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**Article**



**Byrne, PA, Wood, PJ and Reid, I (2011) The impairment of river systems by metal mine contamination: A review including remediation options. Critical Reviews in Environmental Science and Technology, 42 (19). pp. 2017-2077. ISSN 1064-3389**

# 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.

## Acknowledgements

PB gratefully acknowledges the support of a Loughborough University Department of Geography Scholarship which allowed this research to be undertaken.

## References

Abdullah MI, Royle LG. Heavy metal content of some rivers and lakes in Wales. Nature 1972; 238: 329-330.

Aisemberg J, Nahabedian DE, Wider EA, Verrengia Guerrero NR. Comparative study on two freshwater invertebrates for monitoring environmental lead exposure. Toxicology 2005; 210: 45-53.

Albering HJ, van Leusen SM, Moonen EJC, Hoogewerff JA, Kleinjans JCS. Human health risk assessment: A case study involving heavy metal soil contamination after the flooding of the river Meuse during the winter of 1993-1994. Environmental Health Perspectives 1999; 107: 37-43.

Alderton DHM, Serafimovski T, Mullen B, Fairall K, James S. The chemistry of waters associated with metal mining in Macedonia. Mine Water and the Environment 2005; 24: 139-149.

Aleksander-Kwaterczak U, Helios-Rybicka E. Contaminated sediments as a potential source of Zn, Pb, and Cd for a river system in the historical metalliferous ore mining and smelting industry area of South Poland. Journal of Soils and Sediments 2009; 9: 13-22.

Aleva GJJ. Indonesian Fluvial Cassiterite Placers and Their Genetic Environment. Journal of the Geological Society 1985; 142: 815-836.

Amisah S, Cowx IG. Impacts of abandoned mine and industrial discharges on fish abundance and macroinvertebrate diversity of the upper River Don in South Yorkshire, UK. Journal of Freshwater Biology 2000; 15: 237-250.

Armitage PD. The effects of mine drainage and organic enrichment on benthos in the River Nent system, Northern Pennines. Hydrobiologia 1980; 74: 119-128.

Armitage PD, Bowes MJ, Vincent HM. Long-term changes in macroinvertebrate communities of a heavy metal polluted stream: the River Nent (Cumbria, UK) after 28 years. River Research and Applications 2007; 23: 997-1015.

Asta MP, Cama J, Gault AG, Charnock JM, Queralt I. Characterisation of AMD sediments in the discharge of the Tinto Santa Rosa mine (Iberian Pyritic Belt, SW Spain). In: Cidu R, Frau F, editors. International Mine Water Association Symposium 2007: Water in Mining Environments, Cagliari (Mako Edizioni), 2007.

Bahrndorff S, Ward J, Pettigrove V, Hoffmann AA. A microcosm test of adaptation and species specific responses to polluted sediments applicable to indigenous chironomids (Diptera). Environmental Pollution 2006; 139: 550-560.

Balci NC. Effects of bacterial activity on the release of trace metals from sphalerite oxidation. In: Rapantova N, Hrkal Z, editors. Mine Water and the Environment. Ostrava (VSB – Technical University of Ostrava), 2008.

Banks D, Parnachev VP, Frengstad B, Holden W, Vedernikov AA, Kannachuk OV. Alkaline mine drainage from metal sulphide and coal mines: examples from Svalbard and Siberia. In: Younger PL, Robins NS, editors. Mine Water Hydrogeology and Geochemistry. The Geological Society, London, 2002, pp. 287-296.

Banks D, Younger PL, Arnesen RT, Iversen ER, Banks SB. Mine-water chemistry: the good, the bad and the ugly. Environmental Geology 1997; 32: 157-174.

Banks SB, Banks D. Abandoned mines drainage: impact assessment and mitigation of discharges from coal mines in the UK. Engineering Geology 2001; 60: 31-37.

Batty LC. The potential importance of mine sites for biodiversity. Mine Water and the Environment 2005; 24: 101-103.

Batty LC, Auladell M, Sadler J. The impacts of metalliferous drainage on aquatic communities. In: Batty LC, Hallberg KB, editors. Ecology of Industrial Pollution. Cambridge University Press, Cambridge, 2010, pp. 70-100.

Batty LC, Younger PL. The use of waste materials in the passive remediation of mine water pollution. Surveys in Geophysics 2004; 25: 55-67.

Beltman DJ, Clements WH, Lipton J, Cacela D. Benthic invertebrate metals exposure, accumulation and community-level effects downstream from a hard rock mine site. Environmental Toxicology and Chemistry 1999; 18: 299-307.

Benner SG, Blowes DW, Ptacek CJ. A full-scale porous reactive wall for prevention of acid mine drainage. Ground Water Monitoring and Remediation 1997; 17: 99-107.

Berger WH, Parker FL. Diversity of planktonic foraminifera in deep-sea sediments. Science of the Total Environment 1970; 168: 1345-1347.

Berninger K, Pennanen J. Heavy metals in perch (Perca fluviatilis L.) from two acidified lakes in the Salpausselkae esker area in Finland. Water, Air, and Soil Pollution 1995; 81: 283-294.

Biological Monitoring Working Party. Final Report: Assessment and Presentation of Biological Quality of Rivers in Great Britain. Unpublished report. Department of the Environment Water Data Unit, 1978.

Bird G, Brewer PA, Macklin MG, Nikolova M, Kotsev T, Mollov M, et al. Pb isotope evidence for contaminant-metal dispersal in an international river system: The lower Danube catchment, Eastern Europe. Applied Geochemistry 2010; 25: 1070-1084.

Bird SC. The effect of hydrological factors on trace metal contamination in the River Tawe, South Wales. Environmental Pollution 1987; 45: 87-124.

Boult S, Collins DN, White KN, Curtis CD. Metal transport in a stream polluted by acid mine drainage - the Afon Goch, Anglesey, UK. Environmental Pollution 1994; 84: 279-284.

Bradley JB, Cox JJ. The significance of the floodplain to the cycling of metals in the River Derwent catchment, UK. Science of the Total Environment

1990; 97/98: 441-454.

Bradley SB. Flood effects of the transport of heavy metals. International Journal of Environmental Studies 1984; 22: 225-230.

Bradley SB, Foster IDL, Gurnell AM, Webb BW. Long-term dispersal of metals in mineralised catchments by fluvial processes. In: Foster IDL, Gurnell AM, Webb BW, editors. Sediment and Water Quality in River Catchments. John Wiley & Sons Ltd, Chichester, 1995, pp. 161-177.

Bradley SB, Lewin J. Transport of heavy metals on suspended sediments under high flow conditions in a mineralised region of Wales. Environmental Pollution (Series B) 1982; 4: 257-267.

Braungardt CB, Achterberg EP, Elbaz-Poulichet F, Morley NH. Metal geochemistry in a mine-polluted estuarine system in Spain. Applied Geochemistry 2003; 18: 1757-1771.

Brewer PA, Dennis IA, Macklin MG. The use of geomorphological mapping and modelling for identifying land affected by metal contamination on river floodplains: DEFRA, 2005.

Brinkman SF, Johnston WD. Acute toxicity of aqueous copper, cadmium, and zinc to the mayfly Rithrogena hageni. Archives of Environmental Contamination and Toxicology 2008; 54: 466-472.

Brkovic-Popovic I, Popovic M. Effects of heavy metals on survival and respiration rate of tubificid worms: Part 1 - effects on survival. Environmental Pollution 1977; 13: 65-72.

Brumbaugh WG, Mora MA, May TW, Phalen DN. Metal exposure and effects in voles and small birds near a mining haul road in Cape Krusenstern National Monument, Alaska. Environmental Monitoring and Assessment 2010; 170: 73-86.

Burrows IG, Whitton BA. Heavy metals in water, sediments and invertebrates from a metal-contaminated river free of organic pollution. Hydrobiologia 1983; 106: 263-273.

Burton AG. Metal Bioavailability and Toxicity in Sediments. Critical Reviews in Environmental Science and Technology 2010; 40: 852 - 907.

Butler BA. Effect of pH, ionic strength, dissolved organic carbon, time, and particle size on metals release from mine drainage impacted streambed sediments. Water Research 2009; 43: 1392-1402.

Byrne P, Reid I, Wood PJ. Short-term fluctuations in heavy metal concentrations during flood events through abandoned metal mines, with implications for aquatic ecology and mine water treatment. International Mine Water Conference. Water Institute of Southern Africa and International Mine Water Association, Pretoria, South Africa, 2009, pp. 124-129.

Byrne P, Reid I, Wood PJ. Sediment geochemistry of streams draining abandoned lead/zinc mines in central Wales: the Afon Twymyn. Journal of Soils and Sediments 2010; 4: 683-697.

Calmano W, Hong J, Forstner U. Binding and mobilisation of heavy metals in contaminated sediments affected by pH and redox potential. Water Science and Technology 1993; 28: 223-235.

Campbell PGC, Stokes PM. Acidification and toxicity of metals to aquatic biota. Canadian Journal of Fisheries and Aquatic Sciences 1985; 42: 2034-2049.

Canovas CR, Hubbard CG, Olias M, Nieto JM, Black S, Coleman ML.

Hydrochemical variations and contaminant load in the Rio Tinto (Spain) during flood events. Journal of Hydrology 2008; 350: 25-40.

Carlisle DM, Clements WH. Leaf litter breakdown and shredder production in metal-polluted streams. Freshwater Biology 2005; 50: 380-390.

Carpenter J, Odum WE, Mills A. Leaf litter decomposition in a reservoir affected by acid mine drainage. Oikos 1983; 41: 165-172.

Chadwick JW, Canton SP. Inadequacy of diversity indices in discerning metal mine drainage effects on a stream invertebrate community. Water, Air, and Soil Pollution 1984; 22: 217-223.

Chadwick JW, Canton SP, Dent RL. Recovery of benthic invertebrate communities in Silver Bow Creek, Montana, following improved metal mine wastewater treatment. Water, Air and Soil Pollution 1986; 28: 427-438.

Chapa-Vargas L, Mejia-Saavedra JJ, Monzalvo-Santos K, Puebla-Olivares F. Blood lead concentrations in wild birds from a polluted mining region at Villa de La Paz, San Luis Potosi, Mexico. Journal of Environmental Science and Health Part a-Toxic/Hazardous Substances & Environmental Engineering 2010; 45: 90-98.

Cid N, Ibanez C, Palanques A, Prat N. Patterns of metal bioaccumulation in two filter-feeding macroinvertebrates: Exposure distribution, inter-species differences and variability across developmental stages. Science of the Total Environment 2010; 408: 2795-2806.

Cidu R, Di Palma M, Medas D. The Fluminese Mining District (SW Sardinia, Italy): Impact of the past lead-zinc exploitation on aquatic environment. In: Cidu R, Frau F, editors. International Mine Water Association Symposium 2007: Water in the Mining Environment, Cagliari (Mako Edizioni), 2007, pp. 47-51.

Cidu R, Mereu L. The abandoned copper-mine of Funtana Raminosa (Sardinia): Preliminary evaluation of its impact on the aquatic system. In: Cidu R, Frau F, editors. International Mine Water Association Symposium 2007: Water in Mining Environments, Cagliari (Mako Edizioni), 2007, pp. 53-57.

Clements WH. Small-scale experiments support causal relationships between metal contamination and macroinvertebrate community responses. Ecological Applications 2004; 14: 954-967.

Clements WH, Carlisle DM, Lazorchak JM, Johnson PC. Heavy metals structure benthic communities in Colorado mountain streams. Ecological Applications 2000; 10: 626-638.

Clements WH, Cherry DS, Cairns J. The influence of copper exposure on predator-prey interactions in aquatic insect communities. Freshwater Biology 1989; 21: 483-488.

Clements WH, Cherry DS, Van Hassel JH. Assessment of the impact of heavy metals on benthic communities at the Clinch River (Virginia): Evaluation of an index of community sensitivity. Canadian Journal of Fisheries and Aquatic Sciences 1992; 49: 1686-1694.

Clews E, Oormerod SJ. Improving bio-diagnostic monitoring using simple combinations of standard biotic indices. River Research and Applications 2009; 25: 348-361.

Comber SD, Merrington G, Sturdy L, Delbeke K, van Assche F. Copper and zinc water quality standards under the EU Water Framework Directive:

The use of a tiered approach to estimate the levels of failure. Science of the Total Environment 2008; 403: 12-22.

Conesa HM, Perez-Chacon JA, Arnaldos R, Moreno-Caselles J, Faz-Cano A. In situ heavy metal accumulation in lettuce growing near a former mining waste disposal area: Implications for agricultural management. Water, Air and Soil Pollution 2010; 208: 377-383.

Connelly RJ. Rehabilitation and construction issues for Silvermines Abandoned Mine Area, Ireland. International Mine Water Conference. Water Institute of South Africa and International Mine Water Association, Pretoria, South Africa, 2009, pp. 298-307.

Coulthard TJ, Macklin MG. Modelling long-term contamination in river systems from historical metal mining. Geology 2003; 31: 451-454.

Cui H, Li LY, Grace JR. Exploration of remediation of acid rock drainage with clinoptilolite as sorbent in a slurry bubble column for both heavy metal capture and regeneration. Water Research 2006; 40: 3359-3366.

Davies BE, Lewin J. Chronosequences in alluvial soils with special reference to historic lead pollution in Cardiganshire, Wales. Environmental Pollution 1974; 6: 49-57.

Davies BE, Thornton I. Heavy metal contamination from base metal mining and smelting: implications for man and his environment. In: Thornton I, editor. Applied Environmental Geochemistry. Academic Press, London, 1983, pp. 425-462.

Davy-Bowker J, Murphy JF, Rutt GP, Steel JEC, Furse MT. The development and testing of a macroinvertebrate biotic index for detecting the impact of acidity on streams. Archiv fuer Hydrobiologie 2005; 163: 383-403.

Dawson EJ, Macklin MG. Speciation of heavy metals on suspended sediment under high flow conditions in the River Aire, West Yorkshire, UK. Hydrological Processes 1998; 12: 1483-1494.

De Bisthoven JL, Gerhardt A, Guhr K, Soares AMVM. Behavioural changes and acute toxicity to the freshwater shrimp Atyaephyra desmaresti Millet (Decapoda: Natantia) from exposure to acid mine drainage. Ecotoxicology 2006; 15: 215-227.

De Bisthoven JL, Gerhardt A, Soares AMVM. Effects of acid mine drainage on larval Chironomus (Diptera, Chironomidae) measured with the Multispecies Freshwater Biomonitor. Environmental Toxicology and Chemistry 2004; 23: 1123-1128.

De Bisthoven JL, Gerhardt A, Soares AMVM. Chironomidae larvae as bioindicators of an acid mine drainage in Portugal. Hydrobiologia 2005; 532: 181-191.

DeNicola DM, Stapleton MG. Impact of acid mine drainage on benthic communities in streams: the relative roles of substratum vs. aqueous effects. Environmental Pollution 2002; 119: 303-315.

Dennis IA, Coulthard TJ, Brewer PA, Macklin MG. The role of floodplains in attenuating contaminated sediment fluxes in formerly mined drainage basins. Earth Surface Processes and Landforms 2009; 34: 453-466.

Dennis IA, Macklin MG, Coulthard TJ, Brewer PA. The impact of the October-November 2000 floods on contaminant metal dispersal in the River Swale catchment, North Yorkshire, UK. Hydrological Processes 2003; 17: 1641-1657.

Desbarats AJ, Dirom GC. Temporal variation in discharge chemistry and portal flow from the 8-Level adit, Lynx Mine, Myra Falls Operations, Vancouver Island, British Columbia. Environmental Geology 2005; 47: 445-456.

Di Toro DM, Allen HE, Bergman HL, Meyer JS, Paquin PR, Santore RC. Biotic ligand model of the acute toxicity of metals. 1, Technical basis. Environmental Toxicology and Chemistry 2001; 20: 2383-2396.

Dojlido JR, Taboryska B. Exchange of heavy metals between sediment and water in the Wloclawek Reservoir on the Vistula River. In: Peters NE WD, editor. Sediment and Stream Water Quality in a Changing Environment: Trends and Explanations. IAHS Pub. no. 203, Vienna, 1991, pp. 315-320.

Dressing SA, Mass RP, Weiss CM. Effect of chemical speciation on the accumulation of cadmium by the caddisfly, Hydropscyhe sp. Bulletin of Environmental Contamination and Toxicology 1982; 28: 172-180.

Edraki M, Golding SD, Baublys KA, Lawrence MG. Hydrochemistry, mineralogy and sulfur isotope geochemistry of acid mine drainage at the Mt. Morgan mine environment, Queensland, Australia. Applied Geochemistry 2005; 20: 789-805.

Enid Martinez C, McBride MB. Solubility of $Cd2^{+}$, $Cu2^{+}$, $Pb2^{+}$, and $Zn2^{+}$ in aged coprecipitates with amorphous iron hydroxides. Environmental Science and Technology 1998; 32: 743-748.

Environment Agency. Metal Mine Strategy for Wales. Environment Agency Wales, Cardiff, 2002.

Environment Agency. Attenuation of mine pollutants in the hyporheic zone. Environment Agency, Bristol, 2006.

Environment Agency. Abandoned mines and the water environment. Bristol. Environment Agency, 2008a.

Environment Agency. Assessment of metal mining-contaminated river sediments in England and Wales. Environment Agency, Bristol, 2008b.

Ernst WHO. Phytoextraction of mine wastes - options and impossibilities. Chemie der Erde 2005; 65: 29-42.

Esbri JM, Bernaus A, Avila M, Kocman D, Garcia-Noquero EM, Gaona X, et al. XANES speciation of mercury in three mining districts - Almaden, Asturia (Spain), Idria (Slovenia). Journal of Synchrotron Radiation 2010; 17: 179-186 Part 2.

Evangelou VP, Zhang YL. A review - pyrite oxidation mechanisms and acid-mine drainage prevention. Critical Reviews in Environmental Science and Technology 1995; 25: 141-199.

Evans LJ, Adams WA. Chlorite and illite in some lower Palaeozoic mudstones of mid-Wales. Clay Minerals 1975; 10: 387-397.

Farag AM, Woodward DF, Goldstein JN, Brumbaugh W, Meyer JS. Concentrations of metals associated with mining waste in sediments, biofilm, benthic macroinvertebrates, and fish from the Coeur d'Alene River Basin, Idaho. Archives of Environmental Contamination and Toxicology 1998; 34: 119-127.

Fergusson JE. The Heavy Elements. Chemistry, Environmental Impact and Health Effects. Oxford: Pergamon Press, 1990.

Filipek LH, Nordstrom DK, Ficklin WH. Interaction of acid mine drainage with waters and sediments of West Squaw Creek in the West Shasta Mining District, California. Environmental Science and Technology 1987; 21:

388-396.

Ford RG, Bertsch PM, Farley KJ. Changes in transition and heavy metal partitioning during hydrous iron oxide aging. Environmental Science and Technology 1997; 31: 2028-2033.

Forstner U. Sediment dynamics and pollutant mobility in rivers: An interdisciplinary approach. Lakes and Reservoirs. Research and Management 2004; 9: 25-40.

Forstner U. Sediments and priority substances in river basins. Journal of Soils and Sediments 2009; 9: 89-93.

Forstner U, Salomons W. Trends and challenges in sediment research 2008: the role of sediments in river basin management. Journal of Soils and Sediments 2008; 8: 281-283.

Foster IDL, Charlesworth SM. Heavy metals in the hydrological cycle: trends and explanations. Hydrological Processes 1996; 10: 227-261.

Fuge R, Laidlaw IMS, Perkins WT, Rogers KP. The influence of acidic mine and spoil drainage on water quality in the mid-Wales area. Environmental Geochemistry and Health 1991; 13: 70-75.

Galan E, Gomez-Ariza JL, Gonzalez I, Fernandez-Caliani JC, Morales E, Giraldez I. Heavy metal partitioning in river sediments severely polluted by acid mine drainage in the Iberian Pyrite Belt. Applied Geochemistry 2003; 18: 409-421.

Gammons CH, Shope CL, Duaime TE. A 24 h investigation of the hydrogeochemistry of baseflow and stormwater in an urban area impacted by mining: Butte, Montana. Hydrological Processes 2005; 19: 2737-2753.

Gandy CJ, Younger PL. Effect of a clay cap on oxidation of Pyrite within mine spoil. Quarterly Journal of Engineering Geology and Hydrogeology 2003; 36: 207-215.

Garcia-Garcia G, Nandini S. Turbidity mitigates lead toxicity to cladocerans (Cladocera). Ecotoxicology 2006; 15: 425-436.

Gauss JD, Woods PE, Winner RW, Skillings JH. Acute toxicity of copper to three life stages of Chironomous tentans as affected by water hardness-alkalinity. Environmental Pollution (Series A) 1985; 37: 149-157.

Geer R. Reconstructing the geomorphological and sedimentological impacts of a catastrophic flood event, Dale Beck Valley, Caldbeck Fells, Cumbria. MSc thesis. University of Leeds, Leeds, 2004.

Gerhardt A. Review of impact of heavy metals on stream invertebrates with special emphasis on acid conditions. Water, Air, and Soil Pollution 1993; 66: 289-314.

Gerhardt A. Importance of exposure route for behavioural responses in Lumbriculus variegatus Muller (Oligochaeta: Lumbriculida) in short-term exposures to Pb. Environmental Science and Pollution Research 2007; 14: 430-434.

Gerhardt A, De Bisthoven JL, Soares AMVM. Effects of acid mine drainage and acidity on the activity of Choroterpes picteti (Emphemeroptera: Leptophlebiidae). Archives of Environmental Contamination and Toxicology 2005a; 48: 450-458.

Gerhardt A, De Bisthoven LJ, Soares AMVM. Macroinvertebrate response to acid mine drainage: community metrics and on-line behavioural toxicity bioassay. Environmental Pollution 2004; 130: 263-274.

Gerhardt A, De Bisthoven LJ, Soares AMVM. Evidence for the Stepwise Stress Model: Gambusia holbrooki and Daphnia magna under acid mine drainage and acidified reference water stress. Environmental Science and Technology 2005b; 39: 4150-4158.

Geroni JN, Sapsford DJ, Barnes A, Watson IA, Williams KP. Current performance of passive treatment systems in south Wales, UK. International Mine Water Conference. Water Institute of Southern Africa and International Mine Water Association, Pretoria, South Africa, 2009, pp. 486-496.

Giesy JP. Cadmium inhibition of leaf decomposition in an aquatic microcosm. Chemosphere 1978; 7: 467-475.

Gilbert GK. Hydraulic-mining debris in the Sierra Nevada. US Geological Survey Paper 105 1917.

Gilchrist S, Gates A, Szabo Z, Lamothe PJ. Impact of AMD on water quality in critical watershed in the Hudson River drainage basin: Phillips Mine, Hudson Highlands, New York. Environmental Geology 2009; 57: 397-409.

Goodyear KL, McNeill S. Bioaccumulation of heavy metals by aquatic macroinvertebrates of different feeding guilds: a review. Science of the Total Environment 1999; 229: 1-19.

Goodyear KL, Ramsey MH, Thorton I, Rosenbaum MS. Source identification of Pb-Zn contamination in the Allen Basin, Cornwall, S.W. England. Applied Geochemistry 1996; 11: 61-68.

Gower AM, Darlington ST. Relationships between copper concentrations in larvae of Plectrocnemia conspersa (Curtis) (Trichoptera) and in mine drainage streams. Environmental Pollution 1990; 65: 155-168.

Gower AM, Myers G, Kent M, Foulkes ME. Relationships between macroinvertebrate communities and environmental variables in metal-contaminated streams in south-west England. Freshwater Biology 1994; 32: 199-221.

Gray NF. Environmental impact and remediation of acid mine drainage: a management problem. Environmental Geology 1997; 30: 62-71.

Gray NF. Acid mine drainage composition and the implications for its impact on lotic systems. Water Research 1998; 32: 2122-2134.

Gray NF, Delaney E. Comparison of benthic macroinvertebrate indices for the assessment of the impact of acid mine drainage on an Irish river below an abandoned Cu-S mine. Environmental Pollution 2008; 155: 31-40.

Grimshaw DL, Lewin J, Fuge R. Seasonal and short-term variations in the concentration and supply of dissolved zinc to polluted aquatic environments. Environmental Pollution 1976; 11: 1-7.

Groenendijk D, Lucker SMG, Plans M, Kraak MHS, Admiraal W. Dynamics of metal adaptation in riverine chironomids. Environmental Pollution 2002; 117: 101-109.

Groenendijk D, Zenstra LWM, Postma JF. Fluctuating assymetry and mentum gaps in populations of the midge *Chironomous riparius* (Diptera: Chironomidae) from a metal-contaminated river. Environmental Toxicology and Chemistry 1998; 17: 1999-2005.

Guangwei Y, Hengyi L, Tao B, Zhong L, Qiang Y, Xianqiang S. In-situ stabilisation followed by ex-situ composting for treatment and disposal of heavy metals polluted sediments. Journal of Environmental Sciences 2009; 21: 877-883.

Gundersen P, Steinnes E. Influence of temporal variations in river discharge, pH, alkalinity and Ca on the speciation and concentration of heavy metals in some mining polluted rivers. Aquatic Geochemistry 2001; 7: 173-193.

Hallare AV, Seiler T-B, Hollert H. The versatile, changing, and advancing roles of fish in sediment toxicity assessment - a review. Journal of Soils and Sediments 2010; 11.

Hallberg KB, Johnson DB. Mine water microbiology. Mine Water and the Environment 2005; 24: 28-32.

Hammarstrom JM, Seal RR, II., Meier AM, Kornfeld JM. Secondary sulfate minerals associated with acid drainage in the eastern US: recycling of metals and acidity in surficial environments. Chemical Geology 2005; 215: 407-431.

Hawkins JW. Predictability of surface mine spoil hydrologic properties in the Appalachian Plateau. Groundwater 2004; 42: 119-125.

Hedin RS, Nairn RW, Kleinmann RLP. Passive Treatment of Coal Mine Drainage. US Bureau of Mines, 1994.

Hering D, et al. The European Water Framework Directive at the age of 10: A critical review of the achievements with recommendations for the future. Science of the Total Environment 2010; 408: 4007-4019.

Hermann R, Neumann-Mahlkau P. The mobility of zinc, cadmium, copper, lead, iron and arsenic in ground water as a function of redox potential and pH. Science of the Total Environment 1985; 43: 1-12.

Herr C, Gray NF. Seasonal variation of metal contamination of riverine sediments below a copper and sulphur mine in south-east Ireland. Water Science and Technology 1996; 35: 255-261.

Hickey CW, Golding LA. Response of macroinvertebrates to copper and zinc in a stream mesocosm. Environmental Toxicology and Chemistry 2002; 21: 1854-1863.

Hirst H, Juttner I, Ormerod SJ. Comparing the responses of diatoms and macroinvertebrates to metals in upland streams of Wales and Cornwall. Freshwater Biology 2002; 47: 1752-1765.

Howard AG. Aquatic Environmental Chemistry. Oxford: Oxford University Press, 1998.

Hudson-Edwards KA, Macklin MG, Curtis CD, Vaughn DJ. Processes of formation and distribution of Pb, Zn, Cd and Cu bearing minerals in the Tyne Basin, northeast England: Implications for metal-contaminated river systems. Environmental Science and Technology 1996; 30: 72-80.

Hudson-Edwards KA, Macklin MG, Jamieson HE, Brewer PA, Coulthard TJ, Howard AJ, et al. The impact of tailings dam spills and clean-up operations on sediment and water quality in river systems: the Rios Agrio-Guadiamar, Aznalcollar, Spain. Applied Geochemistry 2003; 18: 221-239.

Hudson-Edwards KA, Macklin MG, Taylor M. Historic metal mining inputs to Tees river sediment. Science of the Total Environment 1997; 194/195: 437-445.

Hudson-Edwards KA, Macklin MG, Taylor MP. 2000 years of sediment-borne heavy metal storage in the Yorkshire Ouse basin, NE England, UK. Hydrological Processes 1999a; 13: 1087-1102.
Hudson-Edwards KA, Schell C, Macklin MG. Mineralogy and geochemistry of alluvium contaminated by metal mining in the Rio Tinto area, southwest Spain. Applied Geochemistry 1999b; 14: 1015-1030.
Jage C, Zipper C, Noble R. Factors affecting alkalinity generation by successive alkalinity producing systems: regression analysis. Journal of Environmental Quality 2001; 30: 1015-1022.
Jain CK. Metal fractionation study on bed sediments of River Yamuna, India. Water Research 2004; 38: 569-578.
Jarvis AP, Fox A, Gozzard E, Hill S, Mayes WM, Potter HAB. Prospects for effective national management of abandoned metal mine water pollution in the UK. In: Cidu R, Frau F, editors. International Mine Water Association Symposium 2007: Water in Mining Environments, Cagliari (Mako Edizioni), 2007, pp. 77-81.
Jarvis AP, Moustafa M, Orme PHA, Younger PL. Effective remediation of grossly polluted acidic, and metal-rich, spoil heap drainage using a novel, low-cost, permeable reactive barrier in Northumberland, UK. Environmental Pollution 2006; 143: 261-268.
Jarvis AP, Younger PL. Passive treatment of ferruginous mine waters using high surface area media. Water Research 2001; 35: 3643-3648.
Johnson DB. Chemical and microbiological characteristics of mineral spoils and drainage waters at abandoned coal and metal mines. Water, Air, and Soil Pollution 2003; 3: 47-66.
Johnson DB, Hallberg KB. Acid mine drainage remediation options: A review. Science of the Total Environment 2005; 338: 3-14.
Jop KM. Concentration of metals in various larval stages of four Ephemeroptera species. Bulletin of Environmental Contamination and Toxicology 1991; 46: 901-905.
Jurjovec J, Ptacek CJ, Blowes DW. Acid neutralization mechanisms and metal release in mine tailings: A laboratory column experiment. Geochimica et Cosmochimica Acta 2002; 66: 1511-1523.
Keith DC, Runnells DD, Esposito KJ, Chermak JA, Levy DB, Hannula SR, et al. Geochemical models of the impact of acidic groundwater and evaporative sulfate salts on Boulder Creek at Iron Mountain, California. Applied Geochemistry 2001; 16: 947-961.
Kelly M. Mining and the Freshwater Environment. Barking: Elsevier Science Publishing, 1988.
Kepler D, McCleary E. Successive alkalinity producing systems (SAPS) for the treatment of acid mine drainage. Proceedings of the International Land Reclamation and Mine Drainage Conference, Pittsburgh, PA, USA, 1994.
Kiffney PM. Main and interactive effects of invertebrate density, predation, and metals on a Rocky Mountain stream macroinvertebrate community. Canadian Journal of Fisheries and Aquatic Sciences 1996; 53: 1595-1601.
Kiffney PM, Clements WH. Responses of periphyton and insects to experimental manipulation of riparian buffer width along forest streams. Journal of Applied Ecology 2003; 40: 1060-1076.

Knighton AD. Channel Bed Adjustment Along Mine-Affected Rivers of Northeast Tasmania. Geomorphology 1991; 4: 205-219.

Knott NA, Aulbury JP, Brown TH, Johnston EL. Contemporary ecological threats from historical pollution sources: impacts of large-scale resuspension of contaminated sediments on sessile invertebrate recruitment. Journal of Applied Ecology 2009; 46: 770-781.

Koukouzas N, Vasilatos C, Itskos G, Mitsis I, Moutsatsou A. Removal of heavy metals from wastewater using CFB-coal fly ash zeolithic materials. Journal of Hazardous Materials 2010; 173: 581-588.

Kovacs E, Dubbin WE, Tamas J. Influence of hydrology on heavy metal speciation and mobility in a Pb-Zn mine tailing. Environmental Pollution 2006; 141: 310-320.

Krantzberg G. Metal accumulation by chironomid larvae: the effects of age and body weight on metal body burdens. Hydrobiologia 1989; 188/189: 497-506.

Kuwabara J, Berelson W, Balistrieri L, Woods P, Topping B, Steding D, et al. Benthic flux of metals and nutrients into the water column of Lake Coeur d'Alene, Idaho: report of an August 1999 pilot study. US Geological Survey Water Resources Investigation 00-4132 (CD-ROM), Menlow Park, California, 2000.

Lambing JH, Nimick DA, Cleasby TE. Short-term variation of trace-element concentrations during base flow and rainfall runoff in small basins. U.S. Geological Survey, 1999.

Lee G, Bigham JM, Faure G. Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee. Applied Geochemistry 2002; 17: 569-581.

Leland HV, Fend SV, Dudley TL, Carter JL. Effects of copper on species composition of benthic insects in a Sierra Nevada, California, stream. Freshwater Biology 1989; 21: 163-179.

Lewin J, Bradley SB, Macklin MG. Historical valley alluviation in mid-Wales. Geological Journal 1983; 19: 331-350.

Lewin J, Davies BE, Wolfenden PJ. Interactions between channel change and historic mining sediment. In: Gregory KJ, editor. River Channel Changes. Wiley, Chichester, 1977, pp. 353-367.

Lewin J, Macklin MG. Metal mining and floodplain sedimentation in Britain. In: Gardiner V, editor. International Geomorphology 1986 Part I. John Wiley & Sons Ltd., 1987, pp. 1009-1027.

Licheng Z, Guijiu Z. The species and geochemical characteristics of heavy metals in the sediments of Kangjiaxi River in the Shuikoushan Mine Area, China. Applied Geochemistry 1996; 11: 217-222.

Linge KL. Methods for investigating trace element binding in sediments. Critical Reviews in Environmental Science and Technology 2008; 38: 165-196.

Lord RA, Morgan PA. Metal contamination of active stream sediments in Upper Weardale, Northern Pennine Orefield, UK. Environmental Geochemistry and Health 2003; 25: 95-104.

Lottermoser BG. Mine Waste. Characterization, Treatment, Environmental Impacts. New York: Springer, 2007.

Lund MA, McCullough CD. Biological Remediation of Low Sulphate Acidic Pit

Lake Waters with Limestone pH Neutralisation and Nutrients. International Mine Water Conference. Water Institute of Southern Africa and International Mine Water Association, Pretoria, South Africa, 2009, pp. 519-525.
Luoping Z, Huan F, Xiaoxia L, Xin Y, Youhai J, Tong O. Heavy metal contaminant remediation study of western Xiamen Bay sediment, China: Laboratory bench scale testing results. Journal of Hazardous Materials 2009; 172: 108-116.
Macedo-Sousa JA, Gerhardt A, Brett CMA, Noqueira AJA, Soares AMVM. Behavioural responses of indigenous benthic invertebrates (Echinogammarus meridionalis, Hydropsyche pellucidula and Choroterpes picteti) to a pulse of acid mine drainage: A laboratorial study. Environmental Pollution 2008; 156: 966-973.
Macedo-Sousa JA, Pestana JLT, Gerhardt A, Noqueira AJA, Soares AMVM. Behavioural and feeding responses of Echinogammarus meridionalis (Crustacea, Amphipoda) to acid mine drainage. Chemosphere 2007; 67: 1663-1670.
Macklin MG. Fluxes and storage of sediment-associated heavy metals in floodplain systems: assessment and river basin management issues at a time of rapid environmental change. In: Anderson MG, Walling DE, Bates PD, editors. Floodplain Processes. Wiley, Chichester, 1996, pp. 441-460.
Macklin MG, Brewer PA, Balteanu D, Coulthard TJ, Driga B, Howard AJ, et al. The long-term fate and environmental significance of contaminant metals released by the January and March 2000 mining tailings dam failures in Maramures County, upper Tisa Basin, Romania. Applied Geochemistry 2003; 18: 241-257.
Macklin MG, Brewer PA, Hudson-Edwards KA, Bird G, Coulthard TJ, Dennis IA. A geomorphological approach to the management of rivers contaminated by metal mining. Geomorphology 2006; 79: 423-447.
Macklin MG, Dowsett RB. The chemical and physical speciation of trace elements in fine grained overbank flood sediments in the Tyne Basin, North-East England. Catena 1989; 16: 135-151.
Macklin MG, Johnston EL, Lewin J. Pervasive and long-term forcing of Holocene river instability and flooding in Great Britain by centennial-scale climate change. The Holocene 2005; 15: 937-943.
Macklin MG, Ridgway J, Passmore DG, Rumsby BT. The use of overbank sediment for geochemical mapping and contamination assessment: results from selected English and Welsh floodplains. Applied Geochemistry 1994; 9: 689-700.
Macklin MG, Rumsby BT, Newson MD, Billi P, Hey RD, Tacconi P, et al. Historic overbank floods and vertical accretion of fine-grained alluvium in the lower Tyne valley, north-east England. Dynamics of Gravel-bed Rivers. Proceedings of the Third International Workshop on Gravel-bed Rivers. Wiley, Chichester, 1992, pp. 564-580.
Madzivire G, Petrik LF, Gitari WM, Balfour G, Vadapalli VRK, Ojumu TV. Role of pH in sulphate removal from circumneutral mine water using coal fly ash. Proceedings of the International Mine Water Conference. Water Institute of Southern Africa's Mine Water Division and International Mine Water Association, Pretoria, South Africa, 2009, pp. 462-471.

Malmqvist B, Hoffsten P. Influence of drainage from old mine deposits on benthic communities in central Swedish streams. Water Research 1999; 33: 2415-2423.

Maltby L, Naylor C. Preliminary observations on the ecological relevance of the Gammarus 'scope for growth' assay: effect of zinc on reproduction. Functional Ecology 1990; 4: 393-397.

Marcus WA. Copper dispersion in ephemeral stream sediments. Earth Surface Processes and Landforms 1987; 12: 217-228.

Marques MJ, Martinez-Conde E, Rovira JV. Effects of zinc and lead mining on the benthic macroinvertebrates of a fluvial ecosystem. Water, Air, and Soil Pollution 2003; 148: 363-388.

Marques MJ, Martinez-Conde E, Rovira JV, Ordonez S. Heavy metals pollution of aquatic ecosystems in the vicinity of a recently closed underground lead-zinc mine (Basque Country, Spain). Environmental Geology 2001; 40: 1125-1137.

Marques APGC, Ranqel AOSS, Castro PML. Remediation of heavy metal contaminated soils: Phytoremediation as a potentially promising clean-up technology. Critical Reviews in Environmental Science and Technology 2009; 39: 622-654.

Martinez EA, Moore BC, Schaumloffel J, Dasgupta N. Teratogenic versus mutagenic abnormalities in Chironomid larvae exposed to zinc and lead. Archives of Environmental Contamination and Toxicology 2004; 47: 193-198.

Mayes WM, Gozzard E, Potter HAB, Jarvis AP. Quantifying the importance of diffuse minewater pollution in a historically heavily coal mined catchment. Environmental Pollution 2008; 151: 165-175.

Mayes WM, Potter HAB, Jarvis AP. Novel approach to zinc removal from circum-neutral mine waters using pelletised recovered hydrous ferric oxide. Journal of Hazardous Materials 2009; 162: 512-520.

McGinness S, Johnson BD. Seasonal variation in the microbiology and chemistry of an acid mine drainage stream. Science of the Total Environment 1993; 132: 27-41.

McGregor RG, Blowes DW, Jambor JL, Robertson WD. The solid-phase controls on the mobility of heavy metals at the Copper Cliff tailings area, Sudbury, Ontario, Canada. Journal of Contaminant Hydrology 1998; 33: 247-271.

Mendez MO, Maier RM. Phytostabilisation of mine tailings in arid and semi-arid environments - An emerging remediation technology. Environmental Health Perspectives 2008; 113: 278-283.

Mighanetara K, Braungardt CB, Rieuwerts JS, Azizi F. Contaminant fluxes from point and diffuse sources from abandoned mines in the River Tamar catchment, UK. Journal of Geochemical Exploration 2009; 100: 116-124.

Miller JR. The role of fluvial geomorphic processes in the dispersal of heavy metals from mine sites. Journal of Geochemical Exploration 1997; 58: 101-118.

Miller JR, Hudson-Edwards KA, Lechler PJ, Preston D, Macklin MG. Heavy metal contamination of water, soil and produce within riverine communities of the Rio Pilcomayo basin, Bolivia. Science of the Total Environment 2004; 320: 189-209.

Morillo J, Usero J, Gracia I. Partitioning of metals in sediments from the Odiel River (Spain). Environment International 2002; 28: 263-271.

Morley NJ, Crane M, Lewis JW. Toxicity of cadmium and zinc mixtures to Diplostomum spathaceum (Trematoda: Diplostomidae) cercarial survival. Archives of Environmental Contamination and Toxicology 2002; 43: 28-33.

Mullinger N. Review of environmental and ecological impacts of drainage from abandoned mines in Wales. Cardiff: Environment Agency, 2004.

Munk L, Faure G, Pride DE, Bigham JM. Sorption of trace metals to an aluminium precipitate in a stream receiving acid rock-drainage; Snake River, Summit County, Colorado. Applied Geochemistry 2002; 17: 421-430.

Nagorski SA, McKinnon TE, Moore JN. Seasonal and storm-scale variations in heavy metal concentrations of two mining-contaminated streams, Montana, USA. Journal De Physique IV 2003; 107: 909-912.

Nagorski SA, Moore JN, Smith DB. Distribution of metals in water and bed sediment in a mineral-rich watershed, Montana, USA. Mine Water and the Environment 2002; 21: 121-136.

Netzband A, et al. Sediment management: An essential element of River Basin Management Plans. Journal of Soils and Sediments 2007; 7: 117-132.

Naji A, Ismail A, Ismail AR. Chemical speciation and contamination assessment of Zn and Cd by sequential extraction in surface sediment of Klang River, Malaysia. Microchemical Journal 2010; 95: 285-292.

Natarajan KA, Subramanian S, Braun JJ. Environmental impact of metal mining - biotechnological aspects of water pollution and remediation - an Indian experience. Journal of Geochemical Exploration 2006; 88: 45-48.

Navarro A, Cardellach E, Mendoza JL, Corbella M, Domenech LM. Metal mobilization from base-metal smelting slag dumps in Sierra Almagrera (Almeria, Spain). Applied Geochemistry 2008; 23: 895-913.

Nayar S, Goh BPL, Chou LM. Environmental impact of heavy metals from dredged and resuspended sediments on phytoplankton and bacteria assessed in in situ mesocosms. Ecotoxicology and Environmental Safety 2004; 59: 349-369.

Neal C, Whitehead PG, Jeffrey H, Neal M. The water quality of the River Carnon, west Cornwall, November 1992 to March 1994: the impacts of Wheal Jane discharges. Science of the Total Environment 2005; 338: 23-39.

Newson TA, Fahey M. Measurement of evaporation from saline tailings storages. Engineering Geology 2003; 70: 217-233.

Niyogi S, Wood CM. Biotic ligand model, a flexible tool for developing site-specific water quality guidelines for metals. Environmental Science and Technology 2004; 38: 6177-6192.

Nordstrom DK, Alpers CN, Ptacek CJ, Blowes DW. Negative pH and extremely acidic mine waters from Iron Mountain, California. Environmental Science and Technology 2000; 34: 254-258.

Norton PJ. The control of acid mine drainage with wetlands. Mine Water and the Environment 1992; 11: 27-34.

Novotny V. Diffuse Pollution and Watershed Management. New York: Wiley &

Sons, 2003.

Novotny V, Salomons W, Forstner V, Mader P. Diffuse sources of pollution by toxic metals and impact on receiving waters. Heavy Metals, Problems and Solutions. Springer, New York, 1995, pp. 33-52.

Nuttall CA, Younger PL. Zinc removal from hard circum-neutral mine waters using a novel closed-bed limestone reactor. Water Research 2000; 34: 1262-1268.

Olias M, Nieto JM, Sarmiento AM, Ceron JC, Canovas CR. Seasonal water quality variations in a river affected by acid mine drainage: the Odiel River (South West Spain). Science of the Total Environment 2004; 333: 267-281.

Ouyang Y, Higman J, Thompson J, O'Toole T, Campbell D. Characterisation and spatial distribution of heavy metals in sediment from Cedar and Ortega rivers subbasin. Journal of Contaminant Hydrology 2002; 54: 19-35.

Owens PN, Walling DE, Leeks GJL. Use of floodplain sediment cores to investigate recent historical changes in overbank sedimentation rates and sediment sources in the catchment of the River Ouse, Yorkshire, UK. Catena 1999; 36: 21-47.

Oyarzun J, Maturana H, Paulo A, Pasieczna A. Heavy metals in stream sediments from the Coquimbo Region (Chile): Effects of sustained mining and natural processes in a semi-arid Andean Basin. Mine Water and the Environment 2003; 22: 155-161.

Paquin PR, Gorsuch JW, Apte S, Batley GE, Bowles KC, Campbell PGC, Delos CG, Di Toro DM, Dwyer RL, Galvez F, Gensemer RW, Goss GG, Hogstrand C, Janssen CR, McGeer JC, Naddy RB, Playle RC, Santore RC, Schneider U, Stubblefield WA, Wood KB, Wu. The biotic ligand model: a historical overview. Comparative Biochemistry and Physiology C-Toxicology & Pharmacology 2002; 133: 3-35.

Perkins WT, Hartley S, Pearce NJG, Dinelli E, Edyvean R, Sandlands L. Bioadsorption in remediation of metal mine drainage: The use of dealginated seaweed in the BIOMAN project. Geochimica et Cosmochimica Acta 2006; 70: A482-A482.

Petersen LBM, Petersen RC. Anomalies in hydropsychid capture nets from polluted streams. Freshwater Biology 1983; 13: 185-191.

Petersen W, Willer E, Williamowski C. Remobilization of trace elements from polluted anoxic sediments after resuspension in oxic water. Water, Air and Soil Pollution 1997; 99: 515-22.

PIRAMID Consortium. Engineering guidelines for the passive remediation of acidic and/or metalliferrous mine drainage and similar waste waters. University of Newcastle Upon Tyne, Newcastle, 2003.

Pirrie D, Power MR, Rollinson G, Camm GS, Huges SH, Butcher AR, et al. The spatial distribution and source of arsenic, copper, tin and zinc within the surface sediments of the Fal Estuary, Cornwall, UK. Sedimentology 2003; 50: 579-595.

Pollmann O, van Rensburg L, Lange C. Reforestation and Landscaping on Mine Tailings. International Mine Water Conference. Water Institute of Southern Africa and International Mine Water Association, Pretoria, South Africa, 2009, pp. 837-842.

Poulton BC, Albert AL, Besser JM, Scmitt CJ, Brumbaugh WG. Fairchild, J.F.

A macroinvertebrate assessment of Ozark streams located in lead-zinc mining areas of Viburnum Trend in southeastern Missouri, USA. Environmental Monitoring and Assessment 2010; 163: 619-641.

Pulles W, Heath R. The evolution of passive mine water treatment technology for sulphate removal. International Mine Water Conference. Water Institute of Southern Africa's Mine Water Division and International Mine Water Association, Pretoria, South Africa, 2009, pp. 2-14.

Rauret G, Lopez-Sanchez JF, Sahuquillo A, Rubio R, Davidson C, Ure A, et al. Improvement of the BCR three step sequential extraction procedure prior to certification of new sediment and soil reference materials. Journal of Environmental Monitoring 1999; 1: 57-61.

Reish DJ, Gerlinger TV. The effects of cadmium, lead and zinc on survival and reproduction in the polychaetus annelid Neanthus arenaceodentata (F. Neriedidae). In: Hutchings PA, editor. Proceedings of the First International Polychate Conference. Linean Society, Sydney, 1964.

Ren J, Packman AI. Stream-subsurface exchange of zinc in the presence of silica and kaolinite colloids. Environmental Science and Technology 2004; 38: 6571-6581.

Rhea DT, Harper DD, Farag AM, Brumbaugh WG. Biomonitoring in the Boulder River watershed, Montana, USA: metal concentrations in biofilm and macroinvertebrates, and relations with macroinvertebrate assemblage. Environmental Monitoring and Assessment 2006; 115: 381-393.

Riba I, Garcia-Luque E, Maz-Courrau A, Gonzalez de Canales ML, Delvalls TA. Influence of salinity in the bioavailability of Zn in sediments of the Gulf of Cadiz (Spain). Water, Air and Soil Pollution 2010; 212: 329-336.

Rieuwerts JS, Austin S, Harris EA. Contamination from historic metal mines and the need for non-invasive remediation techniques: a case study from Southwest England. Environmental Monitoring and Assessment 2009; 148: 149-158.

Robb GA. Environmental consequences of coal mine closure. The Geographical Journal 1994; 160: 33-40.

Robb GA, Robinson JDF. Acid drainage from mines. The Geographical Journal 1995; 161: 47-54.

Roline RA. The effects of heavy metals pollution of the upper Arkansas River on the distribution of aquatic macroinvertebrates. Hydrobiologia 1988; 160: 3-8.

Romero FM, Armienta MA, Gonzalez-Hernandez G. Solid-phase control on the mobility of potentially toxic elements in an abandoned lead/zinc mine tailings impoundment, Taxco, Mexico. Applied Geochemistry 2007; 22: 109-127.

Roper DS, Nipper MG, Hickey CW, Martin ML, Weatherhead MA. Burial, crawling and drifting behaviour of the Bivalve Macomona liliana in response to common sediment contaminants. Marine Pollution Bulletin 1995; 31: 471-478.

Rotting TS, Ayora C, Carrera J. Chemical and hydraulic performance of "dispersed alkaline substrate" (DAS) for passive treatment of acid mine drainage with high metal concentrations. In: Cidu R, Frau F, editors. International Mine Water Association Symposium 2007: Water in

Mining Environments, Cagliari (Mako Edizioni), 2007, pp. 255-259.

Routh J, Ikramuddin M. Thrace-element geochemistry of Onion Creek near Van Stone lead-zinc mine (Washington, USA) - chemical analysis and geochemical modeling. Chemical Geology 1996; 133: 211-224.

Salomons W. Adsorption processes and hydrodynamic conditions in estuaries. Environmental Technology Letters 1980; 1: 356-365.

Salomons W. Sediment Pollution in the EEC. Office for Official Publications of the European Communities, Luxembourg, 1993.

Sanchez J, Marino N, Vaquero MC, Ansorena J, Leqorburu I. Metal pollution by old lead-zinc mines in Urumea River Valley (Basque Country, Spain). Soil, biota and sediment. Water, Air, and Soil Pollution 1998; 107: 303-319.

Sanchez Espana J, Lopez Pamo E, Santofimia Pastor E, Reyes Andres J, Martin Rubi JA. The impact of acid mine drainage on the water quality of the Odiel River (Huelva, Spain): Evolution of precipitate mineralogy and aqueous geochemistry along the Concepcion-Tintillo segment. Water, Air and Soil Pollution 2006; 173: 121-149.

Sanden P, Karlsson S, Duker A, Ledin A, Lundman L. Variations in hydrochemistry, trace metal concentration and transport during a rain storm event in a small catchment. Journal of Geochemical Exploration 1997; 58: 145-155.

Sapsford DJ, Williams KP. Sizing criteria for a low footprint passive mine water treatment system. Water Research 2009; 43: 423-432.

Scanferla P, Ferrari G, Pellay R, Ghirardini AV, Zanetto G, Libralato G. An innovative stabilisation/solidification treatment for contaminated soil remediation: demonstration of project results. Journal of Soils and Sediments 2009; 9: 229-236.

Schmitt CJ, Brumbaugh WG, May TW. Accumulation of metals in fish from lead-zinc mining areas of southeastern Missouri, USA. Ecotoxicology and Environmental Safety 2007; 67: 14-30.

Schultheis AS, Sanchez M, Hendricks AC. Structural and functional responses of stream insects to copper pollution. Hydrobiologia 1997; 346: 85-93.

Shannon CE. A mathematical theory of communication. Bell System Technical Journal 1948; 27: 379-423.

Smith H, Wood PJ, Gunn J. The influence of habitat structure and flow permanence on invertebrate communities in karst spring systems. Hydrobiologia 2003; 510: 53-66.

Smolders AJP, Lock RAC, Van der Velde G, Medina Hoyos RI, Roelofs JGM. Effects of mining activities on heavy metal concentrations in water, sediment, and macroinvertebrates in different reaches of the Pilcomayo River, South America. Archives of Environmental Contamination and Toxicology 2003; 44: 314-323.

Sola C, Burgos M, Plazuelo A, Toja J, Plans M, Prat N. Heavy metal bioaccumulation and macroinvertebrate community changes in a Mediterranean stream affected by acid mine drainage and an accidental spill (Guadiamar River, SW Spain). Science of the Total Environment 2004; 333: 109-126.

Sola C, Prat N. Monitoring metal and metalloid bioaccumulation of Hydropsyche (Trichoptera, Hydropsychidae) to evaluate metal pollution

in a mining river. Whole body versus tissue content. Science of the Total Environment 2006; 359: 221-231.
Spehar RL, Anderson RL, Fiandt JT. Toxicity and bioaccumulation of cadmium and lead in aquatic invertebrates. Environmental Pollution 1978; 15: 195-208.
Stiff MJ. The chemical states of copper in polluted fresh water and a scheme of analysis to differentiate them. Water Research 1971; 5: 585-599.
Stoertz MW, Bourne H, Knotts C, White MM. The effects of isolation and acid mine drainage on fish and macroinvertebrate communities of Monday Creek, Ohio, USA. Mine Water and the Environment 2002; 21: 60-72.
Stone M, Droppo IG. In-channel surficial fine grained sediment laminae. Part II: Chemical characteristics and implications for contaminant transport in fluvial systems. Hydrological Processes 1994; 8: 113-124.
Sullivan AB, Drever JI. Spatiotemporal variability in stream chemistry in a high-elevation catchment affected by mine drainage. Journal of Hydrology 2001; 252: 237-250.
Tordoff GM, Baker AJM, Willis AJ. Current approaches to the revegetation and reclamation of metalliferous mine wastes. Chemosphere 2000; 41: 219-228.
Taylor MP. The variability of heavy metals in floodplain sediments: a case study from mid Wales. Catena 1996; 28: 71-87.
Taylor MP, Mackay AK, Hudson-Edwards KA, Holz E. Soil Cu, Pb and Zn contaminants around Mount Isa city, Queensland, Australia: potential sources and risks to human health. Applied Geochemistry 2010; 25: 841-855.
Tessier A, Campbell PGC, Bisson M. Sequential extraction procedure for the speciation of particulate trace metals. Analytical Chemistry 1979; 7: 41-54.
Tokalioglu S, Kartal S, Birol G. Application of a three-stage sequential extraction procedure for the determination of extractable metal contents in highway soils. Turkish Journal of Chemistry 2003; 27: 333-346.
Van Damme A, Degryse F, Smolders E, Sarret G, Dewit J, Swennen R, et al. Zinc speciation in mining and smelter contaminated overbank sediments by EXAFS spectroscopy. Geochimica et Cosmochimica Acta 2010; 74: 3707-3720.
Van Damme PA, Harnel C, Ayala A, Bervoets L. Macroinvertebrate community response to acid mine drainage in rivers of the High Andes (Bolivia). Environmental Pollution 2008; 156: 1061-1068.
Vasile GD, Vladescu L. Cadmium partition in river sediments from an area affected by mining activities. Environmental Monitoring and Assessment 2010; 167: 349-357.
Vermeulen AC. Elaborating chironomid deformities as bioindicators of toxic sediment stress: The potential application of mixture toxicity concepts. Annales Zoologici Fennici 1995; 32: 265-285.
Vermeulen AC, Liberloo G, Dumont P, Ollevier F, Goddeeris B. Exposure of Chironomus riparius larvae (diptera) to lead, mercury and beta-sitosterol: effects on mouthpart deformation and moulting. Chemosphere 2000; 41: 1581-1591.
Vuori K-M. Rapid behavioural and morphological responses of hydropsychid

larvae (trichoptera, hydropsychidae) to sublethal cadmium exposure. Environmental Pollution 1994; 84: 291-299.

Vinod VTP, Sashidar RB, Sukumar AA. Competitive adsorption of toxic heavy metal contaminants by gum kondagogu (*Cochlospermum gossypium*): A natural hydrocolloid. Colloids and Surfaces B: Biointerfaces 2010; 75: 490-495.

Vivian CMG, Massie KS. Trace metals in waters and sediments of the River Tawe, South Wales, in relation to local sources. Environmental Pollution 1977; 14: 47-61.

Walling DE, Owens PN, Carter J, Leeks GJL, Lewis S, Meharg AA, et al. Storage of sediment-associated nutrients and contaminants in river channel and floodplain systems. Applied Geochemistry 2003; 18: 195-220.

Walling DE, Webb BW. The spatial dimension in the interpretation of stream solute behaviour. Journal of Hydrology 1980; 47: 129-149.

Warburton J, Danks M, Wishart D. Stability of an upland gravel-bed stream, Swinhope Burn, Northern England. Catena 2002; 49: 309-329.

Watanabe NC, Harada S, Komai Y. Long-term recovery from mine drainage disturbance of a mcroinvertebrate community in the Ichi-kawa River, Japan. Hydrobiologia 2000; 429: 171-180.

Watzlaf G, Schroeder K, Kairies C. Long-term performance of anoxic limestone drains. Mine Water and the Environment 2000; 19: 98-110.

Waygood CG, Ferreira S. A review of the current strategy for capping mining spoils. International Mine Water Conference. Water Institute of Southern Africa and International Mine Water Association, Pretoria, South Africa, 2009, pp. 738-745.

Webb BW, Walling DE. Stream solute behaviour in the River Exe basin, Devon, UK. Dissolved loads of Rivers and Surface Water Quality/Quantity Relationships. International Association of Hydrological Sciences Publication No. 141, 1983, pp. 153-169.

Whitehead PG, Prior H. Bioremediation of acid mine drainage: An introduction to the Wheal Jane wetlands project. Science of the Total Environment 2005; 338: 15-21.

Wilby RL, Orr HG, Hedger M, Forrow D, Blackmore M. Risks posed by climate change to the delivery of Water Framework Directive objectives in the UK. Environment International 2006; 32: 1043-1055.

Wilkin RT. Contaminant attenuation processes at mine sites. Mine Water and the Environment 2008; 27: 251-258.

Willis M. Analysis of the effects of zinc pollution on the macroinvertebrate populations of the Afon Crafnant, North Wales. Environmental Geochemistry and Health 1985; 7: 98-109.

Winner RW, Boesel MW, Farrell MP. Insect community structure as an index of heavy-metal pollution in lotic ecosystems. Canadian Journal of Fisheries and Aquatic Sciences 1980; 37: 647-655.

Wirt L, Leib KJ, Bove DJ, Mast MA, Evans JB, Meeker GP. Determination of chemical-constituent loads during base-flow and storm-runoff conditions near historical mines in Prospect Gulch, Upper Animas River Watershed, Southwestern Colorado. U.S. Geological Survey, 1999.

Wolfenden PJ, Lewin J. Distribution of metal pollutants in floodplain

sediments. Catena 1977; 4: 317.
Wolfenden PJ, Lewin J. Distribution of metal pollutants in active stream sediments. Catena 1978; 5: 67-78.
Wolkersdorfer C. Mine water literature in ISI's Science Citation Index expanded. Mine Water and the Environment 2004; 23: 96-99.
Wolz JEA, et al. In search for the ecological and toxicological relevance of sediment re- mobilisation and transport during flood events. Journal of Soils and Sediments 2009; 9: 1-5.
Wood PJ, Armitage PD. Biological effects of fine sediment in the lotic environment. Environmental Management 1997; 21: 203-217.
Woodcock TS, Huryn AD. The response of macroinvertebrate production to a pollution gradient in a headwater stream. Freshwater Biology 2007; 52: 177-196.
Yi Y, Wang Z, Zhang K, Yu G, Duan X. Sediment pollution and its effect on fish through food chain in the Yangtze River. International Journal of Sediment Research 2008; 23: 338-347.
Yim JH, Kim KW, Kim SD. Effect of hardness on acute toxicity of metal mixtures using Daphnia magna: prediction of acid mine drainage toxicity. Journal of Hazardous Materials 2006; B138: 16-21.
Yim WWS. Geochemical investigations on fluvial sediments contaminated by tin mine tailings, Cornwall, England. Environmental Geology 1981; 3: 245-256.
Younger PL. The adoption and adaptation of passive treatment technologies for mine waters in the United Kingdom. Mine Water and the Environment 2000; 19: 84-97.
Younger PL. Coalfield closure and the water environment in Europe. Transactions of the Institution of Mining and Metallurgy (Section A: Mining Technology) 2002; 111: A201-A209.
Younger PL, Banwart SA, Hedin RS. Mine Water. Hydrology, Pollution, Remediation. Dordrecht: Kluwer Academic Publishers, 2002.
Younger PL, Coulton RH, Frogatt EC. The contribution of science to risk-based decision-making: lessons from the development of full-scale treatment measures for acidic mine waters at Wheal Jane, UK. Science of the Total Environment 2005; 338: 138-154.
Younger PL, Wolkersdorfer CH. Mining Impacts on the Fresh Water Environment: Technical and Managerial Guidelines for Catchment Scale Management. Mine Water and the Environment 2004; Supplement to Volume 23: S1-S80.
Ziemkiewicz P, Skousen J, Brant D, Sterner P, Lovett R. Acid mine drainage treatment with armoured limestone in open limestone channels. Journal of Environmental Quality 1997; 26: 560-569.
Zoumis T, Schmidt A, Grigorova L, Calmano W. Contaminants in sediments: remobilisation and demobilisation. Science of the Total Environment 2001; 226: 195-202.

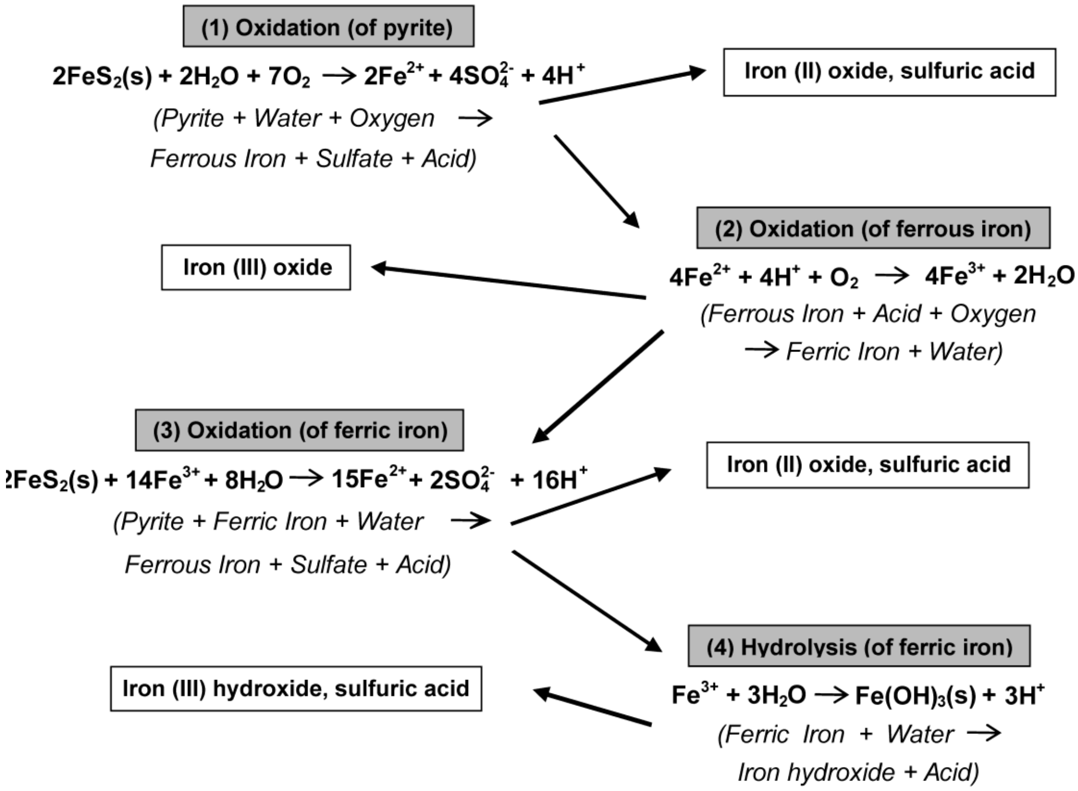


**Figure 1** The process of pyrite weathering in a deep metal mine. Four general equations describe the chemistry of pyrite weathering and the production of AMD – (1) The oxidation of pyrite by oxygen and water in atmospheric conditions to produce dissolved ferrous iron and sulphuric acid; (2) the oxidation 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) |

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| (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) |

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| | | 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* | | | | | |

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| 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) |

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| | | 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) |

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