell functions (Younger et al., 2002). Some micro-organisms will oxidise sulphur to produce sulphuric acid which dissolves acid-soluble minerals such as galena and sphalerite (Balci, 2008). Other micro-organisms are specifically iron-oxidising bacteria (e.g. *Acidithiobacillus ferrooxidans*; *Thiobacillus thiooxidans*; *Leptospirillum ferrooxidans*) and can dissolve the iron oxides produced by pyrite oxidation (ferrous and ferric iron) (Hallberg and Johnson, 2005). The reaction rate is pH dependant proceeding

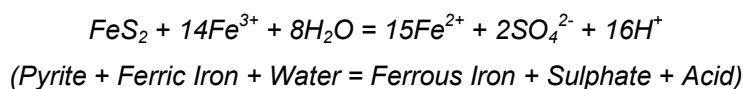
slowly under very acidic conditions (pH 2-3) and several orders of magnitude faster at pH values near 5.

### Reaction (3)



The third reaction involves the hydrolysis (separation of water molecule and metal ion) of ferric iron and the precipitation of iron oxyhydroxide (ochre). Three moles of acidity are generated as a by-product. Many metals are capable of undergoing hydrolysis. The formation of ferric hydroxide precipitate is pH dependant. Solids form if the pH is above about 3.5 but below pH 3.5 little or no solids will precipitate (Bradley, 1995).

### Reaction (4)



The fourth reaction is the oxidation of additional pyrite by the ferric iron which was generated in reaction (2). This reaction does not require oxygen as the ferric iron is the oxidizing agent.

#### Appendix 4.1: Details of sample stations in the Afon Twymyn

Sample station	National Grid Reference		Sample type*	Stream name
1	289080	302765	Su, S, W	A. Laen
2	288774	301619	Su, S, W	A. Twymyn
3	288692	300673	Su, S, W, K	A. Twymyn
4	288183	293430	Su, S, W	A. Twymyn
5	288040	297783	Su, S, W	A. Twymyn
6	287581	296847	Su, S, W	A. Twymyn
7	286618	293890	Su, S, W	A. Twymyn
8	286553	293902	Su, S, W	A. Twymyn
9	286435	293911	Su, S, W	A. Twymyn
10	286322	“93992	Su, S, W	A. Twymyn
11	286251	294013	Su, S, W, K	A. Twymyn
12	286074	293946	Su, S, W	A. Twymyn
13	285821	293512	Su, S, W	A. Twymyn
14	285576	293978	Su, S, W	A. Twymyn
15	285522	293936	Su, S, W	A. Twymyn
16	285394	293898	Su, S, W	A. Twymyn
17	286046	294052	Su, S, W	N. Dropyns
18	285910	294089	Su, S, W	N. Dropyns
19	285813	294197	Su, S, W	N. Dropyns
20	285667	294261	Su, S, W	N. Dropyns
21	285587	294284	Su, S, W	Nant yr lar
22	284721	293886	Su, S, W	Nant yr lar
23	284659	293847	Su, S, W	Nant yr lar
24	284546	293783	Su, S, W, K	Nant yr lar
25	284666	294070	Su, S, W	Nant Yr Lar
26	284735	294004	Su, S, W	N. Dropyns
27	285026	294656	Su, S, W	N. Dropyns
28	284987	294725	Su, S, W	N. Dropyns
29	284919	294783	Su, S, W, K	N. Dropyns
ST	286386	293929	W	Flooded stope
Spr1	285693	293939	W	Spoil spring 1
Spr2	286213	293993	W	Spoil spring 2
MineT	286444	293743	W	Mine tributary
SRF	286343	293938	W	Spoil runoff
AF	287655	297487	W	A. Fachdre
NC	287906	298155	W	N. Caeconroi
CN	288049	297305	W	Creignant
WFT	285359	999043	W	Waterfall tributary
Pond	284803	293964	W	Pwll
Marsh	284695	294964	W	Rhydporthmyn Marsh

\*Key To Sample Type: Su = surber, S = sediment, W = water, K = kick



**Appendix 5.1: Summary of measured discharge data for the Nant Yr Lar (at control station) – based on daily values (2008)**

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
<i>Nant Yr Lar measured flow data (2008)</i>												
Mean flow (m <sup>3</sup> /s)	0.021	0.021	0.020	0.009	0.006	0.006	0.009	0.010	0.010	0.019	0.019	0.032
Max flow (m <sup>3</sup> /s)	0.028	0.080	0.054	0.016	0.011	0.024	0.045	0.042	0.063	0.107	0.062	0.099
Min flow (m <sup>3</sup> /s)	0.017	0.009	0.009	0.005	0.003	0.003	0.004	0.005	0.003	0.006	0.008	0.004
Total flow (million m <sup>3</sup> )	0.059	0.052	0.053	0.024	0.016	0.014	0.023	0.027	0.026	0.052	0.049	0.078
Rainfall (mm)	395	128	238	122	39	134	157	198	215	367	172	125
Runoff (mm)	263	85	159	81	26	89	105	132	143	244	114	83

**Appendix 5.2: Summary of measured discharge data for the Afon Twymyn (at mine station) – based on daily values (2008)**

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
<i>Afon Twymyn measured flow data (2008)</i>												
Mean flow (m <sup>3</sup> /s)	0.233	0.179	0.199	0.133	0.081	0.080	0.100	0.099	0.096	0.175	0.140	0.255
Max flow (m <sup>3</sup> /s)	0.310	0.500	0.318	0.213	0.147	0.192	0.350	0.253	0.381	0.548	0.290	0.685
Min flow (m <sup>3</sup> /s)	0.183	0.073	0.132	0.093	0.063	0.054	0.044	0.052	0.034	0.076	0.051	0.062
Total flow (million m <sup>3</sup> )	0.563	0.449	0.511	0.346	0.212	0.206	0.263	0.261	0.249	0.460	0.363	0.677
Rainfall (mm)	395	128	238	122	39	134	157	198	215	367	172	125
Runoff (mm)	204	66	123	63	20	70	81	102	111	190	89	65

**Appendix 5.3: Summary of measured discharge data for the Afon Gwy (at Cefn Brwyn) – based on daily values (2008)**

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec
<i>Afon Gwy measured flow data (2008)</i>												
Mean flow (m <sup>3</sup> /s)	0.687	0.195	0.374	0.195	0.073	0.133	0.170	0.430	0.329	0.677	0.470	0.288
Max flow (m <sup>3</sup> /s)	3.310	1.034	0.928	0.486	0.215	1.252	1.004	1.523	1.744	3.376	2.064	1.106
Min flow (m <sup>3</sup> /s)	0.085	0.043	0.118	0.080	0.042	0.027	0.065	0.069	0.048	0.162	0.069	0.061
Total flow (million m <sup>3</sup> )	1.841	0.490	1.002	0.504	0.196	0.344	0.668	1.152	0.852	1.814	1.217	0.783
Rainfall (mm)	-	-	-	-	-	-	-	-	-	-	-	-
Runoff (mm)	-	-	-	-	-	-	-	-	-	-	-	-

- No data available

#### Appendix 5.4 Hydrograph characteristics of 14 storms from the control station (2008)

Storm	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Start date/time	31/01	25/02	23/03	24/04	26/06	06/07	10/08	05/08	05/09	23/10	09/11	17/11	09/12	12/12
	03:45	19:45	00:45	04:00	08:45	17:00	20:00	03:00	01:15	10:00	13:30	14:45	07:00	14:30
Rainfall (mm)	14.6	30.2	8.8	9	55.2	17.4	10.4	13.6	61.8	34.2	21.2	10.8	3.8	21.6
Max 15min rainfall (mm)	2.6	1.4	1.2	1.6	3	2.6	1	0.6	7.6	3.2	2.4	1.8	1.2	2.8
Rainfall duration (hrs)	4.75	10.75	6.50	2.75	23.00	3.50	8.75	12.75	36.00	14.00	8.25	10.25	7.00	27.75
Peak Q (m <sup>3</sup> /s)	0.041	0.06	0.014	0.014	0.057	0.025	0.014	0.009	0.06	0.038	0.034	0.024	0.047	0.063
Storm Q (m <sup>3</sup> )	2007	3521	547	452	3612	766	429	576	5691	2287	1655	1608	1111	3810
Time Pk (hrs)	8.75	9.25	4.25	3	12.25	3.5	6.75	6	12.25	8	4.25	4.75	7.5	11.25
Lag (hrs)	0.5	4.75	3.75	2	7	2	3.5	3	-10.5	5.25	1.75	1.25	4	1.75

### Appendix 5.5 Hydrograph characteristics of 14 storms from the mine station (2008)

Storm	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Start date/time	31/01	25/02	23/03	24/04	26/06	06/07	10/08	05/08	05/09	23/10	09/11	17/11	09/12	12/12
	03:45	19:45	00:45	04:00	08:45	17:00	20:00	03:00	01:15	10:00	13:30	14:45	07:00	14:30
Rainfall total (mm)	14.6	30.2	8.8	9	55.2	17.4	10.4	13.6	61.8	34.2	21.2	10.8	3.8	21.6
Max 15min rainfall (mm)	2.6	1.4	1.2	1.6	3	2.6	1	0.6	7.6	3.2	2.4	1.8	1.2	2.8
Rainfall length (hrs)	4.75	10.75	6.50	2.75	23.00	3.50	8.75	12.75	36.00	14.00	8.25	10.25	7.00	27.75
Storm Q (m <sup>3</sup> )	30023	67452	26134	18853	66134	17013	10761	9656	78772	37390	25057	18113	16137	59954
Peak Q (m <sup>3</sup> /s)	0.484	0.443	0.278	0.189	0.574	0.4	0.186	0.085	0.58	0.303	0.433	0.347	0.322	0.607
Time Pk (hrs)	9.5	4	7.25	8	13	3.5	8.25	2.25	2.5	9.25	4.25	5.5	8.75	11.75
Lag (hrs)	1.25	5	4	3	7.45	2	4.5	4	-8	7	1.75	2	5	2

## Appendix 5.6 Pearson correlation coefficients and significance values for control station storms

		Total rainfall	Max15min rainfall	Rainfall length	Storm Q	Peak Q	Time pk	Lag	Hydrograph intensity
Total rainfall	Pearson Correlation	1	.799(**)	.790(**)	.853(**)	.649(*)	.736(**)	-.365	-.616(*)
	Sig. (2-tailed)		.001	.001	.000	.012	.003	.200	.019
	N	14	14	14	14	14	14	14	14
Max15min rainfall	Pearson Correlation	.799(**)	1	.743(**)	.793(**)	.557(*)	.563(*)	-.780(**)	-.464
	Sig. (2-tailed)	.001		.002	.001	.039	.036	.001	.095
	N	14	14	14	14	14	14	14	14
Rainfall length	Pearson Correlation	.790(**)	.743(**)	1	.867(**)	.654(*)	.815(**)	-.502	-.764(**)
	Sig. (2-tailed)	.001	.002		.000	.011	.000	.067	.001
	N	14	14	14	14	14	14	14	14
StormQ	Pearson Correlation	.853(**)	.793(**)	.867(**)	1	.879(**)	.860(**)	-.488	-.757(**)
	Sig. (2-tailed)	.000	.001	.000		.000	.000	.077	.002
	N	14	14	14	14	14	14	14	14
PeakQ	Pearson Correlation	.649(*)	.557(*)	.654(*)	.879(**)	1	.840(**)	-.199	-.632(*)
	Sig. (2-tailed)	.012	.039	.011	.000		.000	.496	.015
	N	14	14	14	14	14	14	14	14
Time pk	Pearson Correlation	.736(**)	.563(*)	.815(**)	.860(**)	.840(**)	1	-.222	-.774(**)
	Sig. (2-tailed)	.003	.036	.000	.000	.000		.446	.001
	N	14	14	14	14	14	14	14	14
Lag	Pearson Correlation	-.365	-.780(**)	-.502	-.488	-.199	-.222	1	.259
	Sig. (2-tailed)	.200	.001	.067	.077	.496	.446		.371
	N	14	14	14	14	14	14	14	14
Hydrograph intensity	Pearson Correlation	-.616(*)	-.464	-.764(**)	-.757(**)	-.632(*)	-.774(**)	.259	1
	Sig. (2-tailed)	.019	.095	.001	.002	.015	.001	.371	
	N	14	14	14	14	14	14	14	14

\*\* Correlation is significant at the 0.01 level (2-tailed).

\* Correlation is significant at the 0.05 level (2-tailed).

### Appendix 5.7 Pearson correlation coefficients and significance values for mine station storms

		Total rainfall	Max15min rainfall	Rainfall length	Storm Q	Peak Q	Time pk	Lag	Hydrograph intensity
Total rainfall	Pearson Correlation	1	.799(**)	.790(**)	.848(**)	.636(*)	.019	-.356	-.066
	Sig. (2-tailed)		.001	.001	.000	.015	.947	.212	.822
	N	14	14	14	14	14	14	14	14
Max15min rainfall	Pearson Correlation	.799(**)	1	.743(**)	.678(**)	.651(*)	-.116	-.772(**)	-.097
	Sig. (2-tailed)	.001		.002	.008	.012	.692	.001	.742
	N	14	14	14	14	14	14	14	14
Rainfall length	Pearson Correlation	.790(**)	.743(**)	1	.790(**)	.609(*)	.090	-.432	-.211
	Sig. (2-tailed)	.001	.002		.001	.021	.759	.123	.468
	N	14	14	14	14	14	14	14	14
Storm Q	Pearson Correlation	.848(**)	.678(**)	.790(**)	1	.794(**)	.152	-.372	-.263
	Sig. (2-tailed)	.000	.008	.001		.001	.603	.190	.364
	N	14	14	14	14	14	14	14	14
Peak Q	Pearson Correlation	.636(*)	.651(*)	.609(*)	.794(**)	1	.273	-.630(*)	.171
	Sig. (2-tailed)	.015	.012	.021	.001		.345	.016	.558
	N	14	14	14	14	14	14	14	14
Time pk	Pearson Correlation	.019	-.116	.090	.152	.273	1	.219	.193
	Sig. (2-tailed)	.947	.692	.759	.603	.345		.453	.508
	N	14	14	14	14	14	14	14	14
Lag	Pearson Correlation	-.356	-.772(**)	-.432	-.372	-.630(*)	.219	1	-.119
	Sig. (2-tailed)	.212	.001	.123	.190	.016	.453		.685
	N	14	14	14	14	14	14	14	14
Hydrograph intensity	Pearson Correlation	-.066	-.097	-.211	-.263	.171	.193	-.119	1
	Sig. (2-tailed)	.822	.742	.468	.364	.558	.508	.685	
	N	14	14	14	14	14	14	14	14

\*\* Correlation is significant at the 0.01 level (2-tailed).

\* Correlation is significant at the 0.05 level (2-tailed).

**Appendix 6.1: Kruskal-Wallis and Mann Whitney U tests of significance for water quality variables between locations and seasons (Afon Twymyn, 2007/2008)**

<b>Main effects</b>	<b>Pb</b>	<b>Zn</b>	<b>Cu</b>	<b>Cd</b>	<b>Fe</b>	<b>Mn</b>	<b>pH</b>	<b>Cond</b>
Season	.014*	.770	.000**	.000**	.000**	.438	.002**	.012*
Location	.000**	.000**	.003**	.000**	.000**	.000**	.000**	.000**
<b>Post-hoc effects</b>								
<b>Season</b>								
Jun07 and Oct07	.010**	.349	.000**	.000**	.550	.746	.488	.006**
Jun07 and Mar08	.026*	.788	.000**	.000**	.000**	.151	.004**	.773
Oct07 and Mar08	.220	.985	.000**	.016*	.000**	.542	.001**	.020*
<b>Location</b>								
Control*Mine	.000**	.000**	.001**	.000**	.000**	.000**	.000**	.000**
Control*Downstream	.006**	.000**	.030*	.031*	.003**	.000**	.000**	.000**
Control*Tributaries	.000**	.000**	.056	.005**	.010**	.000**	.000**	.018*
Mine*Downstream	.000**	.026*	.567	.029*	.003**	.013*	.028*	.000**
Mine*Tributaries	.000**	.000**	.053	.154	.304	.983	.038*	.281
Tributaries*Downstream	.086	.005**	.421	.433	.580	.682	.478	.001**

\*significant at 0.05

\*\*significant at 0.01

**Appendix 6.2: Kruskal-Wallis and Mann Whitney U tests of significance for sediment variables between locations, fractions and extract phases (Afon Twymyn, June 2007)**

<b>Main effects</b>	<b>Pb</b>	<b>Zn</b>	<b>Cd</b>	<b>Cu</b>	<b>Fe</b>	<b>Mn</b>
Fraction	.078	.000**	.005**	.000**	.007**	.000**
Location	.000**	.000**	.000**	.000**	.302	.000**
Extract	.000**	.003**	.000**	.002**	.000**	.000**
<b>Post-hoc effects</b>						
<b>Extract</b>						
Ext1*Ext2	.106	.238	.212	.000**	.000**	.000**
Ext1*Ext3	.000**	.002**	.001**	.183	.013*	.000**
Ext2*Ext3	.000**	.009**	.000**	.056	.000**	.000**
<b>Location</b>						
Control*Mine	.000**	.000**	.000**	.000**	.772	.430
Control*Downstream	.000**	.000**	.038*	.000**	.224	.496
Mine*Downstream	.000**	.000**	.000**	.004**	.122	.100

\*significant at 0.05

\*\*significant at 0.01



**Appendix 6.3: Mean and range (in parenthesis) of non-residual heavy metals in the clay/silt fraction (<63µm) of the Afon Twymyn bed sediments according to site groups (June 2007)**

Variable	Mean		
	Control sites	Mine sites	Downstream sites
Zn	5.90	78	15
(range)	(0.71 – 12)	(32 – 148)	(6.96 – 18)
Pb	4.28	1180	40
(range)	(1.09 – 8.07)	(42 – 2914)	(13 – 65)
Cu	0.63	12	1.90
(range)	(0.20 – 1.37)	(0.56 – 30)	(0.68 – 3.60)
Cd	0.05	0.42	0.10
(range)	(ND – 0.16)	(0.19 – 0.90)	(0.05 – 0.14)
Fe	454	353	67
(range)	(164 – 926)	(213 – 590)	(53 – 77)
Mn	540	196	26
(range)	(16 – 1118)	(53 – 480)	(17 – 32)

ND = not detectable

**Appendix 6.4: Mean and range (in parenthesis) of non-residual heavy metals in the fine sand fraction (64 – 2000µm) of the Afon Twymyn bed sediments according to site groups (June 2007)**

Variable	Mean		
	Control sites	Mine sites	Downstream sites
Zn	0.80	33	5.57
(range)	(0.39 – 1.13)	(4.48 – 100)	(3.58 – 7.03)
Pb	0.58	125	21
(range)	(0.42 – 0.94)	(3.96 – 280)	(11 – 27)
Cu	0.04	5.82	1.72
(range)	(0.02 – 0.09)	(0.09 – 23)	(0.35 – 6.88)
Cd	ND	0.22	0.04
(range)	ND	(0.03 – 0.75)	(0.03 – 0.05)
Fe	58	46	34
(range)	(29 – 116)	(29 – 71)	(25 – 42)
Mn	13	33	17
(range)	(2.31 – 35)	(16 – 57)	(12 – 25)

ND = not detectable

### Appendix 6.5: Correlation matrix of water (D) and sediment (S) variables

Element	PbS	ZnS	CuS	CdS	FeS	MnS	PbD	ZnD	CuD	CdD	FeD	MnD	pH	Cond
PbS	1													
ZnS	.866(**)	1												
CuS	.889(**)	.675(**)	1											
CdS	.634(**)	.917(**)	.399(*)	1										
FeS	-0.126	-0.146	-0.125	-0.080	1									
MnS	-0.272	-0.184	-0.295	-0.053	.697(**)	1								
PbD	.951(**)	.884(**)	.863(**)	.695(**)	-0.132	-0.265	1							
ZnD	.856(**)	.711(**)	.939(**)	.459(*)	-0.229	-0.378	.896(**)	1						
CuD	.618(**)	.506(**)	.820(**)	0.342	-0.132	-0.255	.683(**)	.828(**)	1					
CdD	.852(**)	.705(**)	.931(**)	.449(*)	-0.177	-0.340	.902(**)	.990(**)	.811(**)	1				
FeD	-.524(**)	-.555(**)	-.474(*)	-.480(*)	.473(*)	0.245	-.523(**)	-.574(**)	-.396(*)	-.505(**)	1			
MnD	-0.351	-.418(*)	-0.284	-.402(*)	.599(**)	.535(**)	-0.336	-0.356	-0.177	-0.277	.799(**)	1		
pH	0.230	0.326	0.303	0.321	-0.331	-0.334	0.237	.391(*)	0.316	0.306	-.696(**)	-.720(**)	1	
Cond	0.280	0.224	.392(*)	0.103	-.506(**)	-.418(*)	0.257	.490(*)	.389(*)	.402(*)	-.740(**)	-.595(**)	.781(**)	1

\*\* Correlation is significant at the 0.01 level

\* Correlation significant at the 0.05 level

S denotes sediment-bound metal concentration

D denotes dissolved metal concentration

**Appendix 7.1 Spearman correlation coefficients and significance values for physico-chemical variables, rainfall and discharge at the control (Nant Yr Lar) and mine site (Afon Twymyn) stations**

			Control Q	Mine Q	Rainfall	Control pH	Control Cond	Control Temp	Mine pH	Mine Cond	Mine Temp
Spearman's rho	Control Q	Correlation Coefficient	1.000	.784(**)	.388(**)	-.489(**)	-.540(**)	-.605(**)	-.295(**)	-.308(**)	-.682(**)
		Sig. (2-tailed)	.	.000	.000	.000	.000	.000	.000	.000	.000
		N	338	337	338	268	268	268	338	338	338
	Mine Q	Correlation Coefficient	.784(**)	1.000	.381(**)	-.490(**)	-.381(**)	-.547(**)	-.248(**)	-.338(**)	-.554(**)
		Sig. (2-tailed)	.000	.	.000	.000	.000	.000	.000	.000	.000
		N	337	342	342	273	273	273	342	342	342
	Rainfall	Correlation Coefficient	.388(**)	.381(**)	1.000	-.335(**)	-.203(**)	-.124(*)	-.207(**)	-.179(**)	-.094
		Sig. (2-tailed)	.000	.000	.	.000	.000	.033	.000	.001	.071
		N	338	342	366	296	296	296	366	366	366
	Control pH	Correlation Coefficient	-.489(**)	-.490(**)	-.335(**)	1.000	.719(**)	.266(**)	.773(**)	.547(**)	.361(**)
		Sig. (2-tailed)	.000	.000	.000	.	.000	.000	.000	.000	.000
		N	268	273	296	296	296	296	296	296	296
	Control Cond	Correlation Coefficient	-.540(**)	-.381(**)	-.203(**)	.719(**)	1.000	.318(**)	.657(**)	.785(**)	.357(**)
		Sig. (2-tailed)	.000	.000	.000	.000	.	.000	.000	.000	.000
		N	268	273	296	296	296	296	296	296	296
	Control Temp	Correlation Coefficient	-.605(**)	-.547(**)	-.124(*)	.266(**)	.318(**)	1.000	.134(*)	.067	.978(**)
		Sig. (2-tailed)	.000	.000	.033	.000	.000	.	.021	.247	.000
		N	268	273	296	296	296	296	296	296	296
	Mine pH	Correlation Coefficient	-.295(**)	-.248(**)	-.207(**)	.773(**)	.657(**)	.134(*)	1.000	.517(**)	.108(*)
		Sig. (2-tailed)	.000	.000	.000	.000	.000	.021	.	.000	.039
		N	338	342	366	296	296	296	366	366	366
	Mine Cond	Correlation Coefficient	-.308(**)	-.338(**)	-.179(**)	.547(**)	.785(**)	.067	.517(**)	1.000	-.069
		Sig. (2-tailed)	.000	.000	.001	.000	.000	.247	.000	.	.190
		N	338	342	366	296	296	296	366	366	366
	Mine Temp	Correlation Coefficient	-.682(**)	-.554(**)	-.094	.361(**)	.357(**)	.978(**)	.108(*)	-.069	1.000
		Sig. (2-tailed)	.000	.000	.071	.000	.000	.000	.039	.190	.
		N	338	342	366	296	296	296	366	366	366

\*\* Correlation is significant at the 0.01 level (2-tailed).

\* Correlation is significant at the 0.05 level (2-tailed).

Appendix 8.1a Macroinvertebrate taxa collected in March 2008 (Sites 1 – 14)

Taxa/Site	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Dixidae														
Dytiscidae														
Oreodytes sanmarkii														
Agabus guttatus														
Oxyethira sp.														
Empididae			1					1						
Ephydriidae														
Gyrinidae														
Helophoridae														
Helophorus sp.														
Hydraenidae														
Hydraena sp.														
Hydrophilidae														
Lymnaeidae														
Lymnaea sp.														
Planariidae														
Polycelis nigra					1						1			
Psychodinae														
Scirtidae		1				18								
Sphariidae	1													
Tabanidae														
OLIGOCHAETA	42	2	1		1									
OSTRACODA														
Gammaridae														
Gammarus sp.	1													
Chloroperlidae														
Chloroperla sp.	4	28	15		24	5		5	8	11	7	7	14	20
Leuctridae														
Leuctrid hippopus	5	42	11		2	6		10	16	12	18	9	7	14
Nemouridae														
Nemurella picteti														
Amphinemura sulcicollis						1		13	9	4	8	2	6	14
Protonemura praecox									1				1	
Nemoura sp.					1						1			
Nemoura erratica		2				6		2	4	2			1	
Perlodidae														
Perlodid sp.														
Isoperla grammatica	4	2	1					1	3	1	2	2	6	1
Siphonuridae														
Siphonurus lacustris														
Baetidae														
Baetid sp.	24	18	12		12	4		29	40	34	37	8	74	15
Caenidae														
Emphemerellidae														
Ephemerella ignita														
Heptageniidae														
Heptageniid sp.		23	6		5	6			2	4	4	10	26	29
Ecdyonurus insignis	6													
Glossosomatidae														

Cont.

<b>Glossosoma boltani</b>														
<b>Hydropsychidae</b>														
<b>Hydropsyche siltalai</b>	1	3						1		1				
<b>Hydropsyche contubernalis</b>														
<b>Odontoceridae</b>														
<b>Odontocerum albicorne</b>														
<b>Ploycentropodidae</b>														
<b>Polycentropus flavomaculatus</b>									1					
<b>Plectronemia conspersa</b>														
<b>Rhyacophilidae</b>														
<b>Rhyacophila dorsalis</b>		1	1					1						
<b>Hydroptilidae</b>														
<b>Limnephilidae</b>														
<b>Chaetopteryx villosa</b>														
<b>Drusus annulatus</b>														
<b>Potamophylax latipennis</b>														
<b>Limnephilidae sp.</b>									1					3
<b>Elmidae</b>														
<b>Limnius volckmari</b>										2				
<b>Elmis aenea</b>								1	2	3		2	4	
<b>Oulimnius sp.</b>														
<b>Chironmidae</b>	11	2	1		2	1		1	6	1	6	2	1	4
<b>Simuliidae</b>	1	13				6		2	3	2	1	1	1	5
<b>Tipulidae</b>	1													
<b>Dicranota sp.</b>		1	1					2						
<b>ZYGOPTERA</b>														
<b>ANSIOPTERA</b>														
<b>Cortulegasteridae boltani</b>														

\*Columns in grey represent sites inaccessible or dry at the time of sampling

Appendix 8.1b Macroinvertebrate taxa collected in March 2008 (Sites 15 – 29)

Taxa/Site	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
Dixidae															
Dytiscidae															
Oreodytes sanmarkii															
Agabus guttatus															
Oxyethira sp.															
Empididae															
Ephydriidae															
Gyrinidae															
Helophoridae															
Helophorus sp.															
Hydraenidae															
Hydraena sp.															
Hydrophilidae															
Lymnaeidae															
Lymnaea sp.															
Planariidae															
Polycelis nigra															
Psychodinae															
Scirtidae															
Sphariidae										1					
Tabanidae															
OLIGOCHAETA	14	12		1			1			20		12			10
OSTRACODA															
Gammaridae															
Gammarus sp.		2													
Chloroperlidae															
Chloroperla sp.		4		9	8	22	16			26		28			30
Leuctridae															
Leuctrid hippopus	1	14	3	52	26	31	61			6		2			6
Nemouridae															
Nemurella picteti															
Amphinemura sulcicollis		1		2											
Protonemura praecox															
Nemoura sp.	2														
Nemoura erratica		1	2		1					2		3			4
Perlodidae															
Perlodid sp.							1								
Isoperla grammatica		5	1	3	4	1				7		5			8
Siphonuridae															
Siphonurus lacustris															
Baetidae															
Baetid sp.	32	64	10	15	25	16	19								24
Caenidae															
Emphemerellidae															
Ephemerella ignita															
Heptageniidae															
Heptageniid sp.	1			50	7		22								1
Ecdyonurus insignis						8									
Glossosomatidae															

Cont.

<b>Glossosoma boltani</b>															
<b>Hydropsychidae</b>															
<b>Hydropsyche siltalai</b>	1	3		3											
<b>Hydropsyche contubernalis</b>															
<b>Odontoceridae</b>															
<b>Odontocerum albicorne</b>															
<b>Ploycentropodidae</b>															
<b>Polycentropus flavomaculatus</b>									2		2				1
<b>Plectronemia conspersa</b>															
<b>Rhyacophilidae</b>															
<b>Rhyacophila dorsalis</b>	1	3													1
<b>Hydroptilidae</b>															
<b>Limnephilidae</b>															
<b>Chaetopteryx villosa</b>															
<b>Drusus annulatus</b>															
<b>Potamophylax latipennis</b>															
<b>Limnephilidae sp.</b>		1							1		1				4
<b>Elmidae</b>															
<b>Limnius volckmari</b>	1	6													1
<b>Elmis aenea</b>		2							1						
<b>Oulimnius sp.</b>															
<b>Chironmidae</b>	12	9	1		3		2		10		1				1
<b>Simuliidae</b>	10	7	9	8	5	8	6		23		28				15
<b>Tipulidae</b>											2				2
<b>Dicranota sp.</b>		3			1		2		4		2				1
<b>ZYGOPTERA</b>															
<b>ANSIOPTERA</b>															
<b>Cortulegasteridae boltani</b>															

\*Columns in grey represent sites inaccessible or dry at the time of sampling



Appendix 8.1c Macroinvertebrate taxa collected in June 2007 (Sites 1 – 14)

Taxa/Site	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Dixidae												1		
Dytiscidae						2								
Oreodytes sanmarkii														
Agabus guttatus														
Oxyethira sp.														
Empididae		1												
Ephydriidae														
Gyrinidae														
Helophoridae														
Helophorus sp.						1								
Hydraenidae														
Hydraena sp.			1		1					3			1	
Hydrophilidae														
Lymnaeidae														
Lymnaea sp.														
Planariidae														
Polycelis nigra									4					
Psychodinae		1												
Scirtidae	22	36	2	16		72						1		
Sphariidae												2		
Tabanidae							3							
OLIGOCHAETA	8		1									2		
OSTRACODA														
Gammaridae														
Gammarus sp.														
Chloroperlidae														
Chloroperla sp.	7	12	4	16	20	18		1	1	13	6	4	7	
Leuctridae														
Leuctrid hippopus	173	174	98	133	100	25		7	5	43	39	20	32	
Nemouridae														
Nemurella picteti														
Amphinemura sulcicollis													1	
Protonemura praecox														
Nemoura sp.														
Nemoura erratica														
Perlodidae														
Perlodid sp.														
Isoperla grammatica												2		
Siphonuridae														
Siphonurus lacustris														
Baetidae														
Baetid sp.	76	51	58	95	97	165	127	69	58	131	125	83	75	
Caenidae		1												
Emphemerellidae														
Ephemerella ignita	8	3	6	8		4						22		
Heptageniidae														
Heptageniid sp.		1	2	10						2	4		56	
Ecdyonurus insignis				1										
Glossosomatidae														

Cont.

<b>Glossosoma boltani</b>														
<b>Hydropsychidae</b>														
<b>Hydropsyche siltalai</b>		1		1		3				3		36	6	
<b>Hydropsyche contubernalis</b>												2		
<b>Odontoceridae</b>														
<b>Odontocerum albicorne</b>												3		
<b>Ploycentropodidae</b>														
<b>Polycentropus flavomaculatus</b>								1	1	1	2		5	
<b>Plectronemia conspersa</b>														
<b>Rhyacophilidae</b>														
<b>Rhyacophila dorsalis</b>						4		1				9		
<b>Hydroptilidae</b>														
<b>Limnephilidae</b>														
<b>Chaetopteryx villosa</b>														
<b>Drusus annulatus</b>													3	
<b>Potamophylax latipennis</b>														
<b>Limnephilidae sp.</b>														
<b>Elmidae</b>														
<b>Limnius volckmari</b>						1		2	3	1		4	2	
<b>Elmis aenea</b>									3	12	14		32	
<b>Oulimnius sp.</b>		2	1				2		1			1	3	
<b>Chironmidae</b>	11	44	20	40	33	38	14	1	2	3	1	27	1	
<b>Simuliidae</b>		41	4	9	4	78	17	13	16	2		53	1	
<b>Tipulidae</b>		1	1	1		1	1		1					
<b>Dicranota sp.</b>	1		2	1	5							10		
<b>ZYGOPTERA</b>														
<b>ANSIOPTERA</b>														
<b>Cortulegasteridae boltani</b>														

\*Columns in grey represent sites inaccessible or dry at the time of sampling

Appendix 8.1d Macroinvertebrate taxa collected in June 2007 (Sites 15 – 29)

Taxa/Site	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
Dixidae															
Dytiscidae															
Oreodytes sanmarkii				1	1										
Agabus guttatus											1				
Oxyethira sp.															1
Empididae									2				7		
Ephydriidae															
Gyrinidae															
Helophoridae															
Helophorus sp.											8	3			
Hydraenidae															
Hydraena sp.				1		3	1		1		4		6	6	
Hydrophilidae											1			1	
Lymnaeidae															
Lymnaea sp.															
Planariidae															
Polycelis nigra															
Psychodinae															
Scirtidae														2	
Sphariidae															
Tabanidae															
OLIGOCHAETA				2		1			4	8	3	13	11	7	11
OSTRACODA										1					
Gammaridae															
Gammarus sp.															
Chloroperlidae															
Chloroperla sp.		6		2	11	27	7	1		2	18	2	11	28	6
Leuctridae															
Leuctrid hippopus		7		24	29	3		1				1	11	6	2
Nemouridae															
Nemurella picteti														2	
Amphinemura sulcicollis		1													
Protonemura praecox															
Nemoura sp.															
Nemoura erratica															
Perlodidae															
Perlodid sp.									1	2				2	
Isoperla grammatica		1		3	4	2			5	1	3		6	1	3
Siphonuridae															
Siphonurus lacustris									3	10					
Baetidae															
Baetid sp.		48		27	28	47	9	2	2		25	79	17	37	20
Caenidae															
Emphemerellidae															
Ephemerella ignita													15	12	
Heptageniidae															
Heptageniid sp.		12		42	11	19	10					3			
Ecdyonurus insignis															
Glossosomatidae															

Cont.

Glossosoma boltani															
Hydropsychidae															
Hydropsyche siltalai		2		2	4	21					1	1	2		
Hydropsyche contubernalis					1										
Odontoceridae															
Odontocerum albicorne															
Ploycentropodidae															
Polycentropus flavomaculatus				1		1									
Plectronemia conspersa													1	2	
Rhyacophilidae															
Rhyacophila dorsalis				3	3			1	1				5		1
Hydroptilidae															
Limnephilidae															
Chaetopteryx villosa										1	1				
Drusus annulatus															
Potamophylax latipennis									4						
Limnephilidae sp.															
Elmidae															
Limnius volckmari		2				2								2	
Elmis aenea		30		2		4			2				8	1	
Oulimnius sp.		1												1	
Chironmidae					4	50	15	37	51	8	25	11	76	34	14
Simuliidae				39	32	68	5	1	5	10	292	64	3	42	5
Tipulidae											1				
Dicranota sp.									5		7	19	3	3	4
ZYGOPTERA															
ANSIOPTERA															
Cortulegasteridae boltani															

\*Columns in grey represent sites inaccessible or dry at the time of sampling

Appendix 8.1e Macroinvertebrate taxa collected in October 2007 (Sites 1 – 14)

Taxa/Site	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Dixidae														
Dytiscidae														
Oreodytes sanmarkii														
Agabus guttatus														
Oxyethira sp.														
Empididae								2						1
Ephydriidae				1										
Gyrinidae														
Helophoridae														
Helophorus sp.														
Hydraenidae														
Hydraena sp.			3	1									1	
Hydrophilidae														
Lymnaeidae														
Lymnaea sp.														
Planariidae														
Polycelis nigra														
Psychodinae														
Scirtidae		2	4	28		34								
Sphariidae			1											
Tabanidae	1			2		2						1		
OLIGOCHAETA	20	4	1	1										3
OSTRACODA														
Gammaridae														
Gammarus sp.														
Chloroperlidae														
Chloroperla sp.	3	20	9	8		5	3	6	3	7	7	4		
Leuctridae														
Leuctrid hippopus	9	25	42	43		21	6	5	7	7	35	9	19	
Nemouridae														
Nemurella picteti														
Amphinemura sulcicollis							4	4	20	27				
Protonemura praecox						3	1	4	6	13	14	3	18	2
Nemoura sp.	1													
Nemoura erratica														
Perlodidae														
Perlodid sp.														
Isoperla grammatica											2		13	
Siphonuridae														
Siphonurus lacustris														
Baetidae														
Baetid sp.	17	32	58	284		118	148	107	78	107	238	198	149	81
Caenidae														
Emphemerellidae														
Ephemerella ignita														
Heptageniidae														
Heptageniid sp.	12	3	25	10		3			3	4	5	26	13	
Ecdyonurus insignis														
Glossosomatidae														

Cont.

<b>Glossosoma boltani</b>				1										
<b>Hydropsychidae</b>														
<b>Hydropsyche siltalai</b>			2	3		8	3	6	5		1			1
<b>Hydropsyche contubernalis</b>														
<b>Odontoceridae</b>														
<b>Odontocerum albicorne</b>														
<b>Ploycentropodidae</b>														
<b>Polycentropus flavomaculatus</b>														
<b>Plectronemia conspersa</b>														
<b>Rhyacophilidae</b>														
<b>Rhyacophila dorsalis</b>	1		4	3			1	3				1	1	2
<b>Hydroptilidae</b>														
<b>Limnephilidae</b>		1	2											
<b>Chaetopteryx villosa</b>														
<b>Drusus annulatus</b>														
<b>Potamophylax latipennis</b>														
<b>Limnephilidae sp.</b>														
<b>Elmidae</b>														
<b>Limnius volckmari</b>	2		5	1				1	1	1	10	10	4	
<b>Elmis aenea</b>							4		5	14	6	13	15	
<b>Oulimnius sp.</b>														
<b>Chironmidae</b>	23	5	7	19		4	3	6	5	6	8		14	31
<b>Simuliidae</b>			2	15		46	45	40	21	10	29	50	66	63
<b>Tipulidae</b>		4												
<b>Dicranota sp.</b>		6	3	2			5							1
<b>ZYGOPTERA</b>														
<b>ANSIOPTERA</b>														
<b>Cortulegasteridae boltani</b>														

\*Columns in grey represent sites inaccessible or dry at the time of sampling

Appendix 8.1f Macroinvertebrate taxa collected in October 2007 (Sites 15 – 29)

Taxa/Site	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
Dixidae															
Dytiscidae															
Oreodytes sanmarkii															
Agabus guttatus									1						
Oxyethira sp.															
Empididae					1										
Ephydriidae										2					
Gyrinidae															
Helophoridae															
Helophorus sp.															
Hydraenidae															
Hydraena sp.		1		2			1					2			
Hydrophilidae															
Lymnaeidae															
Lymnaea sp.															
Planariidae															
Polycelis nigra															
Psychodinae															
Scirtidae							1								
Sphariidae															
Tabanidae															
OLIGOCHAETA		14					2			6		1			
OSTRACODA															
Gammaridae															
Gammarus sp.		1				1									
Chloroperlidae															
Chloroperla sp.				2		5	1	9		4		1			
Leuctridae															
Leuctrid hippopus		10		86	107	22	56	11	1	13					
Nemouridae															
Nemurella picteti															
Amphinemura sulcicollis															
Protonemura praecox		1		6	2										
Nemoura sp.						1		2							
Nemoura erratica															
Perlodidae															
Perlodid sp.										8		6			
Isoperla grammatica		11			3	2	3			5					
Siphonuridae															
Siphonurus lacustris															
Baetidae															
Baetid sp.		49		179	86	72	34	1	1	4		2			
Caenidae															
Emphemerellidae															
Ephemerella ignita															
Heptageniidae															
Heptageniid sp.		4		30	18	8	9								
Ecdyonurus insignis															
Glossosomatidae															

Cont.

<b>Glossosoma boltani</b>													1	2	
<b>Hydropsychidae</b>															
<b>Hydropsyche siltalai</b>		7				1	1								
<b>Hydropsyche contubernalis</b>															
<b>Odontoceridae</b>															
<b>Odontocerum albicorne</b>															
<b>Ploycentropodidae</b>															
<b>Polycentropus flavomaculatus</b>						1	1							1	
<b>Plectronemia conspersa</b>															4
<b>Rhyacophilidae</b>															
<b>Rhyacophila dorsalis</b>		11		6											
<b>Hydroptilidae</b>															
<b>Limnephilidae</b>								2		1		1			
<b>Chaetopteryx villosa</b>															
<b>Drusus annulatus</b>															
<b>Potamophylax latipennis</b>															
<b>Limnephilidae sp.</b>															
<b>Elmidae</b>															
<b>Limnius volckmari</b>		11		2	1										
<b>Elmis aenea</b>		8													
<b>Oulimnius sp.</b>															
<b>Chironmidae</b>		9		13	12	3	21	9	10	9		58			
<b>Simuliidae</b>		30		9	13	7	13	2		1		31			
<b>Tipulidae</b>							1								
<b>Dicranota sp.</b>		8		1	1	2	4	5		2		6			
<b>ZYGOPTERA</b>														1	
<b>ANSIOPTERA</b>															
<b>Cortulegasteridae boltani</b>														1	

\*Columns in grey represent sites inaccessible or dry at the time of sampling



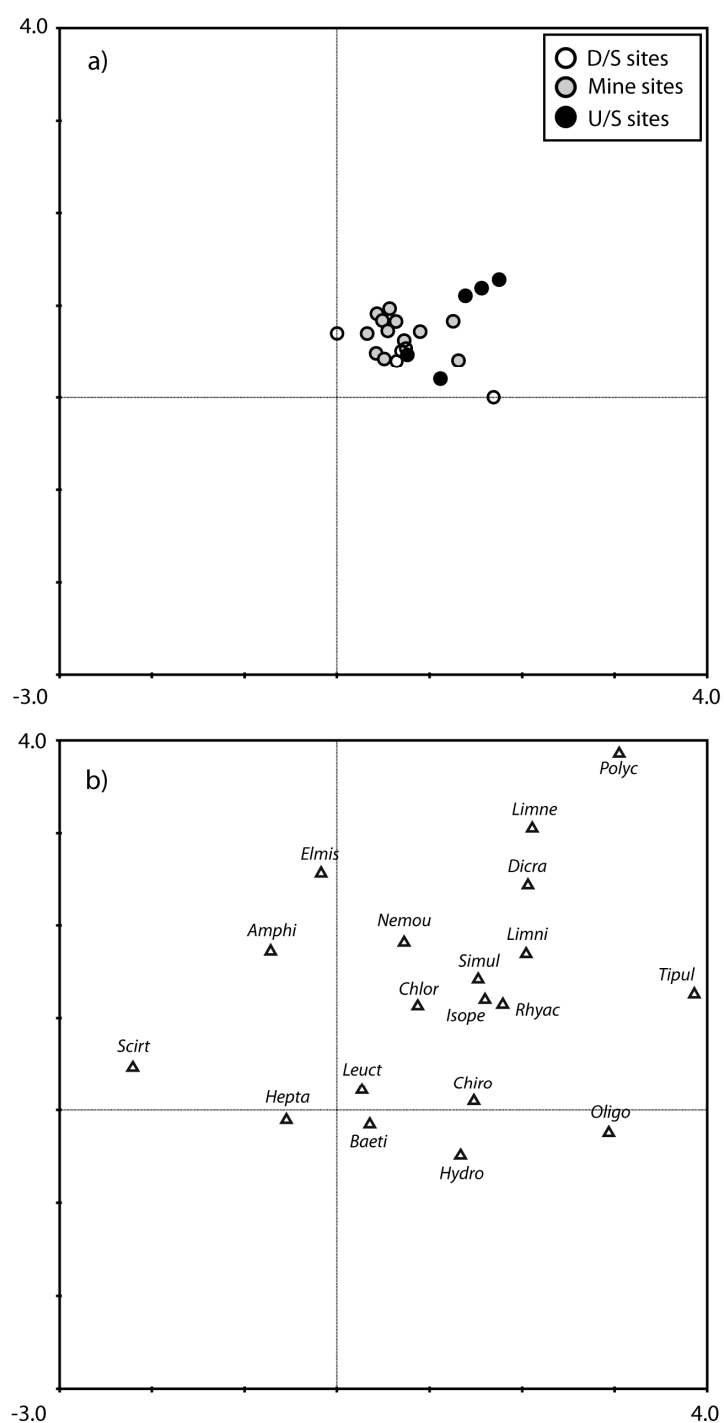
**Appendix 8.2 Kruskal-Wallis and Mann Whitney U tests of significance for biological indices between locations and seasons (Afon Twymyn, 2007/2008)**

<b>Main effects</b>	<b>Diversity</b>	<b>Dominance</b>	<b>No. Taxa</b>	<b>Abundance</b>	<b>No. EPT</b>	<b>BMWP</b>	<b>ASPT</b>	<b>AWIC</b>
	<b>Taxa</b>							
Location	.134	.042*	.793	.018*	.002**	.708	.192	.006**
Season	.057	.087	.754	.002**	.013*	.669	.061	.000**
<b>Post Hoc tests</b>	<b>Diversity</b>	<b>Dominance</b>	<b>No. Taxa</b>	<b>Abundance</b>	<b>No. EPT</b>	<b>BMWP</b>	<b>ASPT</b>	<b>AWIC</b>
	<b>Taxa</b>							
<b>Season</b>								
Jun07 and Oct07	.741	.616	.621	.386	.152	.595	.741	.226
Jun07 and Mar08	.098	.211	.473	.001**	.004**	.694	.057	.000**
Oct07 and Mar08	.014*	.015*	.792	.012*	.120	.375	.062	.007**
<b>Location</b>								
Control*Mine	.191	.095	.453	.451	.001**	.379	.100	.003**
Control*Downstream	.442	.367	.695	.019*	.021*	.705	.616	.006**
Mine*Downstream	.064	.020*	.832	.020*	.306	.680	.167	.998

\*\*significant at 0.01

\*significant at 0.05

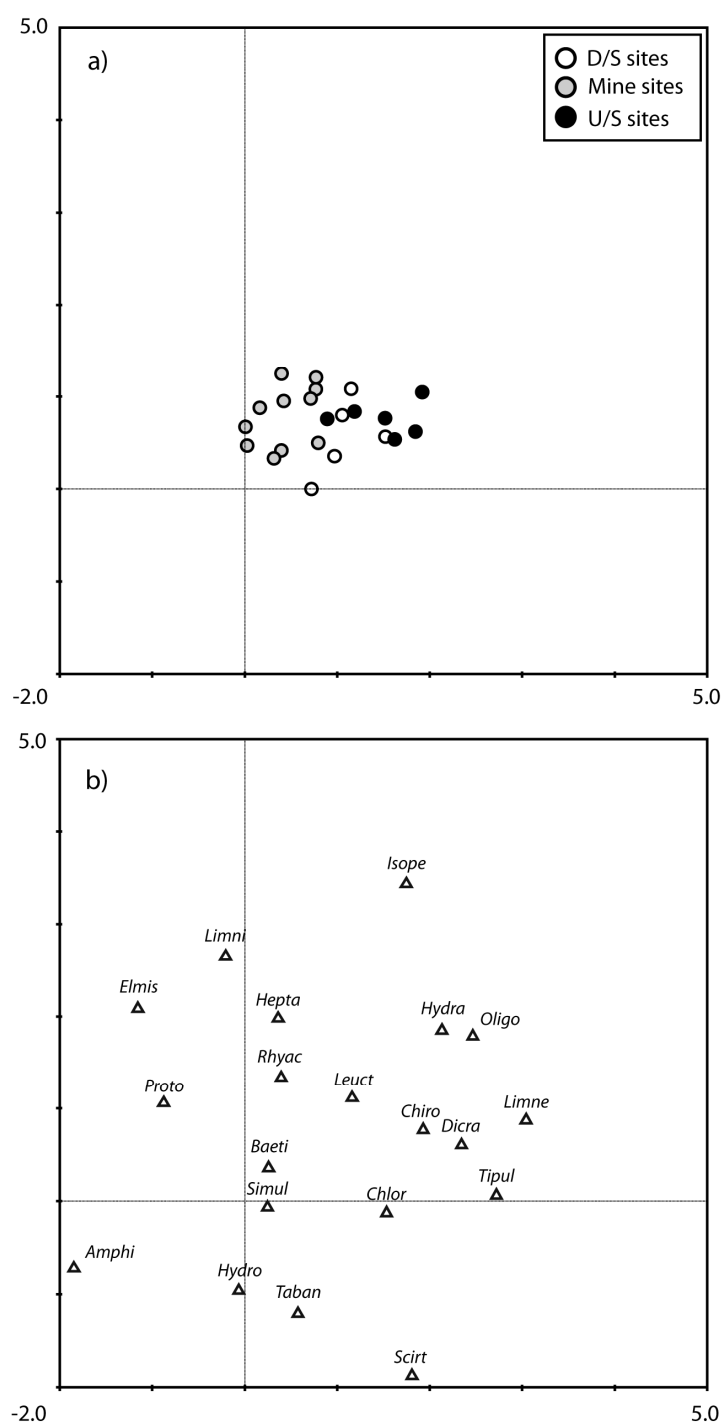
### Appendix 8.3a DCA biplots for Run 1 (March): a) sites and b) species



### Appendix 8.3b Summary of key findings from March DCA analysis (Run 1)

Axis	1	2	3	4
Eigenvalues	0.218	0.080	0.030	0.014
Lengths of gradient	1.759	1.276	1.063	1.137
Cumulative % variance of species data	23.5	32.0	35.3	36.8

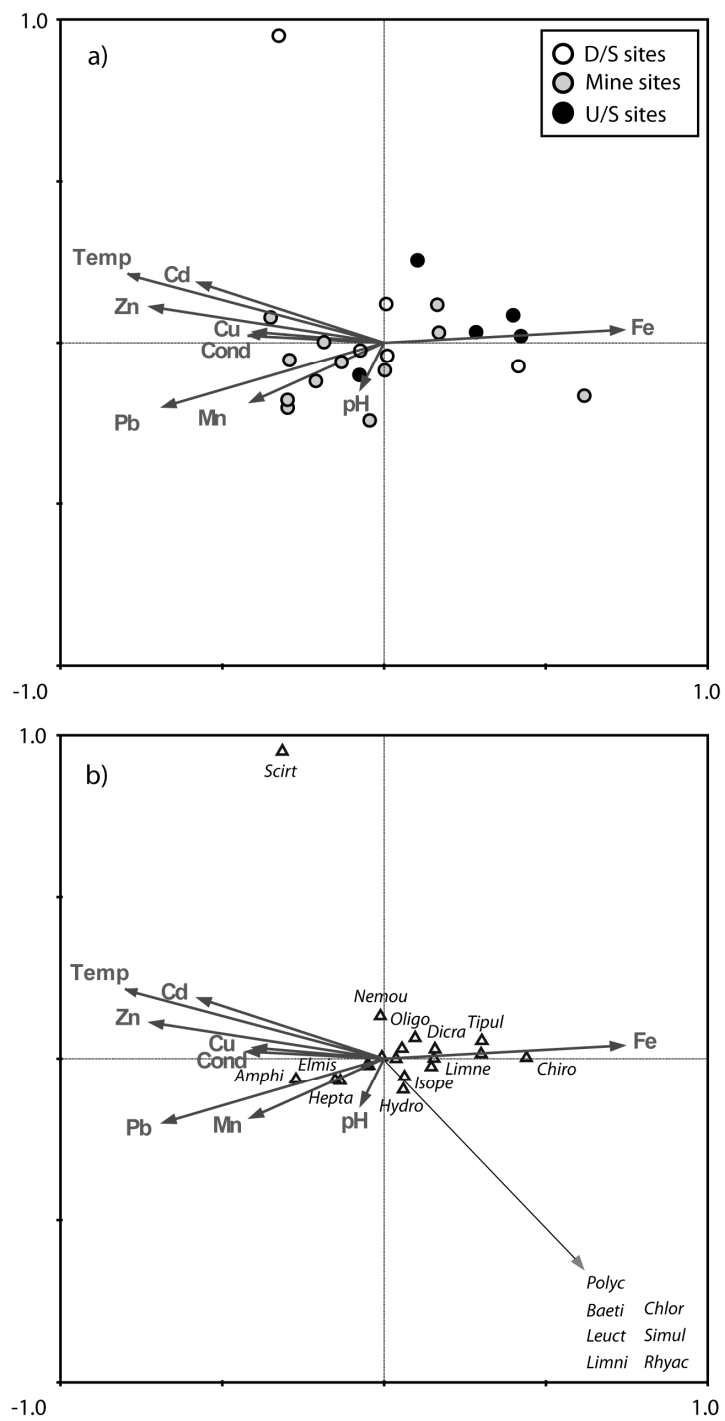
#### Appendix 8.4a DCA biplots for Run 3 (October): a) sites and b) species



#### Appendix 8.4b Summary of key findings from October DCA analysis (Run 3)

Axis	1	2	3	4
Eigenvalues	0.245	0.097	0.033	0.025
Lengths of gradient	1.916	1.265	1.130	1.078
Cumulative % variance of species data	24.9	34.9	38.2	40.8

**Appendix 8.5a CCA biplots for Run 1 (March, water only): a) sites and b) species**



**Appendix 8.5b Rankings for weighted water quality variables in March using unrestricted Monte Carlo significance test (Run 1)**

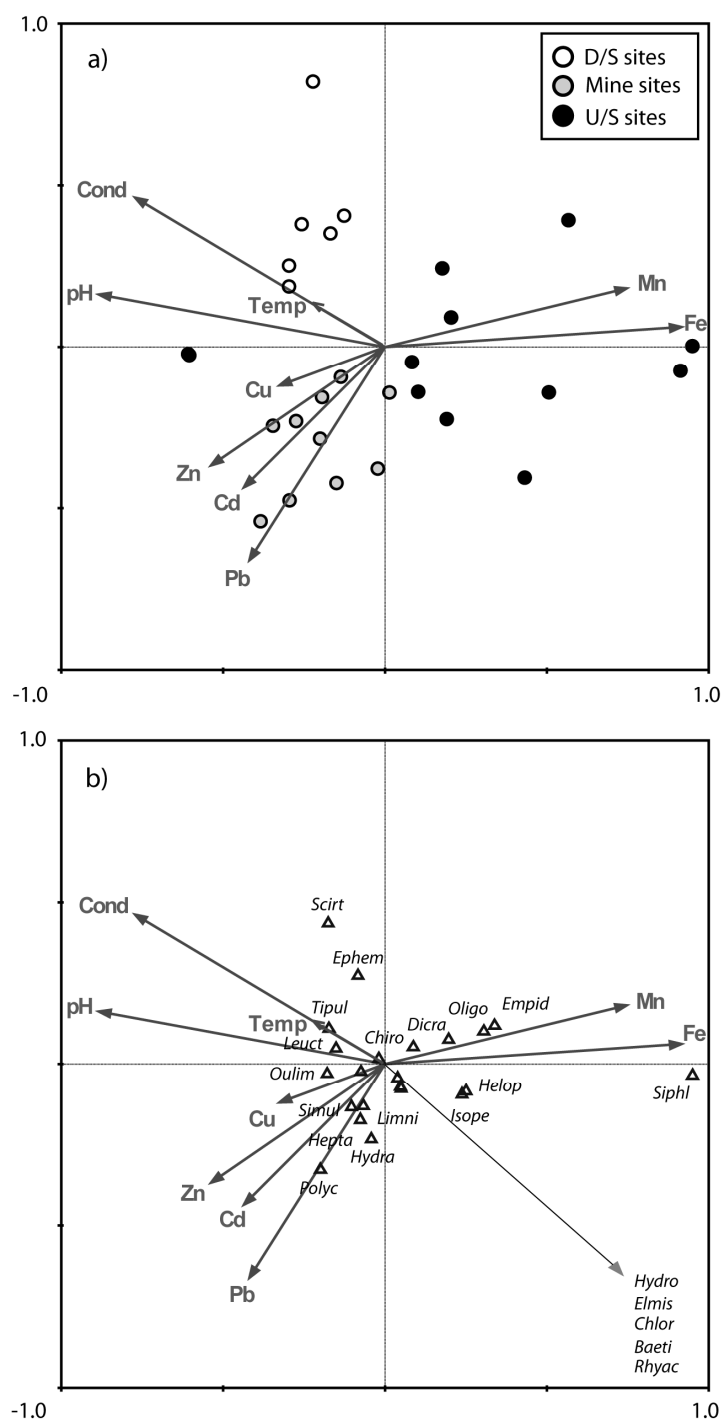
Rank	Variable	Lambda-A	P value	F ratio
1	Temp	0.161	<b>0.001</b>	4.19
2	Fe	0.124	<b>0.034</b>	2.06
3	Zn	0.115	0.289	1.20
4	Pb	0.111	<b>0.022</b>	2.29
5	Cd	0.088	0.269	1.25
6	Cond	0.080	0.634	0.80
7	pH	0.054	0.338	1.14
8	Mn	0.046	0.176	1.44
9	Cu	0.045	0.339	1.12

Significant (p = <0.05) in bold

**Appendix 8.5c Key findings from March water quality data set (Run 1)**

Axis	1	2	3	4
Eigenvalues	0.196	0.123	0.098	0.044
Species-environment correlations	0.956	0.892	0.909	0.771
Cumulative % variance				
a. Species data	21.1	34.3	44.8	49.5
b. Species-environment data	36.1	58.6	76.7	84.7
Significance of first canonical axis			F ratio 3.207	P value 0.004

**Appendix 8.6a CCA biplots for Run 2 (June, water only): a) sites and b) species**



**Appendix 8.6b Rankings for weighted water quality variables in June using unrestricted Monte Carlo significance test (Run 2)**

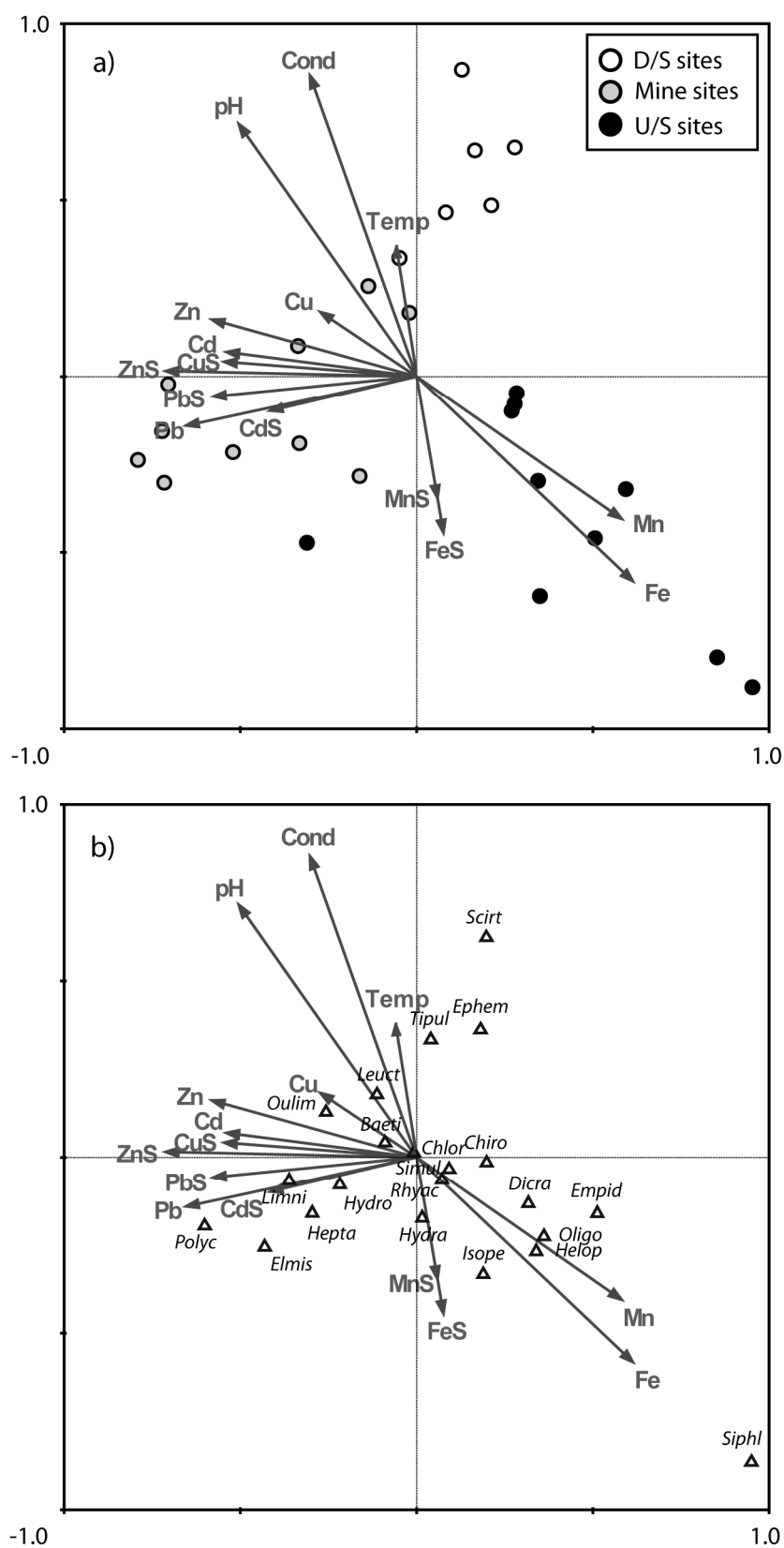
Rank	Variable	Lambda-A	P value	F ratio
1	Fe	0.183	<b>0.001</b>	4.49
2	pH	0.174	0.293	1.17
3	Cond	0.166	<b>0.005</b>	2.66
4	Mn	0.141	0.247	1.24
5	Pb	0.118	<b>0.006</b>	2.44
6	Zn	0.115	0.717	0.73
7	Cd	0.102	0.310	1.20
8	Cu	0.074	0.177	1.36
9	Temp	0.056	0.250	0.121

Significant (p = <0.05) in bold

**Appendix 8.6c Key findings from June water quality data set (Run 2)**

Axis	1	2	3	4
Eigenvalues	0.213	0.144	0.076	0.052
Species-environment correlations	0.886	0.873	0.875	0.725
Cumulative % variance				
a. Species data	18.3	30.7	37.2	41.7
b. Species-environment data	34.8	58.3	70.7	79.2
Significance of first canonical axis			F ratio 3.591	P value 0.018

**Appendix 8.7a CCA biplots for Run 4 (June, water and sediment): a) sites and b) species**





**Appendix 8.7b Rankings for weighted sediment and water quality variables in March using unrestricted Monte Carlo significance test (Run 4)**

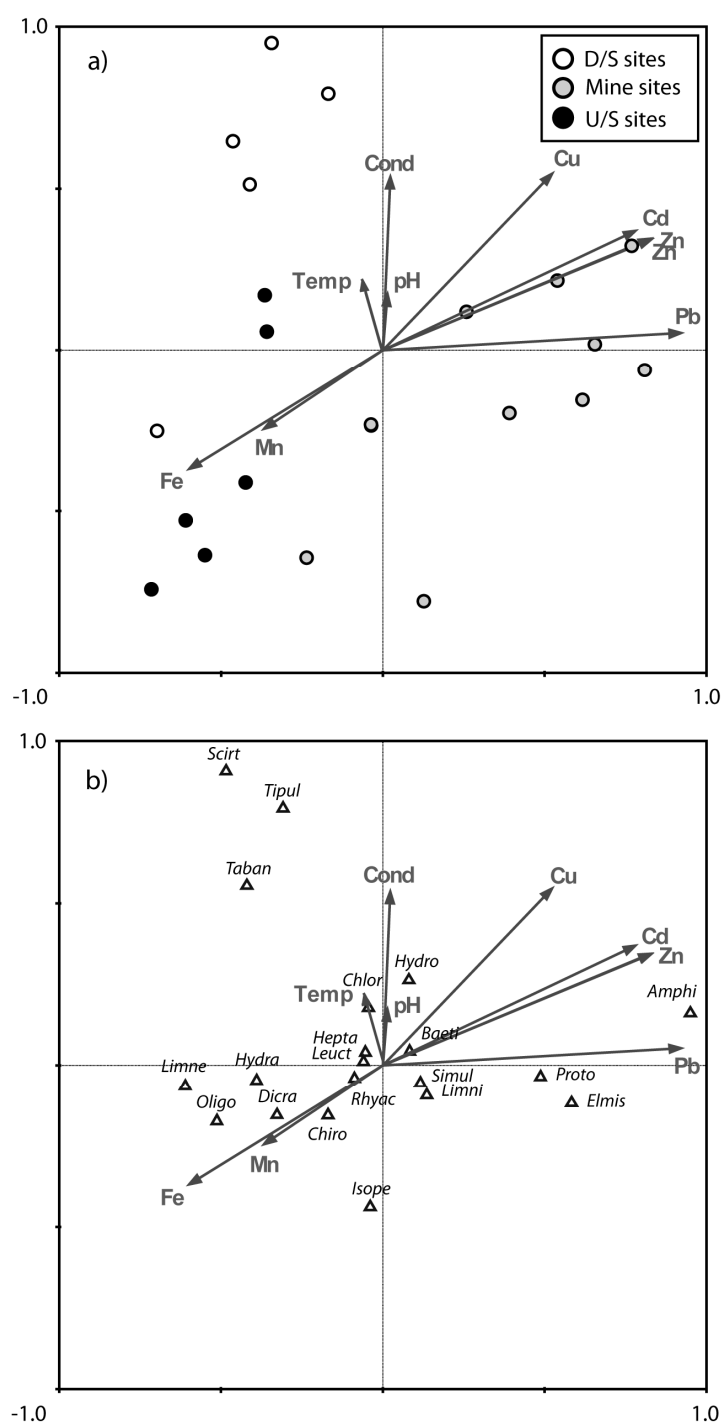
Rank	Variable	Lambda-A	P value	F ratio
1	Cond	0.150	<b>0.001</b>	4.07
2	ZnS	0.118	<b>0.001</b>	3.56
3	Fe	0.074	<b>0.007</b>	2.35
4	CuS	0.057	<b>0.039</b>	1.87
5	FeS	0.045	0.107	1.52
6	Temp	0.039	0.151	1.38
7	CdS	0.039	0.184	1.34
8	pH	0.030	0.349	1.07
9	MnS	0.033	0.282	1.20
10	Cu	0.035	0.233	1.27
11	Pb	0.034	0.247	1.27
12	Mn	0.024	0.562	0.89
13	Zn	0.025	0.540	0.93
14	Cd	0.029	0.403	1.05
15	PbS	0.023	0.593	0.81

Significant (p = <0.05) in bold

**Appendix 8.7c Key findings from June water and sediment quality data set (Run 4)**

Axis	1	2	3	4
Eigenvalues	0.214	0.168	0.070	0.066
Species-environment correlations	0.938	0.957	0.941	0.858
Cumulative % variance				
a. Species data	20.8	37.1	43.9	50.3
b. Species-environment data	28.4	50.7	60.0	68.7
Significance of first canonical axis			F ratio 2.627	P value 0.080

**Appendix 8.8a CCA biplots for Run 5 (October, water only): a) sites and b) species**



**Appendix 8.8b Rankings for weighted water quality variables in October using unrestricted Monte Carlo significance test (Run 5)**

Rank	Variable	Lambda-A	P value	F ratio
<b>1</b>	Pb	0.171	<b>0.001</b>	4.22
<b>2</b>	Zn	0.156	<b>0.002</b>	2.74
<b>3</b>	Cd	0.148	0.545	0.88
<b>4</b>	Fe	0.104	0.214	1.28
<b>5</b>	Cu	0.095	0.852	0.55
<b>6</b>	Mn	0.063	0.238	1.23
<b>7</b>	Cond	0.046	0.085	1.50
<b>8</b>	Temp	0.040	0.185	1.32
<b>9</b>	pH	0.029	0.492	0.98

Significant (p = <0.05) in bold

**Appendix 8.8c Key findings from October water quality data set (Run 5)**

Axis	1	2	3	4
Eigenvalues	0.196	0.113	0.080	0.063
Species-environment correlations	0.932	0.871	0.866	0.773
Cumulative % variance				
a. Species data	20.0	31.5	39.6	46.0
b. Species-environment data	34.3	54.0	68.0	78.9
Significance of first canonical axis			F ratio 2.750	P value 0.030

**Appendix 8.9 Mann Whitney U tests of significance for metal accumulation in organisms between locations and seasons**

	Location (Control/recovery and Impacted)	Season (October '08 and March '09)
<b><i>B. rhodani</i></b>		
Zn	.329	.028*
Pb	.010*	.465
<b><i>H. siltalai</i></b>		
Zn	.548	.010*
Pb	.190	.730
<b><i>L. hippopus</i></b>		
Zn	.222	.019*
Pb	.016*	.257

**Appendix 8.10 Pearson's correlation coefficients between organism tissue metal concentrations and environmental variables**

	Zn Water	Pb Water	Zn Sed	Pb Sed
<b><i>B. rhodani</i></b>				
Zn Oct	.570	.739	.678	.296
Pb Oct	.888*	.978**	.751	-.003
Zn Mar	.897*	.712	.753	.137
Pb Mar	.453	.547	.956*	.770
<b><i>H. siltali</i></b>				
Zn Oct	.913*	.650	.759	.291
Pb Oct	.902*	.713	.686	.131
Zn Mar	.942*	.740	.712	.126
Pb Mar	.968*	.879	.757	.093
<b><i>L. hippopus</i></b>				
Zn Oct	.137	.606	.404	.058
Pb Oct	.168	.551	.568	.412
Zn Mar	.934	.703	.854	.865
Pb Mar	.890	.802	.916	.942

\*\*significant at 0.01

\*significant at 0.05