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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 metalliferous 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 19th and early 20th 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$_2$OH). 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 splay deposits 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;
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
solute (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,
(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.
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 the remediative processes and have the principal
advantages over active remediation of reduced set up and maintenance costs
(Pulle 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 (Fürstner, 2004), and some success has been achieved in the stabilisation and removal of toxic metals (Guangwei et al., 2009; Luoping et al., 2009; Scanferla et al., 2009). However, the principal necessity for the protection of sediment and aquatic systems is considered to be the development of guidelines concerning sediment quality (Burton, 2010; Byrne et al., 2010).

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

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

The character of metal mine drainage after it enters surface waters is affected by many factors including stream discharge, rainfall characteristics, conditions antecedent to rainfall-runoff events and season, and the interaction of a large permutation of processes which must be understood and quantified in order to mitigate effectively. Seasonal variability in metal concentrations is linked to oxidation and dissolution of metal sulphates, leading to elevated metal concentrations in summer and autumn months. At many mine sites, the transport of significant amounts of mine waste is limited to stormflows. Typically, hysteresis is evident in the relationship between metal concentrations and discharge. Peak metal concentrations are achieved before peak discharge, associated with the dissolution of surface oxidised material. Despite the importance of stormflows for the transport of mine wastes, little research has concentrated on investigating toxic metal fluxes and hydrochemical variability under these conditions. Predicted increases in the frequency and magnitude of floods as a function of climate change may result in increased mobilisation and deposition of toxic metals in floodplains across
Europe. Stormflow hydrochemistry in rivers draining mine sites should be studied in more detail in order to quantify metal fluxes more accurately and allow environmental managers to prioritise areas for remediation. Toxic metal flushing during stormflows potentially impacts stream ecosystems by significantly increasing the toxicity of the river water, even if only for short time periods. More research is needed to help understand the potential toxicological impacts of stormflows in mining-affected river catchments. Relatively few studies have investigated mine spoil hydrology and metal attenuation and release processes. Environmental investigations at abandoned metal mine sites should include assessments of mine spoil in terms of mineralogy, metal speciation and hydrology, especially where contamination of groundwater is an issue.

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

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

A management approach which can draw on the expertise of separate but related and relevant disciplines such as hydrology, hydrochemistry, sediment geochemistry, fluvial geomorphology and aquatic ecology affords the opportunity for a more complete understanding of processes and impacts in mining-impacted river catchments. It is hoped that this review will help to contribute to our knowledge and understanding of the impacts of metal mining on aquatic ecosystems and highlight the usefulness of approaching such problems from a multi-disciplinary geographical point of view.
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Figure 1 The process of pyrite weathering in a deep metal mine. Four general equations describe the chemistry of pyrite weathering and the production of AMD – (1) The oxidation of pyrite by oxygen and water in atmospheric conditions to produce dissolved ferrous iron and sulphuric acid; (2) the oxidation of dissolved ferrous iron to ferric iron; (3) the hydrolysis of ferric iron with water to produce iron hydroxide precipitate (ochre) and acidity; (4) the oxidation of additional pyrite by the ferric iron generated in reaction (2) to produce dissolved ferrous iron and sulphuric acid. The acidic conditions generated during these processes can dissolve oxidised trace metals. The process is accelerated by the presence of sulphide and iron-oxidising bacteria.
Table 1 A comparison of dissolved metal (mg/l), sulphate (mg/l) and pH concentrations from waters impacted by historical deep metal mining.

<table>
<thead>
<tr>
<th>Location</th>
<th>Sample type</th>
<th>Pb</th>
<th>Zn</th>
<th>Cu</th>
<th>Cd</th>
<th>Fe</th>
<th>SO₄</th>
<th>pH</th>
<th>Author(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River Carnon, England</td>
<td>Mine drainage</td>
<td>&lt;0.01 - 0.02</td>
<td>0.12 - 23</td>
<td>0.02 - 1.3</td>
<td>&lt;0.01 - 0.02</td>
<td>&lt;0.01 - 49</td>
<td>77 - 789</td>
<td>3.3 - 7.7</td>
<td>Neal et al. (2005)</td>
</tr>
<tr>
<td>River Tamar, England</td>
<td>Adit drainage</td>
<td>&lt;0.01 - 0.17</td>
<td>&lt;0.1 - 2.5</td>
<td>&lt;0.01 - 1.4</td>
<td>&lt;0.01 - 0.01</td>
<td>0.05 - 2.6</td>
<td>10 - 89</td>
<td>3.4 - 7.8</td>
<td>Mighanetara et al. (2009)</td>
</tr>
<tr>
<td>Funtana Raminosa Mining District, Italy</td>
<td>Tailings</td>
<td>&lt;0.01</td>
<td>0.08 - 34</td>
<td>&lt;0.01 - 0.04</td>
<td>&lt;0.01 - 0.85</td>
<td>0.02 - 0.25</td>
<td>22 - 1680</td>
<td>7.1 - 7.8</td>
<td>Cidu and Mereu (2007)</td>
</tr>
<tr>
<td>Buchim Mining district, Macedonia</td>
<td>Mine stream</td>
<td>0.03*</td>
<td>0.03*</td>
<td>0.62*</td>
<td>&lt;0.01*</td>
<td>0.3*</td>
<td>-</td>
<td>5.1*</td>
<td>Alderton et al. (2005)</td>
</tr>
<tr>
<td>Zletovo Mining District, Macedonia</td>
<td>Adit drainage</td>
<td>0.06*</td>
<td>21.57*</td>
<td>0.46*</td>
<td>0.14*</td>
<td>98.2*</td>
<td>-</td>
<td>3.4*</td>
<td>Alderton et al. (2005)</td>
</tr>
<tr>
<td>River Zletovska, Macedonia</td>
<td>Channel</td>
<td>&lt;0.03 - 0.8</td>
<td>0.04 - 70.07</td>
<td>&lt;0.01 - 1.05</td>
<td>&lt;0.01 - 0.24</td>
<td>0.1 - 103.3</td>
<td>-</td>
<td>3.4 - 7.6</td>
<td>Alderton et al. (2005)</td>
</tr>
<tr>
<td>River Bjorgasen, Norway</td>
<td>Channel</td>
<td>-</td>
<td>5.4b</td>
<td>2.7b</td>
<td>0.01b</td>
<td>-</td>
<td>-</td>
<td>3.2b</td>
<td>Gundersen and Stiennes (2001)</td>
</tr>
<tr>
<td>Rio Tinto, Spain</td>
<td>Channel</td>
<td>0.1 - 2.4</td>
<td>0.3 - 420</td>
<td>0.05 - 240</td>
<td>-</td>
<td>-</td>
<td>2800 - 16000</td>
<td>1.4 - 7.6</td>
<td>Hudson-Edwards et al. (1999b)</td>
</tr>
<tr>
<td>Troya Mine, Spain</td>
<td>Tailings pond</td>
<td>0.02 - 0.05</td>
<td>4.99 - 18.95</td>
<td>&lt;0.01 - 0.03</td>
<td>0.01 - 0.03</td>
<td>0.04 - 0.33</td>
<td>-</td>
<td>-</td>
<td>Marques et al. (2001)</td>
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<tr>
<td>River Odiel, Spain</td>
<td>Channel</td>
<td>&lt;0.01 - 1.18</td>
<td>0.17 - 130.23</td>
<td>0.01 - 37.62</td>
<td>&lt;0.01 - 0.38</td>
<td>0.03 - 262.71</td>
<td>50.7 - 3960</td>
<td>2.5 - 6.3</td>
<td>Olias et al. (2004)</td>
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<tr>
<td>Tintillo River, Spain</td>
<td>Mine drainage</td>
<td>0.01 - 0.07</td>
<td>7.3 - 216</td>
<td>3.5 - 115</td>
<td>&lt;0.01 - 0.51</td>
<td>264 - 1973</td>
<td>1300 - 11580</td>
<td>2.3 - 2.8</td>
<td>Sanchez Espana et al. (2006)</td>
</tr>
<tr>
<td>Tinto Santa Rosa Mine, Spain</td>
<td>Mine drainage</td>
<td>&lt;0.01 - 0.08</td>
<td>56 - 85</td>
<td>15 - 23</td>
<td>0.09 - 0.15</td>
<td>234 - 881</td>
<td>2704 - 4026</td>
<td>2.6 - 3.4</td>
<td>Asta et al. (2007)</td>
</tr>
<tr>
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<td>Type</td>
<td>Parameter 1</td>
<td>Parameter 2</td>
<td>Parameter 3</td>
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<td>Parameter 5</td>
<td>Parameter 6</td>
<td>Reference</td>
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<tr>
<td>Fluminesne Mining District, Spain</td>
<td>Mine water</td>
<td>&lt;0.01 - 0.05</td>
<td>0.88 - 40</td>
<td>&lt;0.01 - 0.09</td>
<td>&lt;0.01 - 12</td>
<td>17 - 640</td>
<td>6.3 - 8.2</td>
<td>Cidu et al. (2007)</td>
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<tr>
<td>River Tawe, Wales</td>
<td>Channel</td>
<td>&lt;0.01 - 0.15</td>
<td>0.01 - 8.8</td>
<td>&lt;0.01 - 0.04</td>
<td>&lt;0.01 - 0.16</td>
<td>-</td>
<td>-</td>
<td>Vivian and Massie (1977)</td>
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<tr>
<td>River Rheidol, Wales</td>
<td>Channel</td>
<td>&lt;0.01</td>
<td>0.08 - 0.29</td>
<td>&lt;0.01</td>
<td>-</td>
<td>5.3 - 7.1</td>
<td>5.5 - 6.4</td>
<td>Fuge et al. (1991)</td>
<td></td>
</tr>
<tr>
<td>River Yswyth, Wales</td>
<td>Channel</td>
<td>0.06 - 0.09</td>
<td>0.17 - 0.36</td>
<td>&lt;0.01</td>
<td>-</td>
<td>nd - 5.3</td>
<td>4.1 - 4.6</td>
<td>Fuge et al. (1991)</td>
<td></td>
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<tr>
<td>Cwm Rheidol Mine, Wales</td>
<td>Adit drainage</td>
<td>0.02 - 0.04</td>
<td>38 - 72</td>
<td>0.03 - 0.07</td>
<td>0.04 - 0.11</td>
<td>-</td>
<td>441 - 846</td>
<td>Fuge et al. (1991)</td>
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<tr>
<td>Cwm Yswyth Mine, Wales</td>
<td>Spoil drainage</td>
<td>0.29 - 3.3</td>
<td>1.5 - 4.6</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>-</td>
<td>nd</td>
<td>Fuge et al. (1991)</td>
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<tr>
<td>Cae Coch Pyrite Mine, Wales</td>
<td>Mine water</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2261&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6590&lt;sup&gt;b&lt;/sup&gt;</td>
<td>McGinness and Johnson (1993)</td>
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<tr>
<td>Cwm Rheidol Mine, Wales</td>
<td>Spoil drainage</td>
<td>-</td>
<td>577 - 978</td>
<td>1.2 - 9.35</td>
<td>-</td>
<td>-</td>
<td>2.6 - 2.7</td>
<td>Johnson (2003)</td>
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<td>River Goch, Wales</td>
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<td>&lt;0.01 - 5.99</td>
<td>-</td>
<td>&lt;0.01 - 25.98</td>
<td>-</td>
<td>Boult et al. (1994)</td>
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<td>1.2 - 9.35</td>
<td>-</td>
<td>-</td>
<td>2.6 - 2.7</td>
<td>Johnson (2003)</td>
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<td>West Squaw Creek, USA</td>
<td>Channel</td>
<td>0.01 - 156</td>
<td>&lt;0.01 - 190</td>
<td>-</td>
<td>0.03 - 500</td>
<td>2.6 - 5100</td>
<td>2.4 - 6.9</td>
<td>Filipek et al. (1987)</td>
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</tr>
<tr>
<td>Richmond Mine, USA</td>
<td>Mine water</td>
<td>1 - 120</td>
<td>0.06 - 23.5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.21 - 4.76&lt;sup&gt;a&lt;/sup&gt;</td>
<td>4 - 2110</td>
<td>2.47 - 79.7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>14 - 760&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-3.6 - 1.5</td>
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<tr>
<td>Peru Creek, USA</td>
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<td>-</td>
<td>0.55 - 1.89</td>
<td>0.05 - 0.22</td>
<td>-</td>
<td>0.08 - 0.5</td>
<td>29.6 - 73</td>
<td>4.7 - 5.9</td>
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<td>&lt;0.032&lt;sup&gt;*&lt;/sup&gt;</td>
<td>0.469&lt;sup&gt;*&lt;/sup&gt;</td>
<td>0.246&lt;sup&gt;*&lt;/sup&gt;</td>
<td>&lt;0.01&lt;sup&gt;*&lt;/sup&gt;</td>
<td>2.82&lt;sup&gt;*&lt;/sup&gt;</td>
<td>97.4&lt;sup&gt;*&lt;/sup&gt;</td>
<td>3.3&lt;sup&gt;*&lt;/sup&gt;</td>
<td>Keith et al. (2001)</td>
</tr>
<tr>
<td>Black Foot River, USA</td>
<td>Channel</td>
<td>-</td>
<td>&lt;0.2 - 535</td>
<td>&lt;0.8 - 4</td>
<td>&lt;0.5 - 2.6</td>
<td>&lt;5 - 37</td>
<td>5.5 - 88.8</td>
<td>7.3 - 8.8</td>
<td>Nagorski et al. (2002)</td>
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<tr>
<td>Phillips Mine, USA</td>
<td>Channel</td>
<td>&lt;0.01</td>
<td>&lt;0.01 - 0.17</td>
<td>0.02 - 3.13</td>
<td>-</td>
<td>0.16 - 42.4</td>
<td>25 - 368</td>
<td>2.3 - 6.5</td>
<td>Gilchrist et al. (2009)</td>
</tr>
<tr>
<td>River Dee, Australia</td>
<td>Channel</td>
<td>&lt;0.01 - 0.6</td>
<td>&lt;0.01 - 10.4</td>
<td>&lt;0.01 - 45.03</td>
<td>-</td>
<td>&lt;0.01 - 74</td>
<td>340 - 5950</td>
<td>2.7 - 7.0</td>
<td>Edraki et al. (2005)</td>
</tr>
<tr>
<td>Mt. Morgan Mine, Australia</td>
<td>Open pit</td>
<td>1.51°</td>
<td>21.97°</td>
<td>44.54°</td>
<td>-</td>
<td>253°</td>
<td>1360°</td>
<td>2.7°</td>
<td>Edraki et al. (2005)</td>
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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.

<table>
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<tr>
<th>River location</th>
<th>Geomorphic-type</th>
<th>Grain size fraction</th>
<th>Metal phase extracted</th>
<th>Pb</th>
<th>Zn</th>
<th>Cu</th>
<th>Cd</th>
<th>Author(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River Derwent, England</td>
<td>Channel</td>
<td>&lt;1000 µm</td>
<td>Total</td>
<td>96</td>
<td>82</td>
<td>-</td>
<td>0.6 - 13.8</td>
<td>Burrows and Whitton (1983)</td>
</tr>
<tr>
<td>River Derwent, England</td>
<td>Floodplain</td>
<td>&lt;2000 µm</td>
<td>Total</td>
<td>131</td>
<td>&lt;10</td>
<td>2.9</td>
<td>0.08 - 12.5</td>
<td>Bradley and Cox (1990)</td>
</tr>
<tr>
<td>River Tyne, England</td>
<td>Floodplain</td>
<td>&lt;2000 µm</td>
<td>Total</td>
<td>615</td>
<td>722</td>
<td>11</td>
<td>2.6 - 8</td>
<td>Macklin et al. (1992)</td>
</tr>
<tr>
<td>River Swale, England</td>
<td>Floodplain</td>
<td>&lt;63 µm</td>
<td>Total</td>
<td>56</td>
<td>15</td>
<td>2.9</td>
<td>1 - 18</td>
<td>Macklin et al. (1994)</td>
</tr>
<tr>
<td>River Allen, England</td>
<td>Channel</td>
<td>&lt;170 µm</td>
<td>Total</td>
<td>2330*</td>
<td>1410*</td>
<td>-</td>
<td>-</td>
<td>Goodyear et al. (1996)</td>
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<tr>
<td>River Severn, England</td>
<td>Floodplain</td>
<td>&lt;2000 µm</td>
<td>Total</td>
<td>23</td>
<td>173</td>
<td>30</td>
<td>0.35 - 6.4</td>
<td>Taylor (1996)</td>
</tr>
<tr>
<td>River Tees, England</td>
<td>Channel</td>
<td>&lt;2000 µm</td>
<td>Total</td>
<td>522</td>
<td>404</td>
<td>20</td>
<td>0.95 - 5.95</td>
<td>Hudson-Edwards et al. (1997)</td>
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<tr>
<td>River Aire, England</td>
<td>Channel</td>
<td>&lt;63 µm</td>
<td>Total</td>
<td>90</td>
<td>274</td>
<td>118</td>
<td>-</td>
<td>Walling et al. (2003)</td>
</tr>
<tr>
<td>River Swale, England</td>
<td>Floodplain</td>
<td>&lt;63 µm</td>
<td>Total</td>
<td>10000*</td>
<td>14000*</td>
<td>-</td>
<td>7500*</td>
<td>Dennis et al. (2003)</td>
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<td>River Calder, England</td>
<td>Channel</td>
<td>&lt;63 µm</td>
<td>Total</td>
<td>199</td>
<td>397</td>
<td>141</td>
<td>-</td>
<td>Walling et al. (2003)</td>
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<td>River Avoca, Ireland</td>
<td>Channel</td>
<td>&lt;1000 µm</td>
<td>Total</td>
<td>-</td>
<td>1520*</td>
<td>674*</td>
<td>-</td>
<td>Herr and Gray (1996)</td>
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<tr>
<td>River Mała Panew, Poland</td>
<td>Channel</td>
<td>&lt;63 µm</td>
<td>Total</td>
<td>36</td>
<td>126</td>
<td>3.97</td>
<td>0.18 - 559</td>
<td>Aleksander-Kwaterczak and Helios-</td>
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<td>Location</td>
<td>Environment</td>
<td>Size</td>
<td>Parameter</td>
<td>Lower Limit</td>
<td>Upper Limit</td>
<td>Lower Limit</td>
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<tr>
<td>River Somes, Romania</td>
<td>Channel</td>
<td>&lt;2000 μm</td>
<td>Total</td>
<td>28 - 6800</td>
<td>64 - 19600</td>
<td>12 - 8400</td>
<td>0.8 - 110</td>
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<tr>
<td>River Viseu, Romania</td>
<td>Floodplain</td>
<td>&lt;2000 μm</td>
<td>Total</td>
<td>17 - 850</td>
<td>110 - 2760</td>
<td>32 - 1000</td>
<td>0.5 - 17</td>
<td>-</td>
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<tr>
<td>Gezala Creek, Spain</td>
<td>Channel</td>
<td>&lt;177 μm</td>
<td>Total</td>
<td>10.6 - 37630</td>
<td>216 - 25676</td>
<td>2.7 - 1691</td>
<td>0.22 - 45</td>
<td>-</td>
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<tr>
<td>River Tinto, Spain</td>
<td>Channel</td>
<td>&lt;2000 μm</td>
<td>Total</td>
<td>3200 - 16500</td>
<td>600 - 67300</td>
<td>1800 - 26500</td>
<td>&lt;1 - 23</td>
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<tr>
<td>River Odiel, Spain</td>
<td>Channel</td>
<td>&lt;2000 μm</td>
<td>Total</td>
<td>1900 - 16600</td>
<td>1000 - 74600</td>
<td>3500 - 20900</td>
<td>1.4 - 10.2</td>
<td>-</td>
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<tr>
<td>River Rheidol, Wales</td>
<td>Floodplain</td>
<td>&lt;2000 μm</td>
<td>Total</td>
<td>291 - 2098</td>
<td>242 - 630</td>
<td>21 - 85</td>
<td>0.08 - 3.5</td>
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<tr>
<td>River Tawe, Wales</td>
<td>Channel</td>
<td>&lt;2000 μm</td>
<td>Total</td>
<td>63 - 6993</td>
<td>20 - 31199</td>
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<td>2 - 335</td>
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<tr>
<td>River Rheidol, Wales</td>
<td>Floodplain</td>
<td>&lt;210 μm</td>
<td>Total</td>
<td>813 - 1717</td>
<td>201 - 383</td>
<td>33 - 120</td>
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<tr>
<td>River Towy, Wales</td>
<td>Channel</td>
<td>&lt;2000 μm</td>
<td>Total</td>
<td>36 - 5732</td>
<td>106 - 3722</td>
<td>44 - 259</td>
<td>0.78 - 83</td>
<td>-</td>
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<tr>
<td>River Twymyn, Wales</td>
<td>Channel</td>
<td>&lt;2000 μm</td>
<td>Total</td>
<td>593 - 6411</td>
<td>159 - 6955</td>
<td>44 - 2557</td>
<td>1.5 - 44</td>
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<td>River Ystwyth, Wales</td>
<td>Floodplain</td>
<td>&lt;2000 μm</td>
<td>Total</td>
<td>73 - 4646</td>
<td>123 - 1543</td>
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<td>River Twymyn, Wales</td>
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<td>Non-residual</td>
<td>1.1 - 2914</td>
<td>0.7 - 148</td>
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<tr>
<td>North America</td>
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<td>-</td>
<td>32 - 5940</td>
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<td>West Squaw Creek, USA</td>
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<td>&lt;63 μm</td>
<td>Total</td>
<td>1100 - 8700</td>
<td>1700 - 9600</td>
<td>1400 - 9900</td>
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<td>Black Foot River, USA</td>
<td>Channel</td>
<td>-</td>
<td>Total</td>
<td>4.5 - 420</td>
<td>9.75 - 2050</td>
<td>2.3 - 107</td>
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<td>River Cedar, USA</td>
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<td>&lt;1000 μm</td>
<td>Total</td>
<td>9.9 - 30</td>
<td>9 - 67</td>
<td>31 - 398</td>
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<td>Copper Mine Brook, USA</td>
<td>Channel</td>
<td>&lt;1000 μm</td>
<td>Total</td>
<td>1154 - 8034</td>
<td>124 - 2319</td>
<td>23 - 209</td>
<td>2.6 - 41</td>
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<td>Australasia</td>
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<td>124 - 2319</td>
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<td>2.6 - 41</td>
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<td>River Kangjiaxi, China</td>
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<td>2.6 - 41</td>
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*nd = not detectable, * maximum value,  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.

<table>
<thead>
<tr>
<th>Primary impact reported</th>
<th>Additional information</th>
<th>Author(s)</th>
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<tr>
<td>Community composition</td>
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<tr>
<td>Shift in community structure</td>
<td>Clean sites dominated by Ephemeroptera and Plecoptera; moderately contaminated sites dominated by Plecoptera and Diptera; and heavily contaminated sites dominated by Diptera</td>
<td>Armitage (1980)(^a)</td>
</tr>
<tr>
<td></td>
<td>Clean sites dominated by Ephemeroptera; moderately contaminated sites by Tricoptera; and heavily contaminated sites dominated by Diptera</td>
<td>Winner et al. (1980)(^a)</td>
</tr>
<tr>
<td></td>
<td>Contaminated sites dominated by Orthocladiinae (Chironomidae) and species of net-spinning Tricoptera</td>
<td>Clements et al. (1992)(^a)</td>
</tr>
<tr>
<td></td>
<td>Contaminated sites dominated by Chironomidae</td>
<td>Gray (1998)(^a)</td>
</tr>
<tr>
<td></td>
<td>Ephemeroptera reduced by &gt; 75% in moderately contaminated streams</td>
<td>Clements et al. (2000)(^a)</td>
</tr>
<tr>
<td></td>
<td>Clean sites dominated by Stenopsycheidae (Trichoptera); contaminated sites dominated by Chironomidae and Epeorus latifolium (Ephemeroptera)</td>
<td>Watanabe et al. (2000)(^a)</td>
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<td>Contaminated sites dominated by Chironomidae, Tubificidae, Baeidae and Simulidae</td>
<td>Marques et al. (2003)(^a)</td>
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<td>Heavily contaminated sites dominated by Chironomidae</td>
<td>Smolders et al. (2003)(^a)</td>
</tr>
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<td>Dominance of predators in very acidic mining sites</td>
<td>Gerhardt et al. (2004)(^a)</td>
</tr>
<tr>
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<td>Heavily contaminated sites characterised by high proportion of Chironominae and predatory Tanypodinae</td>
<td>Janssens de Bisthoven et al. (2005)(^a)</td>
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<tr>
<td>Decrease in abundance</td>
<td>Reduction in abundance recorded</td>
<td>Willis (1985)(^a), Gray (1998)(^a), Hirst et al. (2002)(^a)</td>
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<td>Ephemeroptera comprised less than 5% of individuals at one location</td>
<td>Clements et al. (1992)(^a)</td>
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<tr>
<td>Phenomenon</td>
<td>Description</td>
<td>References</td>
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<tr>
<td>Abundance</td>
<td>Significantly lower in experiments with metal mixtures and high predation pressure</td>
<td>Kiffney (1996)</td>
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<td>Abundance</td>
<td>Positively related to stream alkalinity and pH</td>
<td>Malmqvist and Hoffsten (1999)</td>
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<td>Decrease in number of taxa</td>
<td>Reduced number of taxa recorded</td>
<td>Willis (1985), Kiffney (1996), Gray (1998)</td>
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<tr>
<td>Decrease most pronounced in low flow conditions</td>
<td></td>
<td>Clements et al. (1992)</td>
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<tr>
<td>Decrease in EPT taxa</td>
<td>EPT richness positively related to stream pH</td>
<td>Malmqvist and Hoffsten (1999)</td>
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<tr>
<td></td>
<td>Near extinction of mayfly species</td>
<td>Hickey and Golding (2002)</td>
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<tr>
<td></td>
<td>Reduced number of EPT taxa recorded</td>
<td>Gerhardt et al. (2004)</td>
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<td>Decrease in species diversity</td>
<td>Reduced species diversity recorded</td>
<td>Amisah and Cowx (2000), Hirst et al. (2002)</td>
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<td>Dominance of Chironomidae</td>
<td>Smolders et al. (2003)</td>
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<td>Dominance of Chironomidae, Baetidae and Simulida</td>
<td>Van Damme et al. (2008)</td>
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<td>Impaired ecosystem function</td>
<td>Microbial colonisation of leaf material and leaf decomposition inhibited by high Cd concentrations</td>
<td>Giesy et al. (1978)</td>
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<td>Microbial activity and leaf decomposition rates significantly lower at contaminated sites</td>
<td>Carpenter et al. (1983)</td>
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<td>Secondary production of shredders negatively associated with metal contamination; leaf decomposition rates decreased; microbial respiration decreased</td>
<td>Carlisle and Clements (2005)</td>
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<tr>
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<td>Reduced secondary production and organic matter storage</td>
<td>Woodcock and Huryn (2007)</td>
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<td></td>
<td>Greater vulnerability of net-spinning Tricoptera to predation possibly due to spending more time in the open repairing capture nets</td>
<td>Clements et al. (1989)</td>
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</table>

**Macroinvertebrate physiology**
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<td>Differences in metal sensitivity related to trophic status; herbivores and detritivores more sensitive than predators</td>
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<td>Decrease in reproduction rates of Gammurcas pulex (Gammaridae)</td>
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<tr>
<td>Differences in sensitivity related to trophic status; reduced leaf decomposition rates suggests shredders sensitive to pollution</td>
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<td>Increase incident of deformity (mentum structure) in Chironomous riparius (Chironomidae)</td>
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<td>Increased incident of deformity (mentum structure) and decreased moultng success in Chironomous riparius (Chironomidae)</td>
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<td>pH-dependent decrease in locomotion of Atyaephyra desmaersti (Crustacea) in AMD solutions</td>
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<td>Locomotion and ventilation of Choroterpes picteti (Leptophaeidae) greater in acid only solutions than in AMD solutions</td>
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<td>pH-dependent increase in locomotion and ventilation of Gambusia holbrooki (Crustacea) in AMD solutions</td>
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<td>pH-dependent decrease in locomotion and ventilation of Atyaephyra desmaerstiti (Crustacea) in AMD solutions</td>
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<td>Contaminated water causes higher locomotory activity in Lumbriculus variegates (Oligochaeta) than contaminated sediment</td>
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<td>Decrease in pH and increase in dissolved metals caused decrease in locomotion and inhibition of feeding rate in Echinogammarus meridionalis (Crustacea)</td>
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<td>Pulse of AMD caused early warning responses in Echinogammarus meridionalis (Crustacea) consisting of increased locomotion and subsequent increase in ventilation</td>
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<td>Average daily moultng rate of Rithrogena hageni (Heptageniidae) decreased after exposure to aqueous copper, cadmium and zinc</td>
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<td>Anomalies in capture nets of Hydropsychidae</td>
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<td>Morphological deformities</td>
<td>Decrease in burrowing rates and increase in crawling and drifting rates of Macomona liliana (Bivalve)</td>
<td>Roper et al. (1995)</td>
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<td>Cross-breeding of Chironomus riparius (Chironomidae) from contaminated and clean rivers revealed some level of genetic adaptation to metals in offspring</td>
<td>Groenendijk et al. (2002)</td>
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<td></td>
<td>Macroinvertebrate drift and respiration significant correlated with metal concentrations</td>
<td>Clements (2004)</td>
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<td></td>
<td>Increased incident of adult and larval deformities in Chironomous tentans (Chironomidae)</td>
<td>Martinez et al. (2004)</td>
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<td>Decreased locomotory activity of Chironomus sp. (Chironomidae) in AMD solutions</td>
<td>Janssens De Bisthoven et al. (2004)</td>
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<td>Metal bioaccumulation</td>
<td>Younger instars had higher metal concentrations than older instars</td>
<td>Krantzberg (1989)</td>
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<td></td>
<td>Concentration of metals in Ephemeropteran species decreased in consecutive larval stages</td>
<td>Jop (1991)</td>
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<td>Metal bioaccumulation dependent on feeding group; shredders and scrapers accumulated the highest metal concentrations (biofilm contained more metals than sediments)</td>
<td>Farag et al. (1998)</td>
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<td>Whole-body metal concentrations of Hydropsyche sp. (Hydropsychidae) greater in species exposed to dissolved metals than in species exposed to AMD precipitates</td>
<td>DeNicola and Stapleton (2002)</td>
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<td>Chironomus februarius (Chironomidae) exhibited adaptation to and tolerance of metal-polluted sediments</td>
<td>Bahrndorff et al. (2006)</td>
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<td>Macroinvertebrate metrics significantly correlated with metals in biofilm, suggesting biofilm is a better index than macroinvertebrates for monitoring metal impacts on aquatic systems</td>
<td>Rhea et al. (2006)</td>
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<td></td>
<td>Whole-body metal concentrations of Hydropsyche sp. (Hydropsychidae) were strongly positively correlated with metal concentrations in water and sediment</td>
<td>Sola and Prat (2006)</td>
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**Effects of environmental parameters on the toxicity of metal mine discharges**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Water hardness and alkalinity</td>
<td>Increased water hardness and alkalinity reduces metal toxicity in Chironomous tentans (Chironomidae)</td>
<td>Gauss et al. (1985)</td>
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<td></td>
<td>Increasing water hardness reduces community sensitivity to metal contamination</td>
<td>Gower et al. (1994)</td>
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<td></td>
<td>Increased water hardness reduces metal toxicity in Daphnia magna (Daphniidae)</td>
<td>Yim et al. (2006)</td>
</tr>
</tbody>
</table>
Metal mixtures

Abundance of heptageniidae, community respiration and macroinvertebrate drift were more sensitive to metal mixtures than single metal solutions

Survival of Diplostomum spathaceum (Diplostomatidae) greater in metal mixtures than in single metal solutions

Community sensitivity greatest in combined metal mixtures compared to single metal solutions

Morley et al. (2002)\(^c\)

Clements (2004)\(^b\)

Other parameters

Increased turbidity reduces metal toxicity to Cladocera by decreasing bioavailability of metals

Inverse correlation between salinity and lesion index of gills in Ruditapes philippinarum (Bivalvia)

Garcia-Garcia and Nandini (2006)\(^c\)

Riba et al. (2010)\(^a\)
<table>
<thead>
<tr>
<th>Name</th>
<th>Mine water type</th>
<th>Brief description</th>
<th>Advantages</th>
<th>Limitations</th>
<th>Example reference(s)</th>
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<tbody>
<tr>
<td>Passive mine water treatment technologies</td>
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<tr>
<td>Aerobic wetlands</td>
<td>Net alkaline ferruginous</td>
<td>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)</td>
<td>Efficient Fe and Al removal; low maintenance requirement; cost-effective; easy integration into landscape and connection with existing ecosystems</td>
<td>Not suitable for highly toxic, sulphate-rich and acidic mine waters; large land surface area requirement; occasional removal of substrate precipitates required</td>
<td>Robb and Robinson (1995); Johnson and Hallberg (2005)</td>
</tr>
<tr>
<td>Anaerobic wetlands</td>
<td>Net acidic ferruginous with high sulphate concentrations</td>
<td>A thick anoxic substrate of saturated organic material neutralises acidity and generates alkalinity through processes of bacterial sulphate removal; some toxic metal concentrations (especially Zn and Cd); large land surface area requirement; occasional</td>
<td>Often used to neutralise acidity and generate alkalinity prior to discharge to aerobic wetlands; efficient Fe and Al sulphate removal</td>
<td>Not suitable for high toxic metal concentrations</td>
<td>Younger et al. (2002); Johnson and Hallberg (2005)</td>
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<tr>
<td>Anoxic Limestone Drains (ALDs)</td>
<td>Net acidic, low Al and Fe, low dissolved oxygen concentrations</td>
<td>Mine water is routed into a buried limestone trench which neutralises acidity and generates alkalinity</td>
<td>Often used to neutralise acidity and generate alkalinity prior to discharge to aerobic wetlands; efficient Fe and Al removal at low concentrations (&lt;2 mg/l)</td>
<td>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 (&lt;2 mg/l) and dissolved oxygen content (&lt;1 mg/l)</td>
<td>Nuttall and Younger (2000); Watzlaf et al. (2000)</td>
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<tr>
<td>Oxic Limestone Drains</td>
<td>Net acidic, low to An open (exposed to the</td>
<td>Often used to neutralise</td>
<td>Not suitable for high toxic</td>
<td>Ziemkiewicz et al. (1997)</td>
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<td>Systems (RAPS)</td>
<td>Reducing and Net acidic Alkalinity</td>
<td>Producing Systems</td>
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<td></td>
<td><strong>Moderate sulphate atmosphere</strong></td>
<td><strong>Limestone trench</strong></td>
<td><strong>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</strong></td>
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<td></td>
<td><strong>Neutralises acidity and generates alkalinity</strong></td>
<td><strong>Metal mine waters; high flow velocities required to prevent Fe and Al precipitation on the limestone</strong></td>
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<td></td>
<td><strong>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</strong></td>
<td><strong>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 (&gt;1</strong></td>
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<td><strong>Not suitable for high toxic metal mine waters; requires significant hydraulic head</strong></td>
<td><strong>Kepler and McCleary (1994); Jage et al. (2001)</strong></td>
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Surface Catalyzed Net alkaline Oxidation Of Ferrous ferruginous Iron (SCOOFI)

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
<table>
<thead>
<tr>
<th>Permeable reactive Barriers (PRBs)</th>
<th>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.</th>
<th>Useful for mine waters which do not emerge at the surface and instead travel as groundwater plumes.</th>
<th>Limited evidence for removal of toxic metals; limited by depth of aquifer.</th>
<th>Benner et al. (1997); Jarvis et al. (2006)</th>
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<tbody>
<tr>
<td>Physical stabilisation of mine wastes</td>
<td>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.</td>
<td>Immobilises contaminants at source and prevents generation of mine drainage.</td>
<td>Clay caps tend to crack in arid and semi-arid regions from wetting and drying cycles resulting in failure of air-tight cap.</td>
<td>Gandy and Younger (2003); Waygood and Ferriera (2009)</td>
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<tr>
<td>Method</td>
<td>Description</td>
<td>Advantages</td>
<td>Disadvantages</td>
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<tr>
<td>Chemical stabilisation</td>
<td>Addition of a resinous adhesive to form a crust over the mine waste.</td>
<td>Immobilises contaminants at source and prevents generation of mine drainage</td>
<td>Similar to clay caps, crusts are prone to cracking resulting in failure of air-tight cap.</td>
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<td>Phytostabilisation</td>
<td>A vegetative cap on the mine waste to immobilise contaminants by adsorption and accumulation in the rhizosphere.</td>
<td>Immobilises contaminants at source and prevents generation of mine drainage; creates wildlife habitat</td>
<td>Concerns over bioavailability of contaminants to wildlife; need for metal tolerant plants</td>
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<tr>
<td>Phytoextraction</td>
<td>A vegetative cap on the mine waste to immobilise contaminants through hyperaccumulation in plant tissues.</td>
<td>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</td>
<td>Concerns over bioavailability of contaminants to wildlife</td>
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and forestry use