The impairment of river systems by metal mine contamination: A review including remediation options

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Abstract

Contamination of aquatic environments as a consequence of deep metal mining for Pb, Zn, Cu, Cd and Fe is of widespread international concern. Pollution resulting from metal mining activities can result in significant environmental and ecological degradation and can pose serious risks to human health through contamination of food and drinking water. This paper provides a review of the impacts of deep metal mine water discharges on riverine sedimentology, hydrology and ecology and explores strategies for the restoration of rivers draining historically abandoned metal mines.

Physical processes of mine waste dispersal are relatively well understood. Chemical processes are more complex and much research is now focussed on understanding geochemical and mineralogical controls on metal attenuation and release. Recent advances in numerical modelling and geochemical tracing techniques offer the possibility of identifying present and predicted future patterns of contamination at the catchment scale.

The character of mine water has been extensively studied. However, documented impacts on aquatic ecosystems can vary widely depending on a range of hydroclimatological and geochemical factors. Numerous studies have shown that the majority of the annual metal flux in rivers draining mining-impacted regions occurs during the summer and autumn months as a result of water table drawdown, sulphide oxidation and dissolution and flushing of metal salts during subsequent storm periods. There have been few high-

resolution studies of stormflow hydrochemistry, despite the importance of high flows in the translocation of mine wastes.

A growing number of studies have documented chronic and acute toxic effects of mine water contaminants, based on both field and laboratory research, with specific reference to riverine macroinvertebrates. Common bioindices have been used to examine the impacts of mine water contaminants on macroinvertebrate ecology, although the success of these indices has been mixed. Sublethal biomonitoring techniques, as distinct from traditional laboratory bioassays with lethal endpoints, have gained prominence as a means of detecting behavioural and physiological responses of an organism to pulses of contaminants. The development of Biotic Ligand Models (BLMs) has allowed organism physiology and important environmental parameters to be factored into assessments of metal toxicity.

The strategies and technologies available for mine water remediation are considered and key knowledge gaps are highlighted. Passive remediation technologies offer a low cost and sustainable alternative to chemical treatment of deep metal mine discharges. However, at present, these systems generally fail to remove toxic metals associated with metal mine drainage to an acceptable standard. New phytoremediation techniques offer the possibility of immobilisation and extraction of toxic metals in mine spoil and contaminated soils.

We conclude by identifying key recommendations for future research:

(1) Researchers and regulators should consider bioavailable metal fractions in contaminated sediments, as opposed to total metal concentrations, if sediment ecotoxicity is to be accurately measured. In addition, more studies should make use of new spectroscopic techniques (e.g., XANES) capable of providing more detailed information on metal speciation and, therefore, sediment ecotoxicity.

(2) There is a need for better sampling and monitoring of toxic metal concentrations and fluxes during stormflows in mining-impacted river systems, especially given future predicted increases in stormflow occurrence. In addition, further research is required to help understand the potential toxicological impacts of stormflows in mining-impacted catchments.

(3) Further research is required to develop biological indices to identify the impacts of mine water contamination on macroinvertebrate communities.

(4) New substrates and techniques for remediation of metal-rich mine waters are currently being investigated and pilot studies undertaken in the laboratory and field. Many show promising results at the laboratory scale but large-scale pilot treatment plants are required to test the efficiency and long-term sustainability under field conditions.

(5) An interdisciplinary approach, incorporating the collaborative expertise and knowledge regarding sedimentological / geological, hydrological, chemical and ecological consequences of active and historic deep metal mining, is advocated and should be utilised for effective river basin management and the remediation and restoration of impacted sites.

Keywords: metal mine, acid mine drainage, river sediment, flood hydrochemistry, benthic macroinvertebrate, mine remediation

1. Introduction

Environmental impacts of mining on aquatic ecosystems have received increasing attention in recent years (Gray, 1998; Smolders *et al*., 2003; Olias *et al*., 2004; Batty *et al*., 2010). Acidic drainage associated with the abandonment of coal mining activity has been a particular focus of research (Banks and Banks, 2001). Contaminated discharge from abandoned metal mines and their spoil heaps has received less attention, reflecting the highly variable responses associated with the complex and frequently site-specific hydrogeological context of each, and the highly variable hydrogeochemical characteristics of the discharge (Environment Agency, 2008a). However, metal mine discharges have resulted in the severe degradation of many rivers across the globe (Gray, 1998; Gundersen and Stiennes, 2001; Olias *et al*., 2004; Sola *et al*., 2004; Poulton *et al*., 2010).

Metal mining regions occur on all continents except Antarctica and even extend to the continental shelf in certain areas where former floodplains have been submerged by sea-level rise resulting from global warming (Aleva, 1985). As a consequence, significant contamination of the landscape, including riverine and riparian habitats, has been reported internationally (Smolders *et al*., 2003; Asta *et al*., 2007; Edraki *et al*., 2005; Gilchrist *et al*., 2009; Brumbaugh *et al*., 2010). The most severely contaminated discharges typically occur shortly after abandonment of a site, when artificial dewatering has ceased and groundwater levels recover (Robb, 1994). Rising oxygenated groundwater within deep mines interacts with metal sulphides in exposed rockfaces, generating a leachate, typically characterised by low pH and high concentrations of dissolved toxic metals and sulphates (Braungardt *et al*., 2003; Gilchrist *et al*., 2009). Where the water table reaches the surface, leachate may enter rivers and lakes as drainage from mine shafts and mine drainage levels (adits), whilst rainwater may infiltrate through surface spoil heaps and tailings to enter streams and other surface water bodies.

Within riverine systems receiving metalliferrous drainage, the composition and health of plant and animal communities can be severely impaired through the combined toxicity of reactive metals in both the water column and sediments, sulphates and acidity (Sola *et al*., 2004; Schmitt *et al*., 2007; Batty *et al*., 2010; Chapa-Vargas *et al*., 2010). Aqueous metal concentrations generally decline downstream of contaminated sources due to the precipitation of oxide, hydroxide and sulphate phases, and co-precipitation or sorption of metals onto these phases (Hudson-Edwards *et al*., 1999b). However, iron hydroxide ‘ochre’ and other metal precipitates can cover the entire river bed in extreme instances and degrade habitat quality and important breeding and feeding areas for instream organisms (Batty, 2005; Mayes *et al*., 2008). Chronic contamination of riverine systems can be exacerbated by episodic flood events (Bradley 1984; Hudson-Edwards *et al*. 1999a; Dennis *et al*. 2009) or by the failure of tailing dams (Hudson-Edwards *et al*., 2003; Macklin *et al*., 2003; Sola *et al*., 2004). Such events have led to significant ecological degradation in many regions of the world and have severely impacted communities dependent on local rivers and their floodplains for food and livelihood (Macklin *et al*., 2006; Taylor *et al*., 2010).

Environmental degradation resulting from metal mining is not restricted to regions of the world where recent or active mineral exploitation is occurring. In the UK, metal mining reached its peak in the mid-nineteenth century when, for a time, the UK was the largest lead, tin and copper producer in the world (Lewin and Macklin, 1987). Following a global reduction in metal prices associated with the discovery of large deposits of lead and copper in the Iberian Peninsula, South America and Australia during the late 19^{th} and early 20^{th} centuries, a decline of metal mining occurred throughout the UK. Today, the number of abandoned metal mines in England and Wales is estimated at over 3,000 (Jarvis *et al*., 2007). The historical legacy of these mines is still present in the landscape in the form of spoil heaps, abandoned adits and shafts, and derelict structures. The historical metal mining industry, long forgotten and often far removed from manufacturing centre's, has left a significant legacy of environmental contamination which will persist for centuries to millennia (Environment Agency, 2002; Macklin *et al*., 2006). Approximately 20% of all water quality objective failures in England and Wales are due to drainage from abandoned metal mines (Environment Agency, 2006). The severity of the problem is underscored by the view of the Environment Agency of England and Wales that metal mine drainage poses the most serious threat to water quality objectives after diffuse agricultural pollution (Environment Agency, 2006).

Since the 1960s, concerns over the environmental impacts of historic metal mining activities have gained increasing significance and this is reflected in the growing body of literature on the topic (e.g., Macklin *et al*., 2006; Batty *et* *al*., 2010). However, due to the highly variable nature of environmental degradation of surface waters draining metal mines and the site-specific nature of many impacts, the literature is scattered through a wide range of published sources (Wolkersdorfer, 2004). Unlike most review papers to date, which largely focus on specific environmental compartments in relative isolation to the wider aquatic ecosystem, this review paper aims to use an interdisciplinary perspective to critically review: (1) the sedimentological, hydrological and ecological impacts of metal mining activities; and (2) the potential for remediation of metal mine sites and the existing remediation technologies available.

The review is organised into 5 main sections. Mine water chemistry has been studied extensively (e.g., Younger *et al*., 2002) and is generally well understood. Therefore, the purpose of section 2 is to provide a brief overview of the primary variables influencing the generation and character of metal mine drainage. There have been several systematic reviews of the sedimentological impacts of mining on the fluvial environment which have documented the physical and chemical factors controlling metal dispersal and storage in mining affected rivers systems (Lewin and Macklin, 1987; Macklin, 1996; Miller, 1997). In addition, new technologies and approaches to help control and remediate sediment contamination have been widely considered (e.g., Macklin *et al*., 2006). Section 3 provides a review of the recent developments centred on new spectroscopic methods for the measurement of metal mobility and speciation, and evaluate the performance of sediment environmental quality standards. Section 4 of this review examines the catchment hydrological factors which influence the character of metal mine drainage in fluvial systems and discusses the important role of stormflows in transporting mine wastes from mine sites. In section 5, the ecological impacts associated with metal mines are examined with specific reference to benthic macroinvertebrate communities. While a significant body of research has been devoted to examining impacts on fish communities (Hallare *et al*., 2010), the benthic lifestyle of macroinvertebrates makes them more representative of local environmental conditions, and, therefore, more reliable indicators of biological stress. Previous reviews by Gerhardt (1993) and Batty *et al*. (2010) have considered the impact of toxic metals and acidity on macroinvertebrates. The present review builds on previous reviews by considering new developments in biomonitoring techniques and sublethal measurements of toxicity assessment. In the final section, remediation practices and technologies to treat metal mine discharges are evaluated. In each of the four key review sections (sedimentology, hydrology, ecology, remediation), we highlight the key research gaps that remain and identify opportunities for future research.

Given that previous reviews have considered the environmental impacts associated with deep and surficial coal mining (Robb, 1994; Banks and Banks, 2001; Younger, 2002), and in particular acid mine drainage (Robb and Robinson, 1995; Banks *et al*., 1997; Gray, 1997), this review focuses on the impact of deep metal mines on riverine ecosystems with a particular emphasis on the following widely exploited metals: lead (Pb), zinc (Zn), copper (Cu), cadmium (Cd) and iron (Fe). All of these metals frequently occur at high concentrations within waters draining metal mines (Novotny, 1995; Younger *et al*., 2002). The review has broad geographical significance, but highlights several case studies from the UK to illustrate some of the historic impacts of metal mining activities on riverine ecosystems. Two search strategies were used to identify relevant empirical papers. First, key word and title searches of electronic databases were undertaken independently by the authors before comparing results. The databases searched were: ASFA Aquatic Sciences, Biological Sciences, Science Direct, SCOPUS, Toxline, Web of Science and Zetoc. The key search words were: metal mine, heavy metals, toxic metals, acid mine drainage, river sediment, flood hydrochemistry, benthic macroinvertebrate, mine remediation and environmental quality. Databases were searched from inception to December 2010. Second, relevant references within any identified papers were followed up. Searches were limited to papers published in English.

2. Mine water chemistry

Sulphidic minerals such as galena (lead sulphide - PbS), sphalerite (zinc sulphide – ZnS) and pyrite (iron disulphide – FeS_2) are amongst the most commonly mined metal ores (Novotny, 1995). These minerals are formed under reducing conditions in the absence of oxygen and remain 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) through natural weathering processes and long-term landform evolution or anthropogenic activities such as mining (Johnson, 2003). A series of complex biogeochemical reactions occurs in sulphide weathering processes, leading to the generation of a potentially toxic leachate and its release into the environment (**Figure 1;** Younger *et al*., 2002; Johnson, 2003; Evangelou and Zhang, 1995). The leachate generated during the sulphide weathering process is complex and is often referred to as acid mine drainage (AMD) or acid rock drainage (ARD). It is most commonly characterised by high levels of dissolved toxic metals and sulphates and low pH (Robb and Robinson, 1995; Braungardt *et al*., 2003). However, it should be noted that metal mine discharges are not always acidic (Banks *et al*., 2002). In general, an increase in pyrite content of the country rock results in greater acidity; an increase in base-metal sulphides results in greater toxic metal concentrations; while an increase in carbonate and silicate content can result in highly alkaline waters (Oyarzun *et al*., 2003; Alderton *et al*., 2005; Cidu and Mereu, 2007). In the UK, 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, resulting in extremely acidic discharges containing high levels of dissolved toxic metals (Abdullah and Royle, 1972; Fuge *et al*., 1991; Boult *et al*., 1994; Neal *et al*., 2005). In contrast, in those parts of the English Peak District where carbonate lithology predominates (Carboniferous Limestone), neutral to basic mine discharges are common and these have significantly lower concentrations of dissolved toxic metals (Smith *et al*., 2003). Aside from lithology and mineralogy, the character of mine water pollution can vary considerably between regions as a result of the grain size distribution of tailings and spoil (Hawkins, 2004), the exposed mineral surface area

(Younger *et al*., 2002), the concentration of reactants such as dissolved oxygen (Wilkin, 2008), and microbial activity (Hallberg and Johnson, 2005; Natarajan *et al*., 2006; Balci, 2008). The highly variable nature of water chemistry associated with metal mine discharges is outlined in **Table 1**.

3. Sedimentological impacts

During the lifetime of a deep metal mine, ore extraction and processing can release vast quantities of solid waste into the riverine environment (Bird *et al*., 2010). Even after mine abandonment, erosion of material from mine spoil and tailings can continue to introduce contaminated solid wastes into river channels and floodplains for many decades (Macklin *et al*., 2003; Walling *et al*., 2003; Miller *et al*., 2004; Dennis *et al*., 2009). These solid wastes can have a significant impact on the geochemistry of channel and floodplain sediments (e.g., Aleksander-Kwaterczak and Helios-Rybicka, 2009; Byrne *et al*., 2010) and also physical and chemical dispersion patterns of toxic metals (e.g., Hudson-Edwards *et al*., 1999b; Dennis *et al*., 2009).

3.1 Sediment geochemistry

Gross contamination of fluvial sediments both within the channel and on the floodplain has been reported in most metal mining regions of the world (**Table 2**), with metal concentrations in sediments usually being several orders of magnitude greater than that in the water column (Macklin *et al*., 2006). Metal concentrations are greatest in the fine sediment fraction and, in particular, in the clay-silt fraction (< 63 µm; Lewin and Macklin, 1987; Foster and Charlesworth, 1996; Stone and Droppo, 1994; Dennis *et al*., 2003; Förstner, 2004). This reflects the higher surface area per unit mass of smaller particles, and the ion-exchange capacity of silt and clay-sized fractions (which include clay minerals, iron hydroxides, manganese oxides, and organic matter in various states of humification).

Metal speciation is essential to assess geochemical phases and the mobility of potentially toxic elements in contaminated sediments (Tokalioglu *et al*., 2003). Until fairly recently, most investigations of sediment metal concentrations have used strong chemicals (e.g., HNO_3, HCl, $HClO_4$, HF) to extract the total amount of metals in the sediment, often leading to oversimplified interpretations that do not take sediment complexity into account (Linge, 2008). Metals in sediments exist in various geochemical phases which reflect the degree to which they can be re-mobilised from the sediment. For this reason, chemical sequential extraction procedures (SEPs) capable of identifying contaminant partitioning have become increasingly popular over total dissolution of the sediment achieved by single extractions (e.g., Tessier *et al*. 1979; Rauret *et al*., 1999). Various extraction media have been used to target specific geochemical phases, including electrolytes ($CaCl_2$, $MgCl_2$), pH buffers of weak acids (acetic, oxalic acid), chelating agents (EDTA, DTPA) and reducing agents (NH_2OH). In many metal mining regions, the impact on sediment geochemistry has been to increase the proportion of toxic metals in the more mobile (bioavailable) geochemical phases. Studies have identified cadmium (Licheng and Guijiu, 1996; Morillo *et al*., 2002; Vasile and Vladescu, 2010), copper (Jain, 2004), zinc (Morillo *et al*., 2002; Galan *et al*., 2003; Aleksander-Kwaterczak and Helios-Rybicka, 2009;

Naji *et al*., 2010) and lead (Byrne *et al*., 2010) to be highly elevated in the acid-soluble phases. The largest proportion of metals is usually found in the reducible phase bound to Fe and Mn oxides (Macklin and Dowsett, 1989). Copper has been found to associate largely with organic matter in the oxidisable phase (Licheng and Guijiu, 1996).

Sequential extraction procedures have allowed the chemical mobility and toxicological risk posed by contaminated sediments to be established allowing resource managers to prioritise areas for remediation. However, a number of doubts concerning the accuracy of selective chemical extraction schemes have been expressed (Linge, 2008). 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 (Burton, 2010). The multitude of extraction techniques and media used can also lead to great variability in results and, in some instances, limits the ability to make direct comparisons between studies. Since the early 1990s, molecular scale techniques to study elemental binding have become more popular. X-ray absorption spectroscopy (XAS) techniques such as X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) have allowed analysis at the molecular level and direct evidence of surface composition and bonding characteristics of mining-derived sediments (Esbrí *et al*., 2010; Van Damme *et al*., 2010). By investigating metal speciation at the atomic level, it is possible to establish metal toxicity, mobility and bioavailability with far greater accuracy than can be achieved using chemical extraction methods. This allows scientists and environmental managers to more accurately gauge the impact of toxic metals on ecosystems and human health.

3.2 Physical dispersion and downstream attenuation processes

The influx of large volumes of contaminated material into river systems can significantly alter local sediment transport and deposition and affect chemical processes that operate at and beneath the river-bed surface (Gilbert, 1917; Lewin *et al*., 1977; Wood and Armitage, 1997). A number of reviews have historically considered the hydrogeomorphic response of riverine systems to mining activities (e.g., Miller, 1997; Macklin *et al*., 2006) and as a result only limited coverage is provided here. Based on research in the UK, Lewin and Macklin (1987) suggested that disturbances of the river channel due to mining can be categorized as involving processes of '*passive dispersal'* and '*active transformation'*.

Passive Dispersal

During *passive dispersal*, mine waste is transported from the mine site with no significant alteration of the prevailing sediment load of the river. Changes can occur in depositional environments, with slow flowing and deep pools being preferential sites for the deposition of contaminant-enriched fine sediment (< 2000 µm). Transport of coarse sediment (> 2000 µm) may be limited to modest and high flow events. However, fine sediments may be transported under a range of different flows, including extended periods of base-flow. In-channel sediment contamination generally decreases downstream from the contaminant source at rates that vary between systems but which, in many cases, are negatively exponential (Lewin and Macklin, 1987). This pattern is functionally related to the hydraulic sorting of sediment based on density and size of ore particles (e.g., galena is more dense than sphalerite and smaller grains travel less fast than coarser grains - Wolfenden and Lewin 1978); dilution by uncontaminated sediments (Marcus, 1987); hydrogeochemical reactions (Hudson-Edwards *et al*., 1996); and biological uptake (Lewin and Macklin, 1987). In many cases, good fits between metal concentration and distance downstream of mining input can be achieved using regression analysis (Wolfenden and Lewin, 1977; Lewin and Macklin, 1987) or non-linear mixing models which incorporate clean and contaminated sediment sources within a river catchment (Marcus, 1987). However, these models are often specific to both the individual metal and the catchment for which they were developed (Dawson and Macklin, 1998; Miller, 1997). Movement of sediment can also occur in large-scale bed forms or ‘slugs’, which have been identified as associated with highs and lows in an otherwise downward trending metal concentration with distance downstream (Miller, 1997).

Active Transformation

Active transformation occurs in association with a significant increase in the input of mining debris to the fluvial system. This may cause intrinsic thresholds to be exceeded and, consequently, lead to a local loss of hydraulic or geomorphological equilibrium that manifests itself in changes in channel character (Lewin and Macklin, 1987). The type, rate and magnitude of erosional and depositional processes can change (Miller, 1997). Channel aggradation may be associated with sediment inputs from active mining and channel degradation may occur after mining has ceased (Gilbert, 1917; Knighton, 1991). Meandering channels may be transformed into braided forms (Warburton *et al*., 2002). Other depositional features can include scroll bars that arise from rapid accretion of sequentially developing point bars as a response to high sediment loads and channel migration, and substantial overbank floodplain deposits, particularly where overbank splays lead to avulsion channels that cross the flood plain (Miller, 1997; Walling *et al*., 2003; Dennis *et al*., 2009).

Toxic metal contaminants can be extremely persistent within the environment and can remain stored within floodplain deposits for decades to millennia (Miller, 1997). Since the 1970's, a significant amount of research has focussed on the role of historical metal mining in the contamination of floodplains (**Table 2**). Analyses of floodplain overbank sediments in the River Ouse catchment in northeast England revealed contaminated sedimentary successions reflecting over 2000 years of lead and zinc mining (Hudson-Edwards *et al*., 1999a). It has been estimated that over 55% of the agriculturally important River Swale floodplain, a tributary of the Ouse, is significantly contaminated by toxic metals (Brewer *et al*., 2005). It has been estimated that approximately 28% of the lead produced in the Swale catchment remains within channel and floodplain sediments. At present rates of valley-bottom reworking through channel migration and erosion, it may take in excess of 5,000 years for all of the metal-rich sediment to be exported from the catchment (Dennis *et al*., 2009). These studies indicate that large areas of agricultural land are potentially contaminated and that there may be long-term health concerns for those ingesting contaminants via crops produced on this land (Albering *et al*., 1999; Conesa *et al*., 2010).

Recent advances in geochemical tracing techniques and numerical modelling have led to improved understanding and predictability of dispersal rates and patterns of sediment-associated toxic metal contamination. Owens *et al*. (1999) used geochemical fingerprinting to identify the proportion of sediment from mining areas in the River Ouse catchment, UK. Using isotope signatures, several studies have differentiated specific geographical sources in mining-affected catchments (Hudson-Edwards *et al*., 1999a; Bird *et al*., 2010). Bird *et al*. (2010) were able to discriminate between sediments derived from mine waste and river sediments using lead isotope signatures. They surmised that approximately 30% of the sediment load of the lower River Danube was derived from mining. Numerical modelling techniques now allow the prediction of contamination patterns in river catchments now and in the future. For example, the catchment sediment model TRACER has been applied to identify sediment contamination ‘hot spots’ in the River Swale catchment, UK (Coulthard and Macklin, 2003). The model also revealed that over 200 years after the cessation of mining activities, over 70% of the deposited contaminants remain in the Swale catchment.

3.3 Chemical dispersion and attenuation processes

Chemical transportation processes in sediments of metal mining-affected rivers become increasingly important after the closure and abandonment of deep mines (Lewin and Macklin, 1987; Bradley *et al*., 1995). Toxic metals can be attenuated downstream of a mining input through pH buffering, acid neutralisation, and precipitation and adsorption reactions (Routh and Ikramuddin, 1996; Ford *et al*., 1997; Lee *et al*., 2002; Ren and Packman, 2004). The often termed 'master variable' for determining metal speciation in aquatic systems is pH (Kelly, 1988; Younger *et al*., 2002). As pH increases, aqueous metal species generally display an increasing tendency to precipitate as carbonate, oxide, hydroxide, phosphate, silicate or hydroxysulphate minerals (Salomons, 1993). The effects of increasing pH below mine discharges can be seen in some rivers by changes in precipitate mineralogy, with proximal capture by iron hydroxides and distal capture by aluminium oxides (e.g., Munk *et al*., 2002). Therefore, a major control on metal attenuation, acid production and stream pH at abandoned mine sites is the amount of carbonate minerals present in the surrounding geology. Carbonate minerals such as calcite, dolomite and siderite weather quickly and can buffer pH and act as adsorption sites for dissolved toxic metals. Non-carbonate minerals weather slowly and, where they predominate, can be extremely slow to react to changes in pH (Wilkin, 2008). The precipitation of solid-form metals limits the concentration of metals which are transported through the aquatic system as free ion species (Enid Martinez and McBride, 1998). These secondary minerals can also act as sorbents for dissolved metals (Enid-Martinez and McBride, 1998; Asta *et al*., 2007; Wilkin, 2008). Adsorption of metals usually increases at higher pH so that substantial changes in dissolved metal concentrations can occur with small changes in pH, typically over 1 – 1.5 pH units (Salomons, 1993). Aside from pH, several other water quality parameters can influence metal speciation, including the concentration of the metal, presence of ligands, redox conditions, salinity, hardness, and the presence of other metals (Novotny, 2003). High levels of salinity, hardness and organic matter content are known to increase metal attenuation by providing binding sites for metal sorption (Salomons, 1980; Dojlido and Taboryska, 1991; Achterberg *et al*., 2003).

Under invariant environmental conditions, sediment geochemical phases are stable, chemical attenuation of metals will proceed at regular rates and, thus, metals remain immobile in river bed sediments (Morillo *et al*., 2002). However, sediments are not a permanent sink for metals and they may be released into the water column when suitable conditions for dissolution occur. Several studies have reported 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; Zoumis *et al*., 2001; Butler, 2009; Knott *et al*., 2009). In sediments from Hamburg harbour, Calmano *et al*. (1993) observed oxidation episodes to decrease pH in the suspended sediments from 7 to 3.4, leading to the mobilisation of zinc and cadmium. Similarly, oxidation of anoxic sediments from Mulde reservoir, Germany, resulted in the mobilisation of zinc and cadmium and redistribution of toxic metals to more bioavailable geochemical phases (Zoumis *et al*., 2001). Mullinger (2004) reported diffuse discharges of metals from bed sediments accounted for up to 40% of zinc, cadmium and copper entering surface waters of the Cwm Rheidol mine, Wales. 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 the concentration of complexing agents (Fergusson, 1990; Morillo *et al*., 2002) have also been reported to lead to the release of ‘stored’ toxic metals into the wider environment.

The contamination risk posed by toxic metals stored in aquatic sediments of former and current industrial centres (including metal mining regions), and the potential for these toxic metals to contaminate areas beyond the source of contamination, has prompted many national regulatory authorities to introduce sediment environmental quality standards (SEQS) (e.g., Environment Agency, 2008b) based on total metal concentrations in the sediment. The practical application of SEQS is made difficult by a number of factors relating to the nature of heavy metal pollutants, including variation in natural background concentrations, the existence of chemical species, the concentrations of physico-chemical parameters, variations in organism sensitivity, and the fact that some heavy metals are essential elements for organisms (Comber *et al*., 2008). 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; Förstner 2009). As far as is known by the authors, most national monitoring and assessment programmes for freshwater systems measure total metal concentrations in sediments rather than the concentration of metals in different geochemical phases. Measurement of total quantities of metals in sediment provides little information regarding their ecotoxicity and their potential mobility. With the achievement of Good Ecological Status (GES) at the centre of many environmental improvement programmes (e.g., to comply with the European Water framework Directive), it is argued that measurement of bioavailable metals in the sediment, which can interact relatively easily with aquatic organisms, would provide a more comprehensive and robust assessment of ecological risk. In this respect, there is a real risk that such programmes are failing to meet their own objectives.

4. Hydrological impacts

The generation of mine water pollution is a product of many factors including local mineralogy, lithology, contaminant source area, and biogeochemical reactions (Younger *et al*., 2002). The character of mine water pollution in surface waters is strongly influenced by a wide range of hydroclimatological factors (including rainfall characteristics), land use (both catchment-wide and any changes associated with spoil heaps), seasonality, antecedent conditions to rainfall or snow-melt (particularly soil and spoil moisture content but also temperature), dominant hydrological transport pathways, and stream discharge (Gammons *et al*., 2005; Canovas *et al*., 2008). Once released to the water column, metals can move through the aquatic environment, resulting in impaired water quality in reaches of a river or estuary that were unaffected directly by deep mine drainage. Released metals can also interact with aquatic animals, resulting in the deterioration of aquatic ecosystem health (Farag *et al*., 1998).

Traditionally, discharge has been seen as a master variable driving river hydrochemistry (Bradley and Lewin, 1982).Heavy metal ion concentrations in rivers are generally thought to be greatest during low flows and lowest coinciding with high flows, when uncontaminated runoff dilutes solute concentrations (Webb and Walling, 1983). Since the 1970s, many researchers have documented the effects of seasonal variability in stream discharge on toxic metal concentrations (e.g., Grimshaw *et al*., 1976; Keith *et al*., 2001; Sullivan and Drewer, 2001; Nagorski *et al*., 2003; Desbarats and Dirom, 2005; Hammarstrom *et al*., 2005). Annual patterns (hysteresis patterns) of dissolved metal concentrations are apparent in many rivers, reflecting the flushing of oxidised sulphides accumulated over dry summer (low flow) months (Canovas *et al*., 2008). Many researchers have noted maximum toxic metal concentrations as occurring during the first heavy rains of the hydrological year, during the autumn (Bradley and Lewin, 1982; Bird, 1987; Boult *et al*., 1994; Braungardt *et al*., 2003; Desbarats and Dirom, 2005; Olias *et al*., 2004; Mighanetara *et al*., 2009). Contaminant concentrations typically decrease in winter and increase gradually through spring and summer as a result of increased sulphide oxidation and evaporation. Therefore, the timing of maximum contaminant flux will be largely a function of hydroclimatology, catchment characteristics and the minerals present at a mine site.

It is understood that a major part of element transfer in rivers takes place during short episodes of high river flow, i.e. floods (Sanden *et al*., 1997). However, to date, very little research has been directed towards detailing toxic metal fluxes and hydrochemical variability during individual high flow events in former mining regions (Grimshaw *et al*., 1976; Bradley and Lewin, 1982; Sanden *et al*., 1997; Dawson and Macklin, 1998; Lambing *et al*., 1999; Wirt *et al*., 1999; Keith *et al*., 2001; Gammons *et al*., 2005; Canovas *et al*., 2008). One of the earliest studies by Grimshaw *et al*. (1976), on the River Ystwyth, Wales, observed hysteretic behaviour in the relation between metal concentrations and discharge, whereby metal concentrations increased on the rising limb of the flood hydrograph and decreased on the falling limb, associated with flushing and exhaustion (or dilution), respectively. This general pattern has also been reported in a number of more recent studies (e.g., Keith *et al*., 2001; Canovas *et al*., 2008; Byrne *et al*., 2009). In some instances, the source of metals in the initial flush was metal sulphates accumulated on the surface of mine waste (Keith *et al*., 2001) or contaminated groundwater efflux from mine portals (Canovas *et al*., 2008). Metal attenuation on the falling limb is principally due to rain-water dilution and the fact that the available contaminant are scavenged in the first flush (Canovas *et al*., 2008). The frequent occurrence of peak iron, manganese and aluminium concentrations on the falling limb of the hydrograph indicates that adsorption onto, or precipitation with, iron solids may be an important toxic metal attenuation mechanism during stormflow events in some rivers (Lee *et al*., 2002; Asta *et al*., 2007; Byrne *et al*., 2009).

The mobilisation and transport of mine wastes during stormflows and the consequent contamination of agricultural lands is an important issue for environmental managers of former metal mining regions (Dennis *et al*., 2003;

Connelly, 2009). During the 1990s, there was a marked increased interest in toxic metal contamination in floodplains in the UK following a number of devastating floods and an increased focus on the potential effects of climate change on hydrological regimes and sediment transport dynamics (**Table 2**). The autumn and winter floods of 2000-2001 across a substantial part of Europe caused large-scale remobilisation and deposition of contaminated sediments in floodplains and farm-land (Dennis *et al*., 2003; Macklin *et al*., 2003; Macklin *et al*., 2006). In future, predicted increases in the frequency and magnitude of floods as a function of climate change may result in increased mobilisation and deposition of toxic metals in floodplains across Europe (Macklin *et al*., 2006; Environment Agency, 2008b; Förstner and Salomons, 2008). Therefore, there is a need to monitor and assess stormflow events and river hydrochemistry in detail in order to quantify metal fluxes with reasonable levels of accuracy in order to allow environmental managers to prioritise areas for remediation.

Aside from contamination of floodplains, the large-scale movement of mine waste during stormflow events has significance for aquatic ecosystem health. The highly elevated toxic metal concentrations during stormflows undoubtedly cause harm to aquatic communities 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 stormflow 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 stormflows and the potential toxicological impacts (Wolz *et al*., 2009). Understanding the toxicological impacts of stormflows will be important in the achievement of environmental quality standards in mining-affected river catchments.

Most metal mines are associated with significant volumes of waste material deposited as surface spoil heaps and tailings. The hydrological behaviour of these waste deposits can be significantly different to the wider catchment due to the alteration of local surface and sub-surface flow pathways (Younger *et al*., 2002). Considering the important role of spoil material in the production of metal contaminants, comparatively little research has been undertaken into flow pathways and contaminant generating processes within mine spoil. Due to the artificial stratification and the discontinuities in permeability that occur within spoil heaps, they often have ’perched aquifers’ that lie well above the underlying bedrock, producing unique flow paths (Younger *et al*., 2002). The development of a water table in mine spoil depends on the predominant lithology of the spoil. For example, sandstone generally forms highly permeable spoil whereas mudstone produces spoil of low permeability. Highly permeable spoil can contain as much as 25% or more of ore as fines or solutes (Davies and Thornton, 1983). Where rainfall infiltration-excess is typical, because, for instance, fine-grained material produces a surface seal, surface runoff will be the predominant flow path (Younger *et al*., 2002). This will, through gully erosion, transfer large quantities of contaminated solids into the local water course.

Changes in flow paths and direction within mine spoil can occur slowly through the seasons or more rapidly during rainfall events as different flow paths become active with the fluctuation of perched water tables (Walling and Webb, 1980). Differential hydrology can induce variability in toxic metal speciation in mine spoils and tailings (Kovacs *et al*., 2006). Generally, oxidation of sulphide minerals occurs in a shallow oxidation zone near the surface of the spoil (Jurjovec *et al*., 2002). Dissolution and flushing of these oxidised metals can then occur during wet periods (Navarro *et al*., 2008). Several studies of metal flushing during storms have reported the importance of weathered metal salts on and near the surface of mine spoil as responsible for increasing metal concentrations during runoff (Canovas *et al*., 2008; Byrne *et al*., 2009). Below the oxidation zone, a zone of transition from saturated to unsaturated sediments typically occurs, often characterised by a 'hard pan' of metal precipitates (Romero *et al*., 2007). Toxic metals can be attenuated in the mine spoil through a series of precipitation, co-precipitation and adsorption reactions. Reducing conditions in saturated sediments can lead to the formation of insoluble metal sulphides. pH buffering can occur in the shallow oxidizing zone with secondary-phase precipitation occurring near the deeper saturated zone (McGregor *et al*., 1998). In order to effectively plan for mine site remediation, it is essential that mine spoils and tailings are characterised in terms of mineralogy, metal speciation and hydrology, especially where contamination of groundwater is an issue. Such information is necessary to understand the mechanisms controlling the release and attenuation of metals at these sites.

5. Ecological impacts of metal mine contamination on macroinvertebrate communities

As early as the 1960s, the adverse impacts of mining activities on macroinvertebrates were being acknowledged (Reish and Gerlinger, 1964). Metal mine drainage can severely impact aquatic ecosystems by affecting primary and secondary production, nutrient cycling, energy flow and decomposition (Stoertz *et al*., 2002; Knott *et al*., 2009; Younger and Wolkersdorfer, 2004; Batty *et al*., 2010). Freshwater macroinvertebrates fulfil important roles in the river ecosystem, being vital food sources for many aquatic and terrestrial predators and playing a significant part in the cycling of organic matter and nutrients (Gerhardt, 1993). The pivotal position of benthic macroinvertebrates in aquatic food webs means that negative impacts on them can have widespread consequences within aquatic and terrestrial food-webs for primary producers, predators and the wider ecosystem. As a result, macroinvertebrates have increasingly been used as indicators of stream ecosystem health associated with metal mining (e.g., Batty *et al*., 2010; Poulton *et al*., 2010).

5.1 Changes in community composition

A wide range of changes to macroinvertebrate community structure and composition have been reported in the scientific literature associated with metal mining activities. Reductions in abundance, number of taxa and biodiversity are common impacts reported in association with metal mining-activities internationally (e.g., Willis, 1985; Gray, 1998; Amisah and Cowx, 2000; Watanabe *et al*., 2000; Hirst *et al*., 2002; Kiffney and Clements, 2003) (**Table 3**). Investigations have generally revealed that some macroinvertebrate taxa display a tolerance or sensitivity to contamination (**Table 3**). Whilst investigating contaminated stretches of two rivers in Ohio, USA, Winner *et al*. (1980) hypothesised that habitats heavily polluted with toxic metals may be dominated by Chironomidae (Diptera – true fly larvae); moderately polluted habitats by Chironomidae and Trichoptera (caddisfly); and minimally or unpolluted habitats by caddisflies and Ephemeroptera (mayfly). Armitage *et al*. (1980; 2007) examined macroinvertebrate species composition of the mining impacted River Nent. Diptera and Plecoptera (stonefly) were the dominant orders observed in the river system. Trichoptera and mayfly (Ephemeroptera) were not abundant and seemed particularly sensitive to the mine water pollution. In contaminated reaches of the River Vascao, Portugal, the number of predators increased and the number of EPT taxa (Ephemeroptera – Plecoptera - Trichoptera) decreased, probably reflecting the presence of thick layers of metal hydroxides on the river substrate (Gerhardt *et al*., 2004). Sites subject to severe AMD contamination showed high levels of biodiversity due to high species richness of the tolerant species. In general, the order of toxicity of metal mine contamination to the most common macroinvertebrate orders is: Ephemeroptera > Trichoptera > Plecoptera > Diptera. However, there can be considerable variability in metal tolerance between macroinvertebrate taxa and species. For example, Ephemeroptera are generally considered to be highly sensitive to metal contamination despite some species (e.g., *Baetis rhodani* and *Caenis* cf. *luctuosa*) being reported to display some tolerance to metal contaminants

(Roline, 1988; Beltman *et al*., 1999; Gower *et al*., 1994; Gerhardt *et al*., 2004; Gerhardt *et al*., 2005b). Several authors have reported impacts of mine water contamination on ecosystem function (**Table 3**), including reduced secondary production (Carlisle and Clements, 2005; Woodcock and Huryn, 2007), and a reduction in leaf matter (detritus) decomposition rates and microbial respiration (Kiffney and Clements, 2003; Carlisle and Clements, 2005).

Relatively predictable changes in macroinvertebrate community structure as a result of pollution (e.g., decreased abundance and biodiversity, elimination of sensitive taxa) have led to the development of a number of biotic and diversity indices (e.g., Shannon, 1948; Berger and Parker, 1970). However, the performance of biological indices / metrics appear to vary widely when applied to mine water contaminated sites (Smolders *et al*., 2003; Van Damme *et al*., 2008; Chadwick and Canton, 1984; Willis, 1985; Chadwick *et al*., 1986; Rhea *et al*., 2006). Variability in success is likely to be a function of the complicated interplay between the mine water components, other water quality parameters, and natural tolerances and sensitivities of organisms. Gray and Delaney (2008) suggest a modification of the Acid Waters Indicator Community (AWIC) index (Davy-Bowker *et al*., 2005) to incorporate metal toxicity may be required. 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 Biological Monitoring Working Party (BMWP) system (Biological Monitoring Working Party, 1978), based on species' tolerance to acidity and metal contamination, has also been suggested (Gray and Delaney, 2008) and some success has been achieved using a multi-metric approach by considering multiple biological metrics simultaneously (e.g., Clews and Ormerod, 2009). Clearly, there is scope for a biological index designed specifically for detecting the impacts of mine water contamination on aquatic communities. However, 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.

5.2 Changes in macroinvertebrate physiology and behaviour

More subtle community alterations as a result of physiological or behavioural changes are less easy to diagnose (Younger and Wolkersdorfer, 2004) (**Table 3**). For example, Petersen and Petersen (1983) reported anomalies in the construction of filter feeding nets of Hydropsychidae (Trichoptera) in rivers affected by a gradient of toxic metal pollution. Disruption of silk-spinning by contamination caused the caddisfly to spend more time in open habitats repairing the structure and thus more vulnerable to potential predators. Vuori (1994) observed metal exposure to affect the territorial behaviour of Hydropsychidae, relaxing levels of interspecific competition and increasing susceptibility to predation. Brinkman and Johnston (2008) reported decreased moulting rates (*Rhithrogena hageni*: Ephemeroptera) after exposure to high levels of copper, cadmium and zinc. In an experimental stream study, Clements *et al*. (1989) reported that high copper doses increased predation pressure, so much that the numbers of caddisfly, mayfly and chironomids were dramatically reduced. Maltby and Naylor (1990) found high zinc concentrations significantly impacted *Gammarus pulex* reproduction by causing a reduction in energy absorption and an increase in the number of broods aborted. Other behavioural responses reported associated with metal mine contamination include increased drift rates, physical avoidance of contaminated sediments, reduced burrowing / burial rates (Leland *et al*., 1989; Roper *et al*., 1995) and reduced leaf litter processing rates and microbial respiration (Kiffney and Clements, 2003; Carlisle and Clements, 2005). Many of the species specific differences reported within the literature have been attributed to trophic status with herbivores and detritivores typically being more sensitive to contamination than predators (Leland *et al*., 1989; Schultheis *et al*., 1997; Gerhardt *et al*., 2004; Poulton *et al*., 2010). Acute metal contamination can induce deformities and mutations of head and feeding structure in macroinvertebrate fauna (e.g., Groenendijk *et al*., 1998; Vermeulen *et al*., 2000; Groenendijk *et al*., 2002; De Bisthoven *et al*., 2005). Both zinc and lead have been implicated as teratogens (inducing deformities as a result of chronic exposure during the lifetime of the organism) and as a mutagen (inducing deformities in offspring due to DNA damage in parents from chronic exposure) in *Chironomus riparius* (Chironomidae) (Martinez *et al*., 2004).

More recent studies have made use of biomonitoring techniques which are capable of detecting sublethal behavioural and physiological responses in an organism when exposed to a contaminant (e.g., De Bisthoven *et al*., 2004; Gerhardt *et al*., 2004; Gerhardt *et al*., 2005a; De Bisthoven *et al*., 2006; Gerhardt, 2007; Macedo-Sousa *et al*., 2007) (**Table 3**). A conceptual Stepwise Stress Model (SSM), proposed by Gerhardt *et al*. (2005a), postulates that an organism will display a time-dependent sequence of different regulatory and behavioural responses during exposure to contaminants over a certain threshold. Several species have been found to show a pH-dependent response to AMD involving, first, an increase in locomotion, followed by an increase in ventilation (e.g., Gerhardt *et al*., 2005a; De Bisthoven *et al*., 2006). An increased ventilation rate reflects changes in the organism's respiratory and physiological system, and may be due to damage to gill membranes or nerve tissues. Locomotory activity probably represents an avoidance strategy from potentially toxic conditions. Importantly, biomonitoring methods integrate biochemical and physiological processes and so are a more comprehensive method than single biochemical or physiological parameters. In combination with the Stepwise Stress Model, online biomonitoring offers the possibility of a graduated 'early warning' system for the detection of pollution waves (Gerhardt *et al*., 2005a).

5.3 Metal bioaccumulation in macroinvertebrates

A significant body of research has concentrated on evaluating the bioaccumulation of toxic metals in macroinvertebrates as a measure of the bioavailability of contaminants (e.g., Farag *et al*., 1998; Smolders *et al*., 2003; Yi *et al*., 2008). Metals which are bioaccumulated by organisms and plants can be concentrated or magnified in the food chain (Sola *et al*., 2004) (**Table 3**). Benthic primary producers and decomposers are known to accumulate significant amounts of metals with little or no deleterious effects (Farag *et al*., 1998; Sanchez *et al*., 1998). These metals can be transferred to herbivorous and detritivorous macroinvertebrates which in turn can transfer the metals to higher trophic levels (Younger and Wolkersdorfer, 2004). Metal accumulation can vary between species, depending on a great number of physiological (e.g. cuticle type, the presence or absence of external plate gills, the processes which control metal distribution in the cell) and behavioural factors such as an organisms feeding strategy, contact with benthic sediments, larval stage and size (Dressing *et al*., 1982; Farag *et al*., 1998; Goodyear and McNeill, 1999; Sola and Prat, 2006; Cid *et al*., 2010). Metal intake can take place through direct exposure to metals in surface and pore waters or indirectly via food supply. Those metals which, through their chemistry, are almost completely sediment-bound (Fe, Mn, Pb, Al), will usually be most important for particle feeders. Metal intake in the tissue takes place at a cell membrane, typically in the gill or gut, depending on whether the metal is in solution in the surrounding water body or if it was ingested with food. A range of environmental factors determine the potential for metal bioaccumulation including metal concentration in the surrounding water, water hardness, presence of organic matter, feeding group and the ionic state of the metal (Gower and Darlington, 1990; Farag *et al*., 1998; Sola and Prat, 2006). The accumulation of metals in different organisms can also vary greatly as a result of natural or evolved tolerance mechanisms (Spehar *et al*., 1978; Gower and Darlington, 1990; Bahrndorff *et al*., 2006). For example, *Plectrocnemia conspersa* (Trichoptera), common in streams in south-west England affected by metal mine drainage were found to be tolerant of copper pollution (Gower and Darlington 1990). Some controlled microcosm experiments have reported tolerance to metal polluted sediments by *Chironomus februarius* (Chironomidae) (Bahrndorff *et al*. 2006). Mechanisms of tolerance might be methylation, increased metal excretion or decreased metallothionein production. Metallothionein is a metal-binding protein with the principal function of accumulating essential metals for normal metabolic processes (Howard, 1998). Its presence facilitates the accumulation of toxic metals, however decreased production of this protein may allow certain organisms to accumulate lower amounts of toxic metals. Despite the great range of factors which can affect metal bioaccumulation in organisms, bioaccumulation factors (BAFs) which consider tissue metal concentration in relation to the surrounding abiotic medium, are possibly a more robust biodiagnostic method than measurement of metal concentrations in the water column and benthic sediments. If water quality guidelines are to continue to be used, then additional research will need to be undertaken to determine appropriate guidelines (possibly above existing guidelines) to support aquatic communities. In the future, metal bioaccumulation will need to be studied in a greater range of macroinvertebrates in order to fully understand metal-organism interactions in aquatic systems. A review of metal bioaccumulation studies by Goodyear and McNeill (1999) found that most studies primarily considered Ephemeropteran and Dipteran taxa and especially collector-gatherer and predatory functional feeding groups / traits.

5.4 Effects of environmental parameters on the toxicity of mine discharges

Changes in some environmental parameters can affect the chemistry and, therefore, the toxicity of metals to organisms. The effects of salinity, water hardness and alkalinity on metal toxicity have been studied extensively (Stiff, 1971; Brkovic-Popovic and Popovic, 1977; Gauss *et al*., 1985; Gower *et al*., 1994; Yim *et al*., 2006, Riba *et al*., 2010 – **Table 3**). All of these studies reported metal toxicity increases for macroinvertebrate and fish species under low salinity, alkalinity and water hardness conditions. Increased metal toxicity has also been reported at low turbidity (Garcia-Garcia and Nandini, 2006) and DOM (dissolved organic material) levels (Gower *et al*., 1994). In river systems, carbonate minerals, clay minerals and DOM act as sorption sites for toxic metals and, therefore, high levels of these parameters help to reduce the concentration of dissolved toxic metals in bioavailable forms. However, bottom-dwelling organisms will take up sediment-bound metals through ingestion.

While bioassay and microcosm studies have revealed much information on metal ecotoxicity, a possible criticism of them could be that they are too simplistic in seeking to evaluate the response of macroinvertebrate species or communities to a single metal contaminant. In reality, most contaminated mine waters will contain mixtures of different metals in solution (**Table 3**). The simplest solution has been to assume the toxic effects of the metals present in the mixture are additive (Vermeulen, 1995). However, the interaction between metals can result in synergistic effects. For example, Hickey and Golding (2002) reported total abundance of heptageniid mayflies, community respiration and macroinvertebrate drift were most sensitive to solutions with a mixture of zinc and copper. Clements (2004), in stream mesocosms, found negative responses were generally greatest with zinc alone or with zinc and cadmium. A possible explanation for this synergism is the physiological inhibition of metal excretion by one of the metals, allowing the other metal(s) to have greater toxic effects (Berninger and Pennanen, 1995). Mixtures of metals have also been shown to have antagonistic effects. Morley *et al*. (2002) found zinc and cadmium to have an antagonistic effect leading to increased survival of the cercarial stage of the parasitic fluke *Diplostomum spathaceum*. In some cases, antagonistic effects of metal mixtures are probably related to competition between metal ions for common sites of uptake (Younger and Wolkersdorfer, 2004). A study by Vermeulen (1995) illustrated the difficulty in predicting how metal mixtures will affect metal toxicity to organisms. Out of the 26 studies analysed, thirteen reported synergistic effects, six reported antagonistic effects, and seven reported additive effects. The problem of metal mixture toxicity is further compounded by other water quality parameters such as hardness, salinity and organic matter content. These parameters can increase or decrease metal toxicity and comparable mixtures of metals can also show contrasting toxicity effects between different groups, species and populations of organisms (Younger and Wolkersdorfer, 2004).

The task of evaluating metal toxicity is made even more difficult when acidity is considered. Most commonly, a decrease in pH will increase the amount of toxic free metal ions due to changes in metal speciation, mobility and bioavailability (Campbell and Stokes, 1985). However, at low pH, metals tend to desorb from organisms due to competition with hydrogen ions for binding sites (Gerhardt, 1993). The effects of low pH on stream biota in the absence of dissolved metals can be lethal or sublethal, inducing a range of physiological changes including an upset of the ionic balance across organism membranes and hydrolysing of cellular components (Kelly, 1988).

Campbell and Stokes (1985) suggested acidity can affect metal-organism interactions in two key ways. First, if a decrease in pH causes little change in metal speciation and there is only weak binding of metals at biological surfaces, the decrease in pH will decrease the toxicity of the metal due to competition with hydrogen ions for binding sites. Second, if a decrease in pH causes changes in speciation and there is strong binding at biological surfaces, then acidification will increase metal availability and toxicity. In the first instance, acidity will be the primary threat to ecosystems. In the second scenario, low pH and high dissolved metals may both influence toxicity.

The multi-factor nature of contaminated mine discharges (acidity, dissolved metals, metal precipitates, sulphates) and the natural variability in water chemistry between regions means that metal toxicity can be highly variable. Historically, ambient water quality criteria have specified permissible total or dissolved metal concentrations even though metal toxicity is heavily dependent on water chemistry (e.g., hardness, pH, DOM). The Biotic Ligand Model (BLM) (Di Toro *et al*., 2001) was developed to predict metal toxicity by incorporating basic principles of physiology and toxicology, and the effects of water chemistry on metal speciation and bioavailability. The model has gained widespread use amongst the scientific / academic and water industry communities due to its potential for identifying water quality criteria and in facilitating risk assessment of aquatic environments (Paquin *et al*., 2002). In order to gain wider applicability and relevance, BLMs will need to be applied to a wider range of organisms and pollutants in the future, and to be able to incorporate metal mixtures into toxicity predictions (Niyogi and Wood, 2004).

6. Remediation of mining-impacted river systems

The prevention of contaminated discharge from mine sites is now required by law in many countries (Macklin *et al*., 2006). In the USA, the Clean Water Act (1972) was established to minimise the impact of anthropogenic pressures (including mining) on surface waters. In Europe, the adoption of the Water Framework Directive (2000/60/EC), and subsequent Mining Waste Directive (2006/21/EC), has necessitated the development of inventories of contaminant impacts at active and abandoned mine sites (Hering *et al*., 2010). New legislation, based on a greater understanding of water quality and ecological integrity issues arising from mine discharges, have prompted research into remediation technologies aimed at reducing the environmental impact of metal mines (PIRAMID Consortium, 2003).

Mine water remediation technologies can be broadly categorised into active and passive treatment. Active treatment technologies are well established and involve the utilisation of electrical energy and mechanised procedures (Jarvis *et al*., 2006) and are dependent on continuous monitoring and maintenance (Robb and Robinson, 1995). Traditional active treatment processes involve a sequence of oxidation by physical or chemical means, the addition of alkaline chemicals to raise pH and accelerate oxidation and precipitation of metals (Robb and Robinson, 1995; Lund and McCullough, 2009), and settlement and filtration (PIRAMID Consortium, 2003). However, active treatment incurs substantial set-up, material and maintenance costs (PIRAMID Consortium, 2003). In response, passive remediation utilising natural physical, chemical and biological processes and materials has found increasing favour over the past 30 years (Geroni *et al*., 2009). Passive remediation systems use naturally available energy (e.g., topographical gradient, metabolic energy, photosynthesis) to drive he remediative processes and have the principal advantages over active remediation of reduced set up and maintenance costs (Pulles and Heath, 2009). Some passive systems (e.g., wetlands) require significantly greater land area than active treatment systems; although they do not require costly reagents and incur less operational maintenance (Norton, 1992; Hedin *et al*., 1994). Detailed characterisation of contaminant loading over a sufficiently long time period is required prior to implementation of treatment systems, including measurements of seasonal variation and the impact of episodic contaminant flushing events, e.g., associated with spate flows (Younger *et al*., 2005; Byrne *et al*., 2009). Equally important is the linking of all mine water sources with a treatment system. Many abandoned mine sites have substantial diffuse sources (Pirrie *et al*., 2003; Mayes *et al*., 2008; Mighanetara *et al*., 2009; Byrne *et al*., 2010), including mine spoil and mobile metal fractions in the river bed. As a result it may be difficult to collect and route contaminated runoff to treatment areas.

Mine water treatment technologies have been extensively reviewed elsewhere (e.g., Brown *et al*., 2002; Younger *et al*., 2002; PIRAMID Consortium, 2003; Lottermoser, 2007) and so a brief overview is provided (**Table 4**). Both wetlands and Reducing and Alkalinity Producing Systems (RAPS) are now well established remediation technologies throughout North America (e.g., Hedin *et al*., 1994) and Europe (e.g., Whitehead and Prior, 2005) as passive treatment options for sulphate and Fe-rich, net-alkaline and net-acidic coal mine discharges (Batty and Younger, 2004). In anoxic systems, removal of toxic metals (e.g., zinc, lead, copper, cadmium) is hypothesised to occur through the formation of insoluble metal sulphides and carbonates (Younger *et al*., 2002 – See **Table 4**). In aerobic systems, some toxic metals can be removed either by direct precipitation as oxides and hydroxides or carbonate phases or by co-precipitation with iron, manganese and aluminium hydroxides. However, rates of toxic metal removal in these systems (particularly zinc) have, in general, proved insufficient in circum-neutral and net-alkaline mine waters, where chalcophile metals are the principal contaminants (Robb and Robinson, 1995; Nuttall and Younger, 2000). Some success has been achieved using variations of conventional calcite and organic-based treatment systems in laboratory-scale experiments (Nuttall and Younger, 2000; Rotting *et al*., 2007; Mayes *et al*., 2009). A large number of researchers have also demonstrated the potential for organic and inorganic sorbent media to remove toxic metals (Cui *et al*., 2006; Perkins *et al*., 2006; Madzivire *et al*., 2009; Mayes *et al*., 2009; Rieuwerts *et al*., 2009; Koukouzas *et al*., 2010; Vinod *et al*., 2010). However, many of these technologies are still at the experimental stage and will require further refinement and large-scale field pilot studies before their full potential is realised. Frequent blocking of filtering media with metal precipitates and rapid consumption of reactive surfaces limit the metal removal efficiency of many of these systems to very short time scales – hours to days in some instances (Younger *et al*., 2002).

Even with mine water treatment, the legacy of contamination in river sediments and floodplains 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 Status (GCS) and Good Ecological Status (GES) under the EU Water Framework Directive. The historical, preferred method of dealing with contaminated sediment is removal by dredging (Nayar *et al*., 2004). This is an expensive and destructive process which may mobilise vast reservoirs of bioavailable metals as part of the process (Nayar *et al*., 2004; Knott *et al*., 2009). Furthermore, the sediment removed still requires treatment and safe disposal. Recently, geochemical engineering approaches involving in-situ and ex-situ biological and chemical treatment of contaminated soils and sediments have gained attention as alternatives (Förstner, 2004), and some success has been achieved in the stabilisation and removal of toxic 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 considered to be the development of guidelines concerning sediment quality (Burton, 2010; Byrne *et al*., 2010).

Some efforts have focussed on the prevention of the generation of contaminated mine water, so-called source control techniques. Conventional techniques have focussed on physical and chemical stabilisation (Mendez and Maier, 2008). Physical stabilisation involves covering mine waste with inert material (e.g., clay, gravel) to reduce oxygen inflow and water ingress into the contaminated material (Gandy and Younger, 2003; Waygood and Ferriera, 2009). However, clay caps in arid and semi-arid regions have tended to crack from wetting and drying cycles resulting in the failure of the air-tight cap (Newson and Fahey, 2003). Chemical stabilisation is achieved by adding a resinous adhesive to form a crust over the mine waste, however, these also are prone to cracking and failure (Tordoff *et al*., 2000). More recently, phytoremediation (phytoextraction and phytostabilisation) techniques have developed as less costly alternatives (Marques *et al*., 2009). Phytostabilisation creates a vegetative cap on the mine waste which immobilises metals by adsorption and accumulation in the rhizosphere (Mendez and Maier, 2008). Some success has been achieved in laboratory trials investigating reforestation of mine tailings using endemic tree species (Pollmann *et al*., 2009). Phytoextraction offers the possibility of recovery of metals through the hyperaccumulation of metals in plant tissues (Ernst, 2005). However, the long-term performance of these new strategies needs to be evaluated, as does the bioavailability of metals to wildlife which may feed on the vegetative covers.

7. Synthesis and conclusions

This paper provides a critical synthesis of scientific literature related to the sedimentological, hydrological and ecological impacts of metal mining on aquatic ecosystems. It has also highlighted the potential for remediation of mine sites and provided an overview of current research and technological developments in this area.

The important role of sediments in the dispersal, storage and recycling of metal contaminants within the fluvial environment has been highlighted. Significant quantities of contaminated sediment are eroded and transported into aquatic systems from abandoned metal mines and both physical and chemical processes influence the distribution of toxic metals within riverine ecosystems. Physical dispersal processes are generally well understood and can be classified as passive or active (Lewin and Macklin, 1987), the latter prevailing when the addition of mine wastes to a river system results in a threshold crossing event and the collapse of geomorphological equilibrium. Under these circumstances, significant contamination of floodplains by toxic metals can occur, with long-term potential consequences for the environment, society and human health. However, recent advances in geochemical tracing techniques and numerical modelling have led to improved understanding and predictability of dispersal rates and patterns of sediment-associated toxic metal contamination (Coulthard and Macklin, 2003). Chemical dispersal of mine wastes tends to predominate after mine closure and four principal processes result in toxic metal attenuation downstream of inputs – pH buffering, acid neutralisation, precipitation and adsorption. However, river sediments are not a permanent store for toxic metals and they may be released into the water column if there are fluctuations in some important environmental parameters (i.e. pH and redox potential). As a result, establishing metal speciation, bioavailability and potential mobility is essential in order to prioritise sites for remediation. Recently, molecular scale techniques to study elemental binding have become more accessible to researchers. A greater number of geochemical studies should make use of these techniques to provide more accurate information on bonding characteristics of metals in sediments. Environmental regulators are beginning to acknowledge the central role of sediments in maintaining ecological quality in river systems. We have argued that the measurement / quantification of total metal concentrations, as is practiced by many regulators, provides limited information on the potential toxicity of sediments. Measurement of the bioavailable metal fraction within benthic sediments is considered a more accurate gauge of potential metal toxicity.

The character of metal mine drainage after it enters surface waters is affected by many factors including stream discharge, rainfall characteristics, conditions antecedent to rainfall-runoff events and season, and the interaction of a large permutation of processes which must be understood and quantified in order to mitigate effectively. Seasonal variability in metal concentrations is linked to oxidation and dissolution of metal sulphates, leading to elevated metal concentrations in summer and autumn months. At many mine sites, the transport of significant amounts of mine waste is limited to stormflows. Typically, hysteresis is evident in the relationship between metal concentrations and discharge. Peak metal concentrations are achieved before peak discharge, associated with the dissolution of surface oxidised material. Despite the importance of stormflows for the transport of mine wastes, little research has concentrated on investigating toxic metal fluxes and hydrochemical variability under these conditions. Predicted increases in the frequency and magnitude of floods as a function of climate change may result in increased mobilisation and deposition of toxic metals in floodplains across

Europe. Stormflow hydrochemistry in rivers draining mine sites should be studied in more detail in order to quantify metal fluxes more accurately and allow environmental managers to prioritise areas for remediation. Toxic metal flushing during stormflows potentially impacts stream ecosystems by significantly increasing the toxicity of the river water, even if only for short time periods. More research is needed to help understand the potential toxicological impacts of stormflows in mining-affected river catchments. Relatively few studies have investigated mine spoil hydrology and metal attenuation and release processes. Environmental investigations at abandoned metal mine sites should include assessments of mine spoil in terms of mineralogy, metal speciation and hydrology, especially where contamination of groundwater is an issue.

Metal mine contaminants in river systems can have a variety of negative impacts on macroinvertebrate ecology and biology, including changes to community structure, physiological and behavioural impacts as well as direct mortality. Typically, rivers heavily impacted by metal mine drainage have reduced species diversity and abundance, and tend to be dominated by Dipteran species. The order of toxicity in mining-impacted streams generally proceeds in the order Ephemeroptera > Trichoptera > Plecoptera > Diptera. Bioindices are used widely to quantify contaminant impacts on macroinvertebrate communities. However, there effectiveness in discerning the impacts of metal mine contamination is questionable, with widely varying performance reported in the literature. The problem appears to be related to the multi-factor nature of mine discharges. Further research is required to develop a biological index specifically for the detection of the impacts of mine water contamination on macroinvertebrate communities and the wider ecosystem. Traditionally, laboratory bioassay experiments have been used to investigate metal and AMD toxicity, with organism mortality being the test endpoint. Recently, biomonitoring techniques capable of detecting sublethal behavioural and physiological responses in an organism have become popular (e.g., Gerhardt *et al*., 2004). They have the principal advantage over bioassays of integrating both biochemical and physiological processes. A major criticism of bioassay and microcosm studies is that they generally do not consider metal mixtures or the influence of other environmental parameters on metal toxicity. The development of the Biotic Ligand Model has allowed organism physiology and important environmental parameters to be factored into assessments of metal toxicity (Di Toro *et al*., 2001). However, to reach their full potential, BLMs will need to be applied to a wider range of organisms and pollutants, and they will need to be able to incorporate metal mixtures into toxicity predictions.

An increasing range of remediation technologies have been developed for the treatment of contaminated mine water which can be applied in a variety of topographical settings. Chemical treatment of mine waters is expensive and unsustainable over the substantial time periods treatment will be required. Passive remediation technologies offer a low cost and sustainable alternative. Passive systems for the treatment of coal mine discharges, where iron, sulphates and acidity are the principal contaminants, are considered proven technology. However, these systems generally fail to remove toxic metals (e.g., Zn, Pb, Cd), associated with metal mine discharges, to an acceptable standard. New substrates and techniques aimed at removing high concentrations of these toxic metals are being trialled and many show promise at the laboratory scale. However, large-scale pilot treatment plants are needed in order to develop these new systems and to test them in field-relevant conditions. Even with mine water treatment, mine spoil and contaminated soils in mining regions will continue to pose a threat to water and ecological quality for many years into the future. New bio-based source control techniques such as phytoremediation offer the possibility of stabilising, immobilising and extracting toxic metals from soils at low cost, by using plants which hyper-accumulate toxic metals in their tissue. However, the long-term functioning and ecological impact of these new strategies needs to be evaluated.

A management approach which can draw on the expertise of separate but related and relevant disciplines such as hydrology, hydrochemistry, sediment geochemistry, fluvial geomorphology and aquatic ecology affords the opportunity for a more complete understanding of processes and impacts in mining-impacted river catchments. It is hoped that this review will help to contribute to our knowledge and understanding of the impacts of metal mining on aquatic ecosystems and highlight the usefulness of approaching such problems from a multi-disciplinary geographical point of view.

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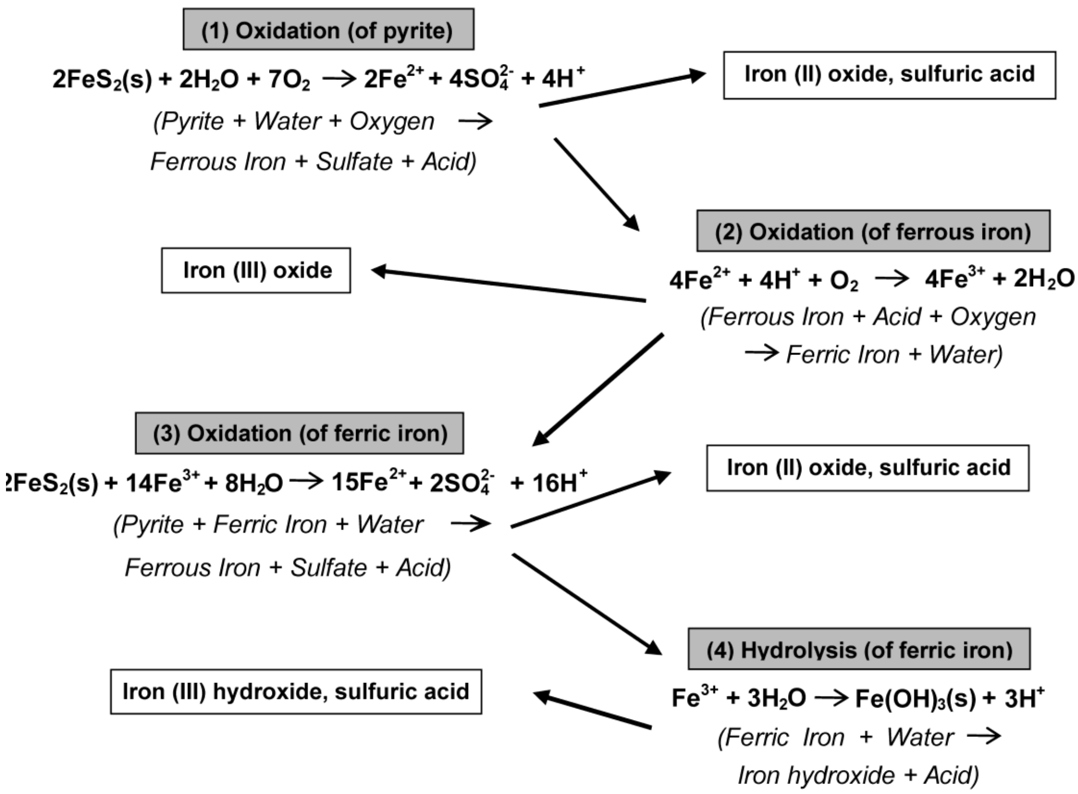

Figure 1 The process of pyrite weathering in a deep metal mine. Four general equations describe the chemistry of pyrite weathering and the production of AMD – (1) The oxidation of pyrite by oxygen and water in atmospheric conditions to produce dissolved ferrous iron and sulphuric acid; (2) the oxidation of dissolved ferrous iron to ferric iron; (3) the hydrolysis of ferric iron with water to produce iron hydroxide precipitate (ochre) and acidity; (4) the oxidation of additional pyrite by the ferric iron generated in reaction (2) to produce dissolved ferrous iron and sulphuric acid. The acidic conditions generated during these processes can dissolve oxidised trace metals. The process is accelerated by the presence of sulphide and iron-oxidising bacteria.

Table 1 A comparison of dissolved metal (mg/l), sulphate (mg/l) and pH concentrations from waters impacted by historical deep metal mining.

Location	Sample type	Pb	Zn	Cu	Cd	Fe	SO_4	pH	Author(s)
Europe									
River Carnon, England	Mine drainage	<0.01 - 0.02	0.12 - 23	0.02 - 1.3	<0.01 - 0.02	<0.01 - 49	77 - 789	3.3 - 7.7	*Neal et al. (2005)*
River Tamar, England	Adit drainage	<0.01 - 0.17	<0.1 - 2.5	<0.01 - 1.4	<0.01 - 0.01	0.05 - 2.6	10 - 89	3.4 - 7.8	*Mighanetara et al. (2009)*
Funtana Raminosa Mining District, Italy	Tailings drainage	<0.01	0.08 - 34	<0.01 - 0.04	<0.01 - 0.85	0.02 - 0.25	22 - 1680	7.1 - 7.8	*Cidu and Mereu (2007)*
Buchim Mining district, Macedonia	Mine stream	0.03*	0.03*	0.62*	<0.01*	0.3*	-	5.1*	*Alderton et al. (2005)*
Zletovo Mining District, Macedonia	Adit drainage	0.06*	21.57*	0.46*	0.14*	98.2*	-	3.4*	*Alderton et al. (2005)*
River Zletovska, Macedonia	Channel	<0.03 – 0.8	0.04 - 70.07	<0.01 - 1.05	<0.01 - 0.24	0.1 - 103.3	-	3.4 - 7.6	*Alderton et al. (2005)*
River Bjorgasen, Norway	Channel	-	5.4[b]	2.7[b]	0.01[b]	-	-	3.2[b]	*Gundersen and Stiennes (2001)*
Rio Tinto, Spain	Channel	0.1 - 2.4	0.3 - 420	0.05 - 240	-	-	2800 - 16000	1.4 - 7.6	*Hudson-Edwards et al. (1999b)*
Troya Mine, Spain	Tailings pond	0.02 - 0.05	4.99 - 18.95	<0.01 - 0.03	0.01 - 0.03	0.04 - 0.33	-	-	*Marques et al. (2001)*
River Odiel, Spain	Channel	<0.01 - 1.18	0.17 - 130.23	0.01 - 37.62	<0.01 - 0.38	0.03 - 262.71	50.7 - 3960	2.5 - 6.3	*Olias et al. (2004)*
Tintillo River, Spain	Mine drainage	0.01 - 0.07	7.3 - 216	3.5 - 115	<0.01 – 0.51	264 - 1973	1300 - 11580	2.3 - 2.8	*Sanchez Espana et al. (2006)*
Tinto Santa Rosa Mine, Spain	Mine drainage	<0.01 - 0.08	56 - 85	15 - 23	0.09 - 0.15	234 - 881	2704 - 4026	2.6 - 3.4	*Asta et al. (2007)*

Fluminese Mining District, Spain	Mine water	<0.01 - 0.05	0.88 - 40	-	<0.01 - 0.09	<0.01 - 12	17 - 640	6.3 - 8.2	*Cidu et al. (2007)*
River Tawe, Wales	Channel	<0.01 – 0.15	0.01 - 8.8	<0.01 - 0.04	<0.01 - 0.16	-	-	-	*Vivian and Massie (1977)*
River Rheidol, Wales	Channel	<0.01	0.08 - 0.29	-	<0.01	-	5.3 - 7.1	5.5 - 6.4	*Fuge et al. (1991)*
River Yswyth, Wales	Channel	0.06 – 0.09	0.17 - 0.36	-	<0.01	-	nd - 5.3	4.1 – 4.6	*Fuge et al. (1991)*
Cwm Rheidol Mine, Wales	Adit drainage	0.02 – 0.04	38 - 72	0.03 - 0.07	0.04 - 0.11	-	441 - 846	2.8 - 3.0	*Fuge et al. (1991)*
Cwm Ystwyth Mine, Wales	Spoil drainage	0.29 - 3.3	1.5 - 4.6	<0.01	<0.01	-	nd	4.1*	*Fuge et al. (1991)*
Cae Coch Pyrite Mine, Wales	Mine water	-	-	-	-	2261[b]	6590[b]	2.4[b]	*McGinness and Johnson (1993)*
River Goch, Wales	Channel	-	<0.01 - 4.19	<0.01 - 5.99	-	<0.01 - 25.98	-	2.3 - 7.7	*Boult et al. (1994)*
Cwm Rheidol Mine, Wales	Spoil drainage	-	577 - 978	1.2 - 9.35	-	-	-	2.6 - 2.7	*Johnson (2003)*
North America									
West Squaw Creek, USA	Channel	-	0.01 - 156	<0.01- 190	-	0.03 - 500	2.6 - 5100	2.4 - 6.9	*Filipek et al. (1987)*
Richmond Mine, USA	Mine water	1 - 120	0.06 – 23.5[a]	0.21 - 4.76[a]	4 - 2110	2.47 – 79.7[a]	14 - 760[a]	-3.6 - 1.5	*Nordstrom et al. (2000)*
Peru Creek, USA	Channel	-	0.55 - 1.89	0.05 - 0.22	-	0.08 - 0.5	29.6 - 73	4.7 - 5.9	*Sullivan and Drever (2001)*
Boulder Creek, USA	Channel	<0.032*	0.469*	0.246*	<0.01*	2.82*	97.4*	3.3*	*Keith et al. (2001)*
Black Foot River, USA	Channel	-	<0.2 - 535	<0.8 - 4	<0.5 - 2.6	<5 - 37	5.5 - 88.8	7.3 - 8.8	*Nagorski et al. (2002)*
Phillips Mine, USA	Channel	<0.01	<0.01 - 0.17	0.02 - 3.13	-	0.16 - 42.4	25 - 368	2.3 – 6.5	*Gilchrist et al. (2009)*
Australasia									
River Dee, Australia	Channel	<0.01 - 0.6	<0.01 - 10.4	<0.01 - 45.03	-	<0.01 - 74	340 - 5950	2.7 - 7.0	*Edraki et al. (2005)*

Mt. Morgan Mine, Australia	Open pit	1.51*	21.97*	44.54*	-	253*	13600*	2.7*	*Edraki et al. (2005)*

nd = not detectable. * single observation. [a] grams per litre. [b] mean value

Table 2 Comparison of metal concentrations (mg/kg) in channel and floodplain sediments from historic deep metal mining impacted rivers.

River location	Geomorphic-type site	Grain size fraction	Metal phase extracted	Pb	Zn	Cu	Cd	Author(s)
Europe								
Red River, England	Channel	<2000 µm	Total	nd - 120	nd - 630	nd - 1320	-	*Yim (1981)*
River Derwent, England	Channel	<1000 µm	Total	96 - 3120	82 - 2760	-	0.6 - 13.8	*Burrows and Whitton (1983)*
River Derwent, England	Floodplain	<2000 µm	Total	131 - 1179	<10 - 1696	2.9 - 64	0.08 - 12.5	*Bradley and Cox (1990)*
River Tyne, England	Floodplain	<2000 µm	Total	615 - 2340	722 - 2340	11 - 42.5	2.6 - 8	*Macklin et al. (1992)*
River Swale, England	Floodplain	<63 µm	Total	56 - 5507	15 - 3066	-	1 - 18	*Macklin et al. (1994)*
River Allen, England	Channel	<170 µm	Total	2330*	1410*	-	-	*Goodyear et al. (1996)*
River Severn, England	Floodplain	<2000 µm	Total	23 - 204	173 - 936	30 - 67	0.35 - 6.4	*Taylor (1996)*
River Tees, England	Channel	<2000 µm	Total	522 - 6880	404 - 1920	20 - 77	0.95 - 5.95	*Hudson-Edwards et al. (1997)*
River Aire, England	Channel	<63 µm	Total	90 - 237	274 - 580	118 - 198	-	*Walling et al. (2003)*
River Swale, England	Floodplain	<63 µm	Total	10000*	14000*	-	7500*	*Dennis et al. (2003)*
River Calder, England	Channel	<63 µm	Total	199 - 343	397 - 907	141 - 235	-	*Walling et al. (2003)*
River Wear, England	Channel	<150 µm	Total	20 - 15000	40 - 1500	<10 - 340	-	*Lord and Morgan (2003)*
Dale Beck, England	Channel	<2000 µm	Total	13693*	442*	206*	-	*Geer (2004)*
River Avoca, Ireland	Channel	<1000 µm	Total	-	1520[a]	674[a]	-	*Herr and Gray (1996)*
River Mala Panew, Poland	Channel	<63 µm	Total	36 - 3309	126 - 11153	3.97 - 483	0.18 - 559	*Aleksander-Kwaterczak and Helios-*

								Rybicka (2009)
River Somes, Romania	Channel	<2000 µm	Total	28 - 6800	64 - 19600	12 - 8400	0.8 - 110	*Macklin et al. (2003)*
River Viseu, Romania	Floodplain	<2000 µm	total	17 - 850	110 - 2760	32 - 1000	0.5 - 17	*Macklin et al. (2005)*
Gezala Creek, Spain	Channel	<177 µm	Total	10.6 - 37630	216 - 25676	2.7 - 1691	0.22 - 45	*Marques et al. (2001)*
River Tinto, Spain	Channel	<2000 µm	Total	3200 - 16500	600 - 67300	1800 - 26500	<1 - 23	*Galan et al. (2003)*
River Odiel, Spain	Channel	<2000 µm	Total	1900 - 16600	1000 - 74600	3500 - 20900	1.4 – 10.2	*Galan et al. (2003)*
River Rheidol, Wales	Floodplain	<2000 µm	Total	291 - 2098	242 - 630	21 - 85	0.08 - 3.5	*Davies and Lewin (1974)*
River Tawe, Wales	Channel	<2000 µm	Total	63 - 6993	20 - 31199	34 - 2000	2 - 335	*Vivian and Massie (1977)*
River Rheidol, Wales	Floodplain	<210 µm	Total	813 - 1717	201 - 383	33 - 120	-	*Wolfenden and Lewin (1977)*
River Towy, Wales	Channel	<2000 µm	Total	36 - 5732	106 - 3722	44 - 259	0.78 - 83	*Wolfenden and Lewin (1978)*
River Twymyn, Wales	Channel	<2000 µm	Total	593 - 6411	159 - 6955	44 - 2557	1.5 - 44	*Wolfenden and Lewin (1978)*
River Ystywth, Wales	Floodplain	<2000 µm	Total	73 - 4646	123 - 1543	-	-	*Lewin et al. (1983)*
River Twymyn, Wales	Channel	<63 µm	Non-residual	1.1 - 2914	0.7 - 148	0.3 - 30	<0.01 - 0.9	*Byrne et al. (2010)*
North America								
West Squaw Creek, USA	Channel	<177 µm	Total	-	32 - 5940	254 - 4090	-	*Filipek et al. (1987)*
Black Foot River, USA	Channel	<63 µm	Total	1100 - 8700	1700 - 9600	1400 - 9900	<1 - 115	*Nagorski et al. (2002)*
River Cedar, USA	Channel	-	Total	4.5 - 420	9.75 - 2050	2.3 - 107	0.07 - 3.8	*Ouyang et al. (2002)*
Copper Mine Brook, USA	Channel	<1000 µm	Total	9.9 - 30	9 - 67	31 - 398	-	*Gilchrist et al. (2009)*
Australasia								
River Kangjiaxi, China	Channel	-	Non-residual	1154 - 8034	124 - 2319	23 - 209	2.6 - 41	*Licheng and Guiju (1996)*

nd = not detectable. * maximum value. [b] mean value.

Table 3 Impacts of metal mine drainage on instream macroinvertebrates reported within the scientific literature. Types of studies are - [a] stream survey, [b] microcosm experiment and [c] laboratory bioassay.

Primary impact reported	Additional information	Author(s)
Community composition		
Shift in community structure	Clean sites dominated by Ephemeroptera and Plecoptera; moderately contaminated sites dominated by Plecoptera and Diptera; and heavily contaminated sites dominated by Diptera	Armitage (1980)[a]
	Clean sites dominated by Ephemeroptera; moderately contaminated sites by Tricoptera; and heavily contaminated sites dominated by Diptera	Winner *et al*. (1980)[a]
	Contaminated sites dominated by Orthocladiinae (Chironomidae) and species of net-spinning Tricoptera	Clements *et al*. (1992)[a]
	Contaminated sites dominated by Chironomidae	Gray (1998)[a]
	Ephemeroptera reduced by > 75% in moderately contaminated streams	Clements *et al*. (2000)[a]
	Clean sites dominated by Stenopsychidae (Trichoptera); contaminated sites dominated by Chironomidae and *Epeorus latifolium* (Ephemeroptera)	Watanabe *et al*. (2000)[a]
	Contaminated sites dominated by Chironomidae, Tubificidae, Baetidae and Simulidae	Marques *et al*.(2003)[a]
	Heavily contaminated sites dominated by Chironomidae	Smolders *et al*. (2003)[a]
	Dominance of predators in very acidic mining sites	Gerhardt *et al*. (2004)[a]
	Heavily contaminated sites characterised by high proportion of Chironominae and predatory Tanypodinae	Janssens de Bisthoven *et al*. (2005)[a]
Decrease in abundance	Reduction in abundance recorded	Willis (1985)[a], Gray (1998)[a], Hirst *et al*. (2002)[a]
	Ephemeroptera comprised less than 5% of individuals at one location	Clements *et al*. (1992)[a]

	Abundance significantly lower in experiments with metal mixtures and high predation pressure	Kiffney (1996)[b]
	Abundance positively related to stream alkalinity and pH	Malmqvist and Hoffsten (1999)[a]
	Ephemeroptera and Plecoptera particularly affected	Clements (2004)[b]
Decrease in number of taxa	Reduced number of taxa recorded	Willis (1985)[a], Kiffney (1996)[b], Gray (1998)[a]
	Decrease most pronounced in low flow conditions	Clements *et al*. (1992)[a]
Decrease in EPT taxa	EPT richness positively related to stream pH	Malmqvist and Hoffsten (1999)[a]
	Near extinction of mayfly species	Hickey and Golding (2002)[a]
	Reduced number of EPT taxa recorded	Gerhardt *et al*. (2004)[a]
Decrease in species diversity	Reduced species diversity recorded	Amisah and Cowx (2000)[a], Hirst *et al*. (2002)[a]
	Dominance of Chironomidae	Smolders *et al*. (2003)[a]
	Dominance of Chironomidae, Baetidae and Simulidae	Van Damme *et al*. (2008)[a]
Impaired ecosystem function	Microbial colonisation of leaf material and leaf decomposition inhibited by high Cd concentrations	Giesy *et al*. (1978)[b]
	Microbial activity and leaf decomposition rates significantly lower at contaminated sites	Carpenter *et al*. (1983)[a]
	Secondary production of shredders negatively associated with metal contamination; leaf decomposition rates decreased; microbial respiration decreased	Carlisle and Clements (2005)[a]
	Reduced secondary production and organic matter storage	Woodcock and Huryn (2007)[a]
	Greater vulnerability of net-spinning Tricoptera to predation possibly due to spending more time in the open repairing capture nets	Clements *et al*. (1989)[b]
Macroinvertebrate physiology		

Physiological response	Differences in metal sensitivity related to trophic status; herbivores and detritivores more sensitive than predators	Leland *et al*. (1989)[a]
	Decrease in reproduction rates of *Gammuras pulex* (Gammaridae)	Maltby and Naylor (1990)[c]
	Differences in sensitivity related to trophic status; reduced leaf decomposition rates suggests shredders sensitive to pollution	Schultheis *et al*. (1997)[a]
	Increase incident of deformity (mentum structure) in *Chironomous riparius* (Chironomidae)	Groenendijk *et al*. (1998)[a]
	Increased incident of deformity (mentum structure) and decreased moulting success in *Chironomous riparius* (Chironomidae)	Vermeulen *et al*. (2000)[c]
	pH-dependent decrease in locomotion of *Atyaephyra desmaersti* (Crustacea) in AMD solutions	Gerhardt *et al*. (2004)[c]
	Locomotion and ventilation of *Choroterpes picteti* (Leptophlebiidae) greater in acid only solutions than in AMD solutions	Gerhardt *et al*. (2005a)[c]
	pH-dependent increase in locomotion and ventilation of *Gambusia holbrooki* (Crustacea) in AMD solutions	Gerhardt *et al*. (2005b)[c]
	pH-dependent decrease in locomotion and ventilation of *Atyaephyra desmaresti* (Crustacea) in AMD solutions	Janssens De Bisthoven *et al*. (2006)[c]
	Contaminated water causes higher locomotory activity in Lumbriculus variegates (Oligochaeta) than contaminated sediment	Gerhardt (2007)[c]
	Decrease in pH and increase in dissolved metals caused decrease in locomotion and inhibition of feeding rate in *Echinogammarus meridionalis* (Crustacea)	Macedo-Sousa *et al*. (2007)[c]
	Pulse of AMD caused early warning responses in *Echinogammarus meridionalis* (Crustacea) consisting of increased locomotion and subsequent increase in ventilitation	Macedo-Sousa *et al*. (2008)[c]
	Average daily moulting rate of *Rithrogena hageni* (Heptageniidae) decreased after exposure to aqueous copper, cadmium and zinc	Brinkman and Johnston (2008)[c]
Behavioural response	Anomalies in capture nets of Hydropsychidae	Petersen and Petersen (1983)[a]

	Decrease in burrowing rates and increase in crawling and drifting rates of *Macomona liliana* (Bivalve)	Roper *et al*. (1995)[c]
Morphological deformities	Cross-breeding of *Chironomous riparius* (Chironomidae) from contaminated and clean rivers revealed some level of genetic adaptation to metals in offspring	Groenendijk *et al*. (2002)[b]
	Macroinvertebrate drift and respiration significant correlated with metal concentrations	Clements (2004)[b]
	Increased incident of adult and larval deformities in *Chironomous tentans* (Chironomidae)	Martinez *et al*. (2004)[c]
	Decreased locomotory activity of *Chironomous* sp. (Chironomidae) in AMD solutions	Janssens De Bisthoven *et al*. (2004)[c]
Metal bioaccumulation	Younger instars had higher metal concentrations than older instars	Krantzberg (1989)[c]
	Concentration of metals in Ephemeropteran species decreased in consecutive larval stages	Jop (1991)[c]
	Metal bioaccumulation dependent on feeding group; shredders and scrapers accumulated the highest metal concentrations (biofilm contained more metals than sediments)	Farag *et al*. (1998)[a]
	Whole-body metal concentrations of *Hydropsyche* sp. (Hydropsychidae) greater in species exposed to dissolved metals than in species exposed to AMD precipitates	DeNicola and Stapleton (2002)[b]
	Chironomus februarius (Chironomidae) exhibited adaptation to and tolerance of metal-polluted sediments	Bahrndorff *et al*. (2006)[b]
	Macroinvertebrate metrics significantly correlated with metals in biofilm, suggesting biofilm is a better index than macroinvertebrates for monitoring metal impacts on aquatic systems	Rhea *et al*. (2006)[a]
	Whole-body metal concentrations of *Hydropsyche* sp. (Hydropsychidae) were strongly positively correlated with metal concentrations in water and sediment	Sola and Prat (2006)[a]
Effects of environmental parameters on the toxicity of metal mine discharges		
Water hardness and alkalinity	Increased water hardness and alkalinity reduces metal toxicity in *Chironomous tentans* (Chironomidae)	Gauss *et al*. (1985)[c]
	Increasing water hardness reduces community sensitivity to metal contamination	Gower *et al*. (1994)[a]
	Increased water hardness reduces metal toxicity in *Daphnia magna* (Dapniidae)	Yim *et al*. (2006)[c]

Metal mixtures	Abundance of heptageniidae, community respiration and macroinvertebrate drift were more sensitive to metal mixtures than single metal solutions	Hickey and Golding (2002)[c]
	Survival of *Diplostomum spathaceum* (Diplostomatidae) greater in metal mixtures than in single metal solutions	Morley *et al*. (2002)[c]
	Community sensitivity greatest in combined metal mixtures compared to single metal solutions	Clements (2004)[b]
Other parameters	Increased turbidity reduces metal toxicity to Cladocera by decreasing bioavailability of metals	Garcia-Garcia and Nandini (2006)[c]
	Inverse correlation between salinity and lesion index of gills in *Ruditapes philippinarum* (Bivalvia)	Riba *et al*. (2010)[c]

Table 4 Typology of common passive mine water treatment units and source control techniques: indicating the nature of mine water drainage and the principal advantages and limitations of each method.

Name	Mine water type	Brief description	Advantages	Limitations	Example reference(s)
Passive mine water treatment technologies					
Aerobic wetlands	Net alkaline ferruginous	A system of shallow ponds, cascades and vegetated substrate encourage aeration of mine waters and oxidation, hydrolysis and precipitation of some heavy metals (mainly Fe and Al)	Efficient Fe and Al removal; low maintenance requirement; cost-effective; easy integration into landscape and connection with existing ecosystems	Not suitable for highly toxic, sulphate-rich and acidic mine waters; large land surface area requirement; occasional removal of substrate precipitates required	Robb and Robinson (1995); Johnson and Hallberg (2005)
Anaerobic wetlands	Net acidic ferruginous with high sulphate concentrations	A thick anoxic substrate of saturated organic material neutralises acidity and generates alkalinity through processes of bacterial	Often used to neutralise acidity and generate alkalinity prior to discharge to aerobic wetlands; efficient Fe and sulphate removal; some toxic	Not suitable for high toxic metal concentrations (especially Zn and Cd); large land surface area requirement; occasional	Younger *et al*. (2002); Johnson and Hallberg (2005)

		sulphate reduction and calcite dissolution; heavy metals (mainly Fe and Al) are removed as precipitates	metals are removed through precipitation of sulphides and adsorption to organic matter; low maintenance requirement; cost-effective; easy integration into landscape and connection with existing ecosystems	removal of substrate precipitates required; requires high sulphate (>100 mg/l) concentrations; often produce hydrogen sulphide gas	
Anoxic Limestone Drains (ALDs)	Net acidic, low Al and Fe, low dissolved oxygen concentrations	Mine water is routed into a buried limestone trench which neutralises acidity and generates alkalinity	Often used to neutralise acidity and generate alkalinity prior to discharge to aerobic wetlands; efficient Fe and Al removal at low concentrations (<2 mg/l)	Not suitable for high toxic metal mine waters; vulnerable to precipitation of Al and Fe on limestone; only suitable for mine waters above pH 5 with low ferric Fe, Al (<2 mg/l) and dissolved oxygen content (<1 mg/l)	Nuttall and Younger (2000); Watzlaf *et al*. (2000)
Oxic Limestone Drains	Net acidic, low to	An open (exposed to the	Often used to neutralise	Not suitable for high toxic	Ziemkiewicz *et al*. (1997)

(OLDs)	moderate sulphate	atmosphere) limestone trench which neutralises acidity and generates alkalinity	acidity and generate alkalinity prior to discharge to aerobic wetlands; good rates of alkalinity generation with low water residence times; easy to construct and low cost alternative to more technically challenging and costly systems	metal mine waters; high flow velocities required to prevent Fe and Al precipitation on the limestone	
Reducing and Alkalinity Producing Systems (RAPS)	Net acidic	A layer of limestone beneath a thick anoxic substrate of organic material neutralises acidity and generates alkalinity through processes of bacterial sulphate reduction and calcite dissolution; heavy metals (mainly Fe and Al) are	Often used to neutralise acidity and generate alkalinity prior to discharge to aerobic wetlands; efficient Fe and sulphate removal; suitable for net acidic mine waters with high ferric Fe, Al and dissolved oxygen content (>1	Not suitable for high toxic metal mine waters; requires significant hydraulic head	Kepler and McCleary (1994); Jage *et al*. (2001)

		removed as precipitates	mg/l); low footprint		
Surface Catalyzed Oxidation Of Ferrous Iron (SCOOFI)	N*et* *al*kaline ferruginous	Containers are packed with high specific surface area inorganic media (e.g. plastic trickle filter, ochre, blast furnace slag) which encourage sorption and oxidation of ferrous Fe and accretion of ferric oxyhydroxide	More efficient Fe removal than aerobic wetlands; low footprint	Not suitable for high toxic metal mine waters; requires significant hydraulic head; requires regular cleaning and replacing of filtering media	Younger (2000); Jarvis and Younger (2001); Sapsford and Williams (2009)
Source control technologies and techniques					

Permeable reactive Barriers (PRBs)	Net acidic	PRBs provide a vertical and permeable compost-based medium in the path of polluted mine water which neutralises acidity and promotes the generation of alkalinity through bacterial sulphate reduction and calcite dissolution	Useful for mine waters which do not emerge at the surface and instead travel as groundwater plumes	Limited evidence for removal of toxic metals; limited by depth of aquifer	Benner *et al*. (1997); Jarvis *et al*. (2006)
Physical stabilisation of mine wastes	-	Covering of mine waste with inert material (e.g. clay, gravel) to reduce oxygen inflow and water ingress into the contaminated material and, hence, the concentrations of contaminants in drainage	Immobilises contaminants at source and prevents generation of mine drainage	Clay caps tend to crack in arid and semi-arid regions from wetting and drying cycles resulting in failure of air-tight cap	Gandy and Younger (2003); Waygood and Ferriera (2009)

		waters			
Chemical stabilisation of mine wastes	-	Addition of a resinous adhesive to form a crust over the mine waste	Immobilises contaminants at source and prevents generation of mine drainage	Similar to clay caps, crusts are prone to cracking resulting in failure of air-tight cap	Tordoff *et al*. (2000)
Phytostabilisation	-	A vegetative cap on the mine waste to immobilise contaminants by adsorption and accumulation in the rhizosphere	Immobilises contaminants at source and prevents generation of mine drainage; creates wildlife habitat	Concerns over bioavailability of contaminants to wildlife; need for metal tolerant plants	Mendez and Maier (2008); Pollmann *et al*. (2009)
Phytoextraction	-	A vegetative cap on the mine waste to immobilise contaminants through hyperaccumulation in plant tissues	Immobilises contaminants at source and prevents generation of mine drainage; creates wildlife habitat; offers the possibility of recovery of metals from plant tissues; improves land for agriculture	Concerns over bioavailability of contaminants to wildlife	Ernst (2005)

	and forestry use
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