

# Attenuation of mining-derived pollutants in the hyporheic zone: a review

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## Abstract

Mine water pollution is a major cause of surface- and groundwater pollution in former mining districts throughout Europe. It is a potential barrier to achieving good status water bodies, which is a requirement of the EU Water Framework Directive. In the UK, a concerted effort has been made over the last decade or so to address the scientific and practical challenges relating to the remediation of mine water pollution. However, most of this work has focused on remediation of point sources of pollution (typically arising from abandoned mines and shafts), while the behaviour of mine water at the groundwater - surface water interface (the “hyporheic zone”) has received far less attention in relevant scientific and engineering literature. The extent of mine water pollution and capacity for its attenuation at the hyporheic zone has not been well quantified while, furthermore, the complex chemical and microbial processes occurring there (specifically with reference to mining-derived pollutants) have not been investigated in any depth. The absence of such data may relate, in a large part, to the difficulty in physically measuring volumes and concentrations associated with these river inputs / exports. A far greater body of literature addresses biogeochemical processes at the hyporheic zone (especially relating to manganese), albeit many such articles relate to aqueous metal dynamics in general, rather than mine water

specifically. This paper presents a review of the natural attenuation processes that may limit the movement and availability of mining-derived pollutants at the groundwater – surface water (GW-SW) interface, and specifically within the hyporheic zone. A substantial part focuses on precipitation and adsorption processes at the hyporheic zone, as well as discussing the role of microbial processes in governing metal ion mobility.

## **Keywords**

Mine water; pollution; hyporheic; attenuation; aquifer; river

## **Introduction**

Discharges from abandoned mines and spoil heaps are a major source of surface- and groundwater pollution worldwide. The Environment Agency's 'initial characterisation' of water bodies in England and Wales for the Water Framework Directive (WFD) indicated that mine water pollution is one of the most significant causes of water bodies being at risk of failing their WFD environmental objectives ([www.environment-agency.gov.uk](http://www.environment-agency.gov.uk); Potter and Jarvis, 2006). After diffuse agricultural pollution, mining poses the most widespread pollution threat to status objectives in England and Wales. The assessment estimated that 26 out of 356 groundwater bodies (7.3%, but 14% by land surface area) and 226 out of 5868 surface water bodies (3.9%, but 7% by river length) are 'at risk' due to mine water pollution. Mine waters are typically rich in metals such as iron, manganese, copper and zinc, and may also be highly acidic (Younger, *et al.*, 2002). Left uncontrolled, they can cause severe faunal impoverishment in receiving watercourses (e.g. Scullion and Edwards, 1980; Jarvis and Younger, 1997).

Understanding attenuation processes at the GW-SW interface is important for WFD implementation. It is needed to a) assess and predict the future behaviour and

consequences of mine pollutants as they migrate through catchments, and b) provide a basis for developing effective ‘programmes of measures’ to restore poor status surface water bodies. Past focus on mine water pollution has been largely directed at point discharges to rivers (e.g. from adits). The WFD requires more integrated management of groundwater and surface water, and the transitional zone becomes important in understanding and managing indirect fluxes to rivers via groundwater, and for understanding the behaviour of pollutants during stream – hyporheic exchange. Diffuse, groundwater-fed pollution of rivers may be caused by the discharge of polluted groundwater rising in previously de-watered aquifers, and by the discharge of leachate from mine spoil heaps via the shallow subsurface. Mullinger (2004) describes how diffuse discharges account for 30 – 40% of the zinc, cadmium and copper entering the surface water systems around the Cwm Rheidol mine (west Wales), but for silver, diffuse discharges contribute around 91% of the flux. In north east England, Mayes *et al.* (2005) calculated that the majority of the iron export from a former coal field to the river Gaunless was by diffuse processes. Hames and Sabine (1998) similarly reported ca. 35% of the iron in rivers draining Welsh coalfields was from diffuse sources.

The term ‘hyporheic zone’ has various detailed definitions depending on the discipline within which it is being considered. However, the general consensus is that it refers to the water saturated transitional zone between surface water and groundwater (Smith, 2005), across which there is exchange of water (Bencala, 2005). The hyporheic zone is often divided into two zones, the “surface hyporheic” zone, composed of water which is almost identical in chemical composition to the surface water, and the “interactive hyporheic” zone, which is a mixing zone composed of

between 10% and 98% surface water (Triska *et al.*,1989). In recent years, the hyporheic zone has been increasingly recognised as a distinct biogeochemical environment and has its own distinct biota, termed the “hyperheos” (Jones and Mulholland, 2000; Hancock, 2002). Ecologists have established the importance of this zone, not only as a biologically rich ecotone, but also as a significant interface to the entire river’s ecology (Brunke and Gonser, 1997). It is a unique habitat (Biksey and Gross, 2001), and represents a transition zone between groundwater and surface water ecosystems. The microbial community within the hyporheic zone provides a food base for small organisms, which in turn provide food for benthic macroinvertebrates, while the zone itself provides a refuge from predators. In addition, advection and diffusion-facilitated cycling of nutrients and carbon between the groundwater and surface water ecosystems allow the hyporheic zone to act as both a source and sink of nutrients, potentially regulating biotic productivity (Moser *et al.*, 2003). Studies of biologic communities in hyporheic zones have shown that they are important sites of refuge, dwelling and development for freshwater fauna (Nagorski and Moore, 1999).

The flux of acidic, metal-rich waters into the hyporheic zone can have an adverse impact, not only on the hyporheic zone, but on the ecology of an entire river. As pointed out by Biksey and Gross (2001), the hyporheic zone is particularly vulnerable since it is exposed to up-welling groundwater contaminants before they reach, and are subject to dilution within, the surface water ecosystem. The sudden influx of toxic metals can result in the death of hyporheic organisms (Brunke and Gonser, 1997). Nelson and Rioline (1999) studied the recovery of a hyporheic invertebrate community structure in a river recovering from metals contamination and concluded that, despite efforts to remediate surface water pollution, community recovery in the

hyporheic zone may take longer than surface macroinvertebrate recovery due to the continued release of metals by reductive dissolution. A similar conclusion was reached by Jarvie et al. (2005) and Neal et al. (2005) relating to the release of phosphorus from river bed sediments.

Biogeochemical processes taking place within the hyporheic zone can impact the fate and transport of mining-derived pollutants. Important transformations occur that can influence the chemistry of both the overlying surface water and the underlying groundwater (Bourg and Bertin, 1993). In some cases, the hyporheic zone can act as a barrier between surface water and groundwater, preventing or retarding the movement of pollution from one to the other (Benner et al., 1995). The extent of natural attenuation in a stream is dependent on the accessibility of zones favourable for relevant natural attenuation reactions to reactive solutes. In this way, exchange of surface water in the hyporheic zone can enhance metal attenuation by transporting metals into zones where removal processes are more favourable (Fuller and Harvey, 2000). The zone can act as a filtering mechanism to pollutants, allowing precipitation or sorption of dissolved minerals and metals. This is enhanced due to the flow of surface water in the hyporheic zone increasing the effective reactive site density per volume of surface water by providing contact of dissolved metals with potential reaction or sorption sites (Fuller and Harvey, 2000).

A complete knowledge of the processes taking place within the hyporheic zone requires a multi-disciplinary approach and, with this in mind, this review draws on work undertaken in a wide range of disciplines, including hydrology, hydrogeology, microbiology and ecology, as well as pollutant transport and hydrogeochemical

studies. Such processes vary depending on the nature of the pollutants involved, but for mining-derived pollutants they are principally sorption, complexation and precipitation reactions, together with dilution and mixing processes. Although mine water discharges from point sources are well documented, and the fate of metals and acidity from such discharges as they enter surface water and groundwater have been extensively studied, the scope of this review is the passage of mine water through permeable riverbed sediments (i.e., the hyporheic zone).

### **Pollutant attenuation and release processes in the hyporheic zone**

#### *Precipitation and adsorption processes*

#### The importance of redox conditions

A number of authors have studied the precipitation and adsorption processes which take place during the exchange of metals between groundwater or surface water and the hyporheic zone. Some of these studies investigate the attenuation of mining-derived pollutants while others investigate heavy metals in general. Precipitation and adsorption processes are dependent upon redox conditions. A redox scale is shown in Fig. 1 which gives sequences of redox processes at different values of Eh, calculated in this case at pH 7 and 25°C. Notwithstanding the important influence of pH, discussed later in this article, it is generally observed in natural environments that redox processes proceed sequentially from the highest energy yield downward (Appelo and Postma, 1993). In Fig. 1, the oxidised species or phase incorporating the element is shown on the left hand side of the scale while the reduced form is on the right. It is thermodynamically favourable to transfer electrons from a reduced species

to an oxidised species that lies higher on the scale. Therefore, changes in key elements occur with changes in redox potential.

#### Precipitation of iron and manganese oxides

Manganese is often not the most toxic metal in mine water discharges but its importance within the hyporheic zone is clearly evident from work carried out by a number of authors (e.g. Harvey and Fuller, 1998; Fuller and Harvey, 2000; Bourg and Bertin, 1993; Benner *et al.*, 1995). As well as microbially enhanced oxidation of dissolved manganese (to form manganese oxide precipitates) (Harvey and Fuller, 1998), manganese oxidation continuously produces new sorption sites, in the form of manganese oxide coatings on sediments, which enhance removal of trace metals (Fuller and Harvey, 2000). This is based on the affinity of metals for sorption or co-precipitation by manganese oxides, and suggests that manganese oxides are an important sorbent phase within the hyporheic zone. Similarly, iron oxides have also been found to be important sorption sites within the hyporheic zone, particularly for arsenic (Nagorski and Moore, 1999) and uranium (Winde and Van der Walt, 2004). However, Fuller and Harvey (2000) noted the absence of dissolved iron, and the presence of low colloidal iron concentrations, which suggests, at least in their study, that iron oxides have a minor role to play in the uptake of metals in the hyporheic zone. The authors also suggest that the ongoing formation of manganese coatings has probably covered any pre-existing iron oxide surfaces. It is certainly not the case that hydrous ferric oxide (HFO) has a minor role in all streams investigated. HFO is a major precipitate on the bed sediment, and in the hyporheic zone, of the streams studied by Benner *et al.* (1995) (see below) and Mayes *et al.* (2005). Given that iron is often the major metal contaminant of discharges from abandoned coal mines, its

potential importance in influencing the behaviour of other ions should never be ruled out.

Oxidation of dissolved manganese, to form manganese oxide precipitates, is thought to be enhanced by the input of stream water to the hyporheic zone as it increases the contact of aerobic stream water with sediment and microbes, i.e. reaction surfaces and mediators (Harvey and Fuller, 1998). In addition, the input of streamflow raises the pH and dissolved oxygen concentration in the hyporheic zone, which further stimulates the rate of manganese oxidation (Fig. 2). The change from a reducing environment in groundwater to well oxygenated river water, with mixing within the pores of the hyporheic sediments causing dissolved iron and manganese in groundwater to become oxidised and precipitate, is also described by Winder and Van der Walt (2004) and Wielinga *et al.* (1999). It appears most likely, from Harvey and Fuller (1998)'s work, that oxidation of dissolved manganese occurs in contact with surface coatings on sediments such as iron oxides or manganese-oxidising bacteria, each of which potentially has a role in catalysing the reaction. Uptake of dissolved manganese by stream sediments occurs by reversible and irreversible processes. Reversible uptake of dissolved manganese (in the form of  $Mn^{2+}$ ) includes uptake by adsorption and cation exchange, while irreversible uptake is due to oxidation of  $Mn^{2+}$  to  $Mn^{3+}$  or  $Mn^{4+}$ , which is enhanced by the presence of oxide surfaces or by microbial processes. These oxidation states ( $Mn^{3+}$  and  $Mn^{4+}$ ) are highly insoluble at the pH and dissolved oxygen concentration typically present within the hyporheic zone, so oxidation, rather than reductive dissolution, is favoured (Harvey and Fuller, 1998).

Extensive orange, iron-rich coatings were observed by Benner *et al.* (1995) on the stream bed of a small creek in western Montana, which is underlain by acidic, metal-rich groundwater, as well as within the hyporheic zone, indicating precipitation of iron oxides to a depth of 80cm. Below this depth, iron concentrations were found to be elevated in the aqueous phase but low in the solid phase, suggesting that the boundary between the hyporheic zone and groundwater is also the geochemical boundary of iron oxide stability (Fig. 3). It is predicted that this phase change may be induced by a change in redox potential or pH, or a combination of the two, as both decrease with depth. A similar pattern was observed by Nelson and Rioline (1999), with metals present in the aqueous phase in deep sediments and precipitated onto substrate near the surface. Manganese, on the other hand, was shown by Benner *et al.* (1995) to accumulate in the stream sediment and surface hyporheic zone but only to a small extent in the interactive hyporheic zone, indicating that the manganese oxide stability boundary lies at the transition between surface water and the hyporheic zone (Fig. 3). In addition, high aqueous manganese concentrations were noted in the groundwater and interactive hyporheic zone but low concentrations in the surface water and surface hyporheic zone, an observation also made by Nelson and Rioline (1999).

#### Adsorption of metals onto iron and manganese oxides

Significant uptake of dissolved metals during interaction of groundwater and surface water with hyporheic zone sediments has been noted by a number of authors, particularly in relation to iron and manganese oxides acting as sorbent phases. Over a 5.3 km reach of a mine water contaminated creek in Arizona, studied by Fuller and Harvey (2000), a net attenuation of metals was observed, ranging from 12 to 68%

(depending on flow and climatic conditions), which was attributed to metal uptake, by sorption to manganese oxides, in the hyporheic zone. The average metal removal into the hyporheic zone on the reach was: manganese 22%, cobalt 52%, nickel 27% and zinc 36%. Consistent with these observations, concentrations of cobalt, nickel, zinc and manganese were typically elevated by a factor of two or more in bed sediments of the active hyporheic zone, compared to deeper sediments. The depth range of elevated sediment metal concentrations (less than 15cm) coincides with the zone where reactive metal uptake was calculated and is consistent with metal uptake occurring within the streambed. It should be noted that the percentage manganese uptake calculated by Harvey and Fuller (1998), and that subsequently calculated with a new data set (Fuller and Harvey, 2000), varied substantially; an average manganese uptake of ~ 9% using the 1994 and 1995 data, but an average of 22% using the 1997 data (above). In this case, this is attributed to the higher pH of the surface waters during the 1997 survey (Fuller and Harvey, 2000). More generally, however, this is illustrative of the potential for substantial temporal and spatial variability of the relative importance of processes in the hyporheic zone. The work of Harvey and Fuller (1998) and Fuller and Harvey (2000) was all conducted in May and June, presumably when hydrological conditions were similar, but Mayes *et al.* (2005) and Gozzard *et al.* (2006) have illustrated how metal concentrations and fluxes may vary significantly on a seasonal basis. Therefore, there appears to be a need to recognise this potential for spatial and temporal variability, particularly when interpreting the results of discrete studies for the purposes of large-scale water management (e.g. in the pursuit of meeting EU WFD objectives).

Benner et al. (1995) noted the removal of cadmium, copper and zinc from solution within the interactive hyporheic zone (Fig. 3). As the precipitation of solid phase minerals containing these elements is unlikely, they believe their removal to be the result of adsorption onto iron oxyhydroxides. Measurable concentrations of arsenic and lead were also found within stream sediments and the interactive hyporheic zone, despite not being detected in solution, suggesting that these elements are also undergoing precipitation / adsorption within the interactive hyporheic zone. In the same way, Wielinga et al. (1999) noticed a marked increase in zinc and manganese associated with iron hydroxide layers in the hyporheic zone and Bencala et al. (1990) observed adsorption of manganese and zinc onto previously precipitated hydrous oxides in the streambed of an acidic and metal-rich mountain stream in Colorado, resulting in small losses of these solutes from the stream. The importance of HFO as a sink for other metals would appear to relate to the absolute concentration of iron in the stream under investigation, and therefore its propensity for non-conservative behaviour; the concentration of iron in the stream investigated by Fuller and Harvey (2000), who conclude that it is of limited importance as a sink for other metals, is at least an order of magnitude lower than the iron concentrations in the streams studied by Bencala et al. (1990) and Wielinga et al. (1999).

Nagorski and Moore (1999) discovered iron precipitation zones at the streambed-surface water interface of the same Montana creek as studied by Benner et al. (1995), with elevated metal and arsenic concentrations associated with the precipitation zones. Since the dissolved arsenic concentrations are significantly lower in both the surface water and groundwater, the authors believe that the elevated concentrations in the hyporheic zone can not be generated by simple physical mixing and suggest they

arise from chemical reactions within the hyporheic zone substrate, involving the contaminated sediments. This reflects how pH-controlled adsorption-desorption reactions, along with redox conditions (a change from oxic surface water to anoxic, acidic groundwater), strongly control the movement of arsenic and iron species between dissolved and solid phases. The authors believe that sorption onto iron oxyhydroxides transfers arsenic from the aqueous phase to the particulate phase and manganese oxyhydroxides catalyse redox reactions transforming soluble arsenic (III) to the less toxic particulate arsenic (V) (Fig. 4). In the creek studied, manganese and iron oxyhydroxides with bound arsenic are readily supplied to the streambed by eroded floodplain sediments largely composed of oxidised mine tailings. Under anoxic-sulphidic conditions, arsenic (III) sulphides transform into arsenic (V) particulates, including minerals such as arsenopyrite. Smedley and Kinniburgh (2002) conducted a thorough review of arsenic behaviour in natural waters, and confirm the importance of iron oxide as an adsorbant for arsenic. Amorphous ferric hydroxide has a particular affinity for arsenic (Smedley and Kinniburgh, 2002), which is significant in mine drainage since large accumulations of amorphous HFO are typical of streambeds affected by poor quality mine drainage. Reductive- and acid-dissolution may lead to subsequent release of arsenic from iron oxide and HFO, and Kiemowitz *et al.* (2005) recently noted the potential for temporal variations (from diurnal to annual) in sediment-bound arsenic flux.

Uranium attenuation has also been observed in hyporheic sediments (Winde and Van der Walt, 2004) as it migrated, along with other heavy metals, from tailings deposits of gold mines, via groundwater, into rivers. This retardation is thought to be triggered by either redox-initiated co-precipitation of uranium in the matrix of precipitating iron

and manganese oxides and hydroxides, or by adsorption onto the large reactive surface area of freshly precipitated gels. The authors also regard varying pH and Eh conditions to be influential in the mobility of uranium, with pH affecting precipitation of iron- and manganese oxides and hydroxides, and thus uranium removal, as well as controlling the adsorption of uranium onto precipitated gels. As the freshly precipitated gels are protected from fluvial erosion, being within sediment pores, the hyporheic zone acts as a medium- to long-term sink for these metals, thereby reducing stream pollution (Winde and Van der Walt, 2004).

#### *Reductive dissolution of iron and manganese oxides*

Changes in redox conditions during infiltration of contaminated river water into an alluvial aquifer can lead to the reductive dissolution of iron and manganese oxides in reduced zones within the hyporheic zone (Bourg and Bertin, 1993). An important mediator in the dissolution of these oxides, as shown by Bourg and Bertin (1993, 1994) and Wielinga *et al.* (1999), is biological activity within the sediments. Respiration by micro-organisms, and oxidative degradation of organic matter, leads to the creation of a reduced zone in which dissolved oxygen is consumed and other species, e.g. dissolved iron and manganese, produced (Bourg and Bertin, 1993). In the study undertaken by Bourg and Bertin (1994), located in south west France, a threshold temperature of 10°C was found to be necessary to trigger the bacterial activity. The microbial reduction of iron and manganese oxides can result, however, not only in the release of iron and manganese, but a wide variety of toxic metals that have previously sorbed to, or co-precipitated with, the oxides (Wielinga *et al.*, 1999). An example is the release of arsenic sorbed or co-precipitated to iron oxides which

underwent reductive dissolution, as observed by Nagorski and Moore (1999). This had the effect of increasing total arsenic concentrations and encouraging the reduction of arsenic (V) to the more toxic arsenic (III) (Fig. 4).

Further along the pathway, when microbial action decreases, and additional oxygen can be supplied by diffusion through the permeable unsaturated zone, the water environment may become oxidised again, leading to the removal of metals from solution by a combination of oxidation, precipitation and adsorption reactions, as observed by e.g. Harvey and Fuller (1998), Fuller and Harvey (2000) and Benner *et al.* (1995).

#### *Diurnal variations in stream contamination*

Several authors have noted diurnal differences in stream contamination, with higher metal concentrations at night. Brick and Moore (1996) suggest that this is due to changes in biogeochemical processes within the hyporheic zone, resulting from variations in pH and dissolved oxygen concentration at night. Nimick *et al.* (2003) identify instream geochemical processes, such as groundwater exchange, manganese redox reactions and adsorption as likely causes of diel variation. More recently, however, Shope *et al.* (2006) suggest that streamflow and hyporheic exchange are not in fact the cause of such diel variation, but ascribe the phenomenon to the influence of the solar cycle on pH and water temperature. Winde and Van der Walt (2004) can explain their observed high metal concentrations at night by the discharge of contaminated groundwater into the river during high stream flow conditions (due to

pumping-related flow conditions within the catchment) at night, with the reverse occurring under low stream flow conditions during the day.

Such diurnal fluctuations in metal concentrations may have important implications for sampling exercises for the purposes of river water quality regulation. For example, with the introduction of the WFD in the European Union, the question arises as to whether achievement of ‘good chemical and ecological status’ will be demonstrable with current sampling strategies, which are understandably based on samples collected during daylight hours? In some catchments, what might appear to be good chemical status may not be reflected in good ecological status if there are substantial increases in ecotoxic metal concentrations during the night. Therefore, in some river basins, particularly those affected by mining-related pollution, and where (biotically-mediated) hyporheic processes are deemed important (cf Brick and Moore, 1996), periodic sampling exercises to identify diurnal variation in metal concentrations may be necessary.

#### *Hydrological and geomorphological controls*

The passage of mining-derived metals through the hyporheic zone is controlled by hydrological exchange processes between surface water and groundwater. These may range from local up- and down-wellings determined by geomorphological features, such as streambed topography, to large scale exchange processes determined mainly by the geological and hydrological properties of the catchment (Brunke and Gonser, 1997). The process of colmation (i.e. clogging of the top layer of the channel sediments), which includes all processes leading to a reduction of pore volume and

decreased permeability of the streambed, can hinder exchange processes between surface water and groundwater and may affect the passage of mining-derived pollutants through the hyporheic zone (Brunke and Gonser, 1997).

Several authors have studied the effects of different sediment types on pollutant attenuation in the hyporheic zone. Brunke and Gonser (1997) show how the grain size and porosity of the sediment layers determine the permeability of the hyporheic zone while Walling et al. (2003) highlight the control of sediment grain size on retardation, storage and transport in different river catchments. Similarly, Younger et al. (1993) point out that a fine grain size provides a low hydraulic conductivity while a high clay and organic matter content makes the sediments highly sorptive. In fact, Younger et al. (1993) consider that the effect of organic matter on sorption is so great that where the organic content of a sediment exceeds 1% by weight, the contribution of mineral surfaces to the total sorption in the sediment is negligible. However, it should be pointed out that this is only likely to be the case for organic contaminants and may not apply to mining-derived pollutants.

Colloids are normally assumed to be readily transported without deposition but Ren and Packman (2002, 2004a, 2004b) show how they can have a significant effect on pollutant transport as they are often transported into, and deposit within, streambeds, due to a combination of physical and chemical mechanisms. These exchanges with the subsurface can result in bed sediment and pore water becoming a significant reservoir for storage of pollutants within a stream system. Since colloidal particles have a large reactive surface area, the authors believe that they can carry contaminants that would otherwise be transported primarily as dissolved species. The amount of

sediment deposited is primarily controlled by the local hydrological and geomorphological conditions, which can result in a situation where a downstream decrease in metal content of channel bed sediment (related to distance from source) is offset by a downstream increase in the amounts of sediment stored (Walling *et al.*, 2003)

### *Microbiological processes*

Over the past two decades, studies on the hyporheic zone have shown that this is a region of high biological activity, and that these processes are very important to stream ecosystem function. To date, however, there have been relatively few studies performed which look directly at hyporheic ecology and microbial processes, as microbial ecologists have tended to focus their attentions on riverbed, lake, marsh / wetland and marine sediments (Storey *et al.*, 1999). Studies of the microbiology of the hyporheic zone have principally focused on microbial productivity, since the microbial diversity of this environment is anticipated to be high (due to reduced groundwaters meeting aerobic surface waters, providing a range of environmental conditions for interstitial organisms, e.g. McClain *et al.* (1994), Jones *et al.* (1995), Storey *et al.* (1999)).

Bacterially-mediated oxidation (and reduction) of iron and manganese is widely cited as a potentially significant mechanism of immobilisation of these metals (see, for example, Madigan and Martinko (2006) for a summary). In the very broadest terms, there are two routes by which iron may be oxidised in the presence of microbial communities: aerobic oxidation of ferrous iron by *Acidithiobacillus ferrooxidans* and

Leptospirillum ferrooxidans, and the precipitation of iron oxides on the sheaths of sheathed bacteria, of which Leptothrix is the most commonly cited (Madigan and Martinko, 2006). The latter mechanism is particularly prevalent in locations where there is a rapid change from anoxic to oxic conditions (Emerson and Revsbech, 1994), and therefore we might anticipate the presence of such precipitates across the anoxic-oxic interface of the hyporheic zone. However, as Emerson and Revsbech (1994) point out, there have been very few studies of the relative importance of direct microbial oxidation of iron and precipitation on bacterial sheaths.

Manganese and iron are not thought to contribute significantly to the productivity of the hyporheic zone, despite the sometimes obvious evidence of iron- and manganese-oxidisers (in the form of visible metal precipitates). Wielinga *et al.* (1994) found that the precipitation of iron oxides throughout the hyporheic zone was largely generated abiotically, whereas manganese oxidation in the hyporheic zone of the same stream was predominantly microbially-mediated. By contrast, sulphur-oxidisers may play a major role in microbial productivity, presuming conditions in the hyporheic zone are initially amenable to the reduction of sulphate (i.e. for circumneutral waters, redox potential of below -150 mV) (Storey *et al.*, 1999). We might, therefore, anticipate that the hyporheic zones of mine water-impacted rivers may have a particularly abundant microbial community, but the authors are aware of no literature that explicitly examines this hypothesis.

The most detailed investigations of the microbial dynamics of metal-impacted watercourses have been undertaken by Feris *et al.* (2003, 2004a, 2004b). Their work has focused on establishing the influence of heavy metal contamination on microbial

community structure, rather than investigating the role of such microbial groups in attenuating or mobilising metal contaminants in the hyporheic zone (cf. Wielinga *et al.*, 1994). A strong positive correlation was identified between heavy metal contamination and community structure. Communities responded rapidly to exposure to elevated metal loads (less than 7 days). However, communities also recovered from these metal treatments, albeit different phylogenetic groups recovered to differing degrees, and in a unique manner. Feris *et al.* (2004b) suggest that these microbial communities may respond to metal loads that vary by an order of magnitude less than those necessary to induce a measurable response from benthic macroinvertebrates, and therefore such organisms may be a very sensitive indicator of pollution. A potential disadvantage of such organisms as indicators of pollution is that such an assessment requires high cost, time-consuming, laboratory techniques, whereas assessment by macroinvertebrate community abundance and diversity is a quick, low-cost, system that requires relatively limited expertise.

## **Conclusions**

Although the hyporheic zone has been recognised for a number of years as an important biogeochemical interface between groundwater and surface water, there has been little specific focus on its role as an environment for mobilisation and / or attenuation of metal pollutants. The existing literature certainly suggests that the hyporheic zone may be an important sink for metal pollutants, but investigations have not been sufficiently detailed, to date, to understand fully how the processes occurring vary spatially and temporally.

A fundamental problem is that there appears to have been no concerted effort to quantify the extent to which the hyporheic zone serves as either a source of, or sink for, metal contamination. This omission is probably, in large part, due to the difficulty of physically measuring the volumes of water transferred across the hyporheic zone (under differing hydrological conditions), and the metal loads associated with these fluxes. Consequently, the best information available in this regard is anecdotal evidence from those river basins that have previously been the subject of detailed investigations of mine water pollution. The hyporheic zone may play an important role in dictating the contribution of diffuse sources of mine water pollution to rivers, but this is not clear as yet. Recent work by Mayes *et al.* (2005) for the river Gaunless, in north east England, suggests that diffuse mining-related pollution may make a very significant overall contribution to the loading of metals to this river, principally because mine water rebound in the area, which was complete by the early 1980's (Younger, 2000), has resulted in a very shallow water table. It is hoped that it will be revealed as part of this ongoing research, at least for one catchment in the north east of England, the extent of mine water pollution at the hyporheic zone, on a catchment scale.

In terms of specific metals, the fate of manganese in the hyporheic zone has received the most attention, possibly because its attenuation is microbially-mediated. The major pollutant of most mine water, iron, on the other hand, has received less attention in the literature. There is clear evidence in stream sediments that oxidation and precipitation of iron is occurring in the hyporheic zone, in the form of red oxide crusts, but little insight into the specific processes and rates that control its fate. Similarly, little research has been undertaken into the fate of other, potentially

important, metals in the context of mine water pollution, such as zinc, copper and lead. Adsorption, precipitation and microbial processes appear to be central to the fate of these contaminants, but the precise mechanics and reaction rates are not currently clear.

From the literature reviewed here, a set of generic conditions can be defined for the attenuation or release of mining-derived pollutants within the hyporheic zone (Fig. 5). In general, the hyporheic zone represents a mixing zone where high pH and high dissolved oxygen concentrations within surface waters meet low pH and low dissolved oxygen concentrations within groundwater. The increase in dissolved oxygen from surface water stimulates the activity of aerobic micro-organisms which increase the rate of iron and manganese oxidation. Simultaneously, other metals (such as zinc, arsenic, copper) are co-precipitated (or adsorbed) along with the iron and manganese oxides. Alternatively, following respiration by micro-organisms, and oxidative degradation of organic matter, dissolved oxygen may become depleted within the hyporheic zone, and reducing conditions are generated. This encourages the dissolution of iron and manganese oxides and the associated metals previously adsorbed to them, leading to the release of metals into solution. Further along the pathway, where redox conditions may change and become oxidising, metal precipitation and adsorption will again take place.

The literature reviewed here illustrates the hyporheic zone to be an important environment for the release and attenuation of metal contaminants. Quantification of pollutant attenuation and release in the hyporheic zone is clearly difficult, requiring capital intensive instrumentation and monitoring facilities. The situation is further

complicated by diurnal and seasonal variations in contaminant fluxes. However, such investment may well pay dividends. The hyporheic zone may play a crucial role as a source of diffuse pollution in river catchments affected by mining activities, but also as a sink for point source surface discharges. In meeting the increasingly stringent limits of metal concentrations imposed by national and international legislation, fully understanding these processes could be essential. Furthermore, the effective immobilisation of metals in the hyporheic zone, reported in some of the literature reviewed here, may provide important guidance in terms of new developments in passive treatment technologies for mine water pollution remediation (see Younger *et al.*, 2002 for a thorough review of passive treatment technologies). For example, re-creation of the particular geochemical conditions that encourage the immobilisation of manganese, and co-precipitation of metals such as zinc and nickel (Fuller and Harvey, 2000), might offer treatment solutions for the remediation of waste streams containing such metals which, to date, have proven difficult to attenuate by passive means.

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## Figure Captions

Figure 1 A redox scale showing the various redox couples of specific elements at varying Eh values

Figure 2 Schematic diagram showing factors that enhance oxidation of manganese within the hyporheic zone (modified from Harvey and Fuller, 1998, by permission of American Geophysical Union)

Figure 3 Chemical conditions within the hyporheic zone of Silver Bow Creek, Montana, where SHZ is the surface hyporheic zone and IHZ is the interactive hyporheic zone (after Benner *et al.*, 1995)

Figure 4 Effect of changes in redox conditions on arsenic mobility in the hyporheic zone

Figure 5 Generic redox and pH conditions for attenuation or release of mining-derived pollutants within the hyporheic zone

Figure 1

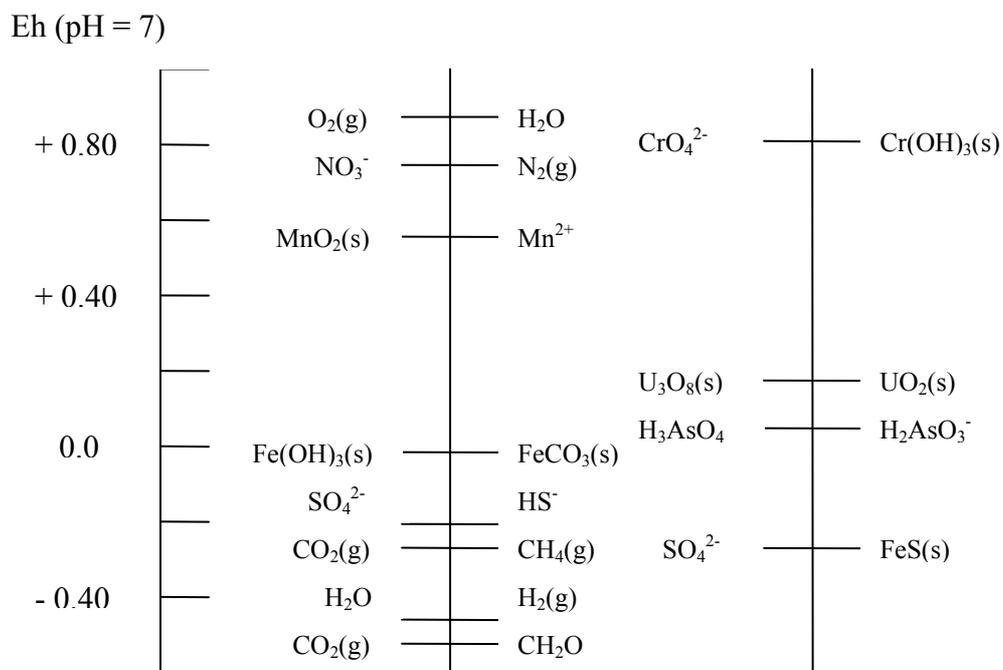


Figure 2

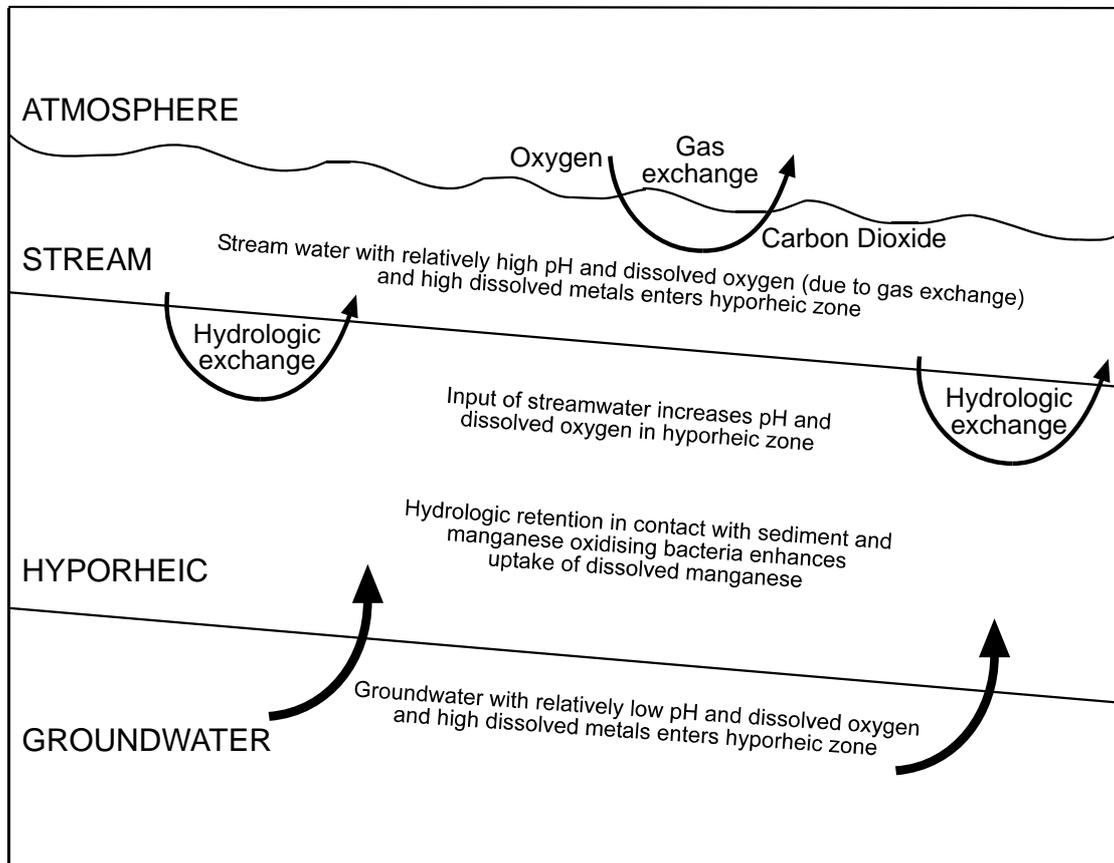


Figure 3

Surface water		Fe oxides		
OXIDISING	pH 7.8-9.1	Mn oxides		
SHZ	pH 7.8-7.9	Fe oxides	Mn oxides	Boundary Mn oxide stability
		Fe oxides		
IHZ	pH 6.2-6.9	dissolved Mn		
		$Cd_{(s)}$ , $Cu_{(s)}$ , $Zn_{(s)}$		
Groundwater		dissolved Fe		Boundary Fe oxide stability
	pH 4.4-4.9	dissolved Mn		
REDUCING		$Cd_{(aq)}$ , $Cu_{(aq)}$ , $Zn_{(aq)}$		

Figure 4

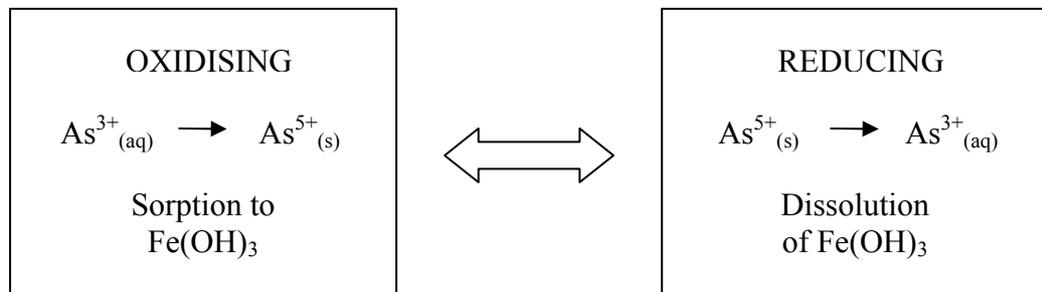


Figure 5

