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Attenuation of mine pollutants in the hyporheic zone

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Steve Killeen

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Executive Summary

Mine water pollution is a major cause of surface water and groundwater pollution in former mining districts of England and Wales, and consequently represents a potential barrier to the successful implementation of the EU Water Framework Directive. A concerted effort has been made over the last decade to address the scientific and practical challenges of cleaning up mine water pollution in the UK. However, the vast majority of this work has focused on point sources of pollution, which typically arise from abandoned mine adits and shafts. This report has been commissioned to review our current understanding of mine water behaviour at the hyporheic zone - the zone between surface water and groundwater - since this has received far less attention in the scientific and engineering literature. The extent of mine water pollution and its attenuation at the hyporheic zone has not been quantified. Furthermore, the complex chemical and microbial processes occurring at the groundwater-surface water interface have not been investigated in any detail with reference to mine water pollution.

The absence of data on mine water pollutants in the hyporheic zone may well relate to the difficulty of physically measuring volumes and concentrations associated with the movement of pollutants. A far greater body of literature addresses biogeochemical processes at the hyporheic zone (especially relating to manganese), although many articles cover aqueous metal dynamics generally rather than mine water pollution specifically. A substantial part of this review therefore focuses on precipitation and adsorption processes at the hyporheic zone, as well as discussing the role of microbial processes in governing metal ion mobility. Section 3.4 of this report reviews the methods employed to characterise these biogeochemical processes.

The hyporheic zone is a region in which high concentrations of metals may be present. For this reason, and because the hyporheic zone is often an important zone for benthos, Section 4 of this report reviews the biological impacts of mine pollution in the hyporheos.

The report reveals gaps in this field of research, where further studies are required to answer the following questions:

- How important, quantitatively, is the hyporheic zone in governing the overall loading of metal contaminants to rivers, and how does it affect the proportions of mine pollution arising as point sources or diffuse sources?
- What are the key biogeochemical processes, and associated rates, that result in the attenuation of metals in the hyporheic zone, and could these processes be recreated in a treatment system to remove some of the 'problematic' metals such as manganese (Mn), zinc (Zn) and lead (Pb)?
- What is the most appropriate, and accurate, method for monitoring the hyporheic zone to answer these questions?
- Is it feasible to resolve the scale-dependence of these biogeochemical processes, in order to understand the role of the hyporheic zone in mine water-affected freshwaters for entire catchments?

Contents

1 Introduction

This report reviews our knowledge of processes occurring at the hyporheic zone, or groundwater-surface water interface, relating to mine pollutants. It describes the importance of these processes for pollutant attenuation in both up-welling areas, where groundwater moves upward into streams, and down-welling areas, where stream water infiltrates through the bed sediment into the groundwater, or aquifer, below. Complete knowledge of the processes taking place within the hyporheic zone requires a multi-disciplinary approach; thus, the report draws on work in a wide range of disciplines, including hydrology, hydrogeology, microbiology and ecology, as well as pollutant transport and hydrogeochemical studies.

The term 'hyporheic zone' has various definitions depending on the discipline with 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). A number of processes (physical, chemical and biological) take place within it and can reduce or attenuate pollutant concentrations and masses. These processes vary depending on the nature of the pollutants, but for mining-derived pollutants they principally involve sorption, complexation and precipitation reactions as well as dilution and mixing processes.

Discharges from abandoned mines and spoil heaps are a major source of water pollution worldwide. In England and Wales, mine water pollution was recently confirmed as one of the most significant sources of freshwater pollution in the Environment Agency's pressure and impact assessment exercise for the Water Framework Directive (WFD) (www.environment-agency.gov.uk). Mine waters are typically highly acidic and rich in metals such as iron, manganese, copper and zinc (Younger *et al.*, 2002). Left uncontrolled, the mine waters can cause severe faunal impoverishment in receiving watercourses. This report will focus on the fate of metals as they pass through the hyporheic zone, particularly the attenuation potential of the zone, where affected waters pass from polluted rivers or streams into aquifers and vice versa, where polluted groundwater interacts with surface water. Although mine water discharges from, for example, adits 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 report is the transport of mine water through the hyporheic zone.

The report begins by looking at the occurrence and extent of mine water at the hyporheic zone and reviews existing literature on the principal attenuation processes for mine pollutants within the hyporheic zone, which can be grouped into chemical processes, such as sorption and precipitation, and microbiological processes. The report then looks at the biological impacts of mining-derived pollutants on the hyporheic zone and finally identifies gaps in the existing literature that require further research.

2 Mine water at the hyporheic zone

Concerted efforts to quantify the presence of mine water at the hyporheic zone, and the resulting impact on both surface water and groundwater, have never been made. To a large degree this probably relates to the difficulty of physically measuring the volume of pollutant inputs to (or exports from) rivers and streams. Consequently, the best information available is anecdotal evidence from river basins that have previously been the subject of detailed investigations of mine water pollution. Examples of mine water pollution arising from the hyporheic zone include catchments of the north-east of England, such as the upper and lower River Wear, and the upper reaches of the River Tyne.

The River Gaunless, which has its confluence with the River Wear at the town of Bishop Auckland, is perhaps more acutely affected by mine water intrusion via the hyporheic zone than many other catchments, principally because mine water rebound in this area, which was complete by the early 1980s (Younger, 2000), has resulted in a very shallow water table. During storm events, visual observations suggest that elevation of the water table results in increased baseflow to the river via the hyporheic zone. Mayes *et al*. (2005) have studied the influence of point and diffuse mine water pollution to the River Gaunless. Preliminary results of this work suggest that diffuse mine pollution may make a very significant overall contribution to the loading of metals to this river; as much as 50 per cent of total metal loading during summer and greater than 90 per cent during winter. Identification of the precise sources of this diffuse pollution is an ongoing subject of investigation, but direct input of mine waters via the hyporheic zone is one of the possible sources cited, along with diffuse run-off from exposed spoil heaps, and re-suspension of previously deposited metal precipitates in river channels during storm events.

Beyond this study of the River Gaunless, there do not appear to have been any studies at the catchment scale of the extent of mine water pollution from the hyporheic zone. Such information may arise as a result of the ongoing work of Mayes *et al*. (2005), but regional and national investigations have not been undertaken to the knowledge of these authors. This is therefore a potential area for future research.

3 Biogeochemical processes in the hyporheic zone

3.1   Overview

Biogeochemical processes taking place within the hyporheic zone can potentially affect the fate and transport of mine pollutants, where important transformations can influence the chemistry of both the overlying surface water and the underlying groundwater. 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 per cent and 98 per cent surface water (Benner *et al*., 1995; Fuller and Harvey, 2000). A number of authors have shown how the mobility of ions is altered at the interface between infiltrating surface water and groundwater and much of this work has suggested that the interactions between the aqueous and solid phases play an important role in controlling solute behaviour. The volume and rate of exchanges taking place within the hyporheic zone vary greatly and are governed by surface water-groundwater head distributions, river bed structure and composition, and ambient chemical and biological conditions (Hancock, 2002).

The presence of metals, including those from mine water discharges, in water passing through the hyporheic zone can limit both the hydrological exchange and the biological activity of the hyporheic zone. 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. The extent of natural attenuation in a stream depends on the accessibility of reactive solutes to zones favourable for chemical reactions. 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. The chemical conditions within the zone can act as a filtering mechanism to pollutants, allowing precipitation or sorption of dissolved minerals and metals. This is enhanced by the flow of surface water in the hyporheic zone increasing the reactive site density per volume of surface water via contact of dissolved metals with potential reaction or sorption sites (Fuller and Harvey, 2000). A review of existing literature on biogeochemical processes occurring in the hyporheic zone is described below.

3.2   Precipitation and adsorption processes

Precipitation and adsorption processes are dependent upon redox conditions. As can be seen from Figure 3.1, a redox scale can be created to give sequences of redox processes at different values of Eh, calculated at pH 7 and 25°C. In natural environments, redox processes are generally observed to proceed sequentially from the highest energy yield downward (Appelo and Postma, 1993). In Figure 3.1, 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. Any reduced form is thermodynamically favoured to transfer electrons to any oxidised form above it on the scale. Therefore, changes in key elements occur up and down the redox scale.

Eh (pH = 7)
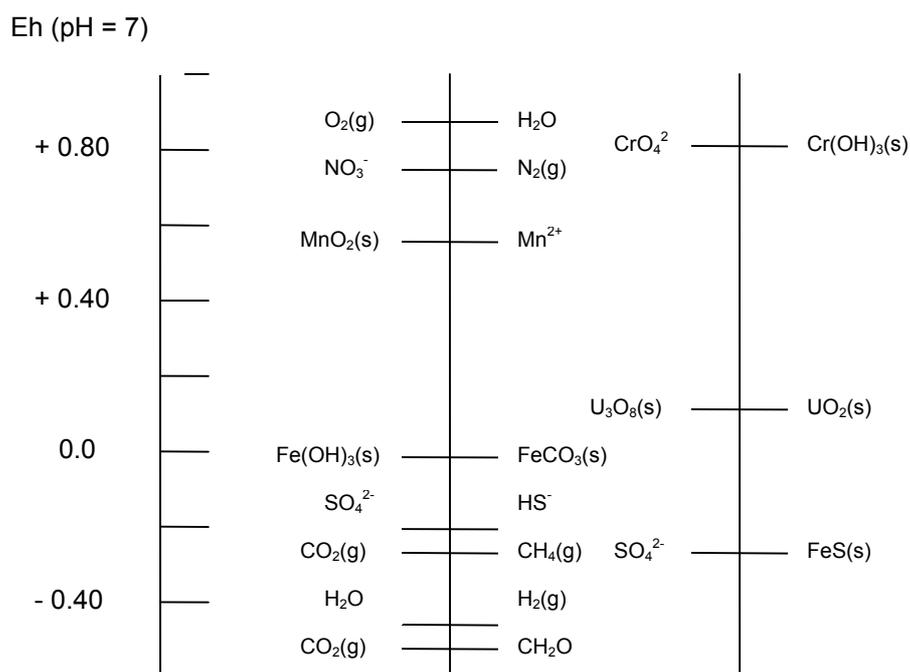
Figure 3.1: A redox scale showing redox couples of specific elements at different Eh values

A number of authors have studied the biogeochemical processes which take place during the exchange of metals between groundwater or surface water and the hyporheic zone. Fuller and Harvey (2000) studied the uptake of metals in the hyporheic zone of a mine water-contaminated creek in Arizona, where groundwater chemistry was dominated by elevated metal concentrations (82.5 mg/l manganese, 1.2 mg/l cobalt, 1.5 mg/l nickel and 1.6 mg/l zinc). They noticed that a significant uptake of dissolved metals occurred during the interaction of groundwater and surface water with hyporheic zone sediments. Previously, they determined (Harvey and Fuller, 1998) that microbially enhanced oxidation of dissolved manganese (to produce manganese oxide precipitates) in the hyporheic zone of the same creek resulted in a net decrease of 20 per cent in the manganese load flowing out of the drainage basin.

Fuller and Harvey (2000) hypothesise that manganese oxidation continuously forms new sorption sites, in the form of manganese oxide coatings on sediments, that should enhance removal of trace metals. 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. In contrast, the absence of dissolved iron and low colloidal iron concentrations suggests that iron oxides have a minor role to play in the uptake of metals. In addition, Fuller and Harvey (2000) suggest that the ongoing formation of manganese coatings has probably covered any pre-existing iron oxide surfaces. Over a 5.3 km reach of the creek, the authors observed a net attenuation of metals ranging from 12% to 68% (depending on flow and climatic conditions), which could be attributed to metal uptake (by sorption to manganese oxides) in the hyporheic zone. The average metal removal into the hyporheic zone was: manganese 22%, cobalt 52%, nickel 27% and zinc 36%.

Fuller and Harvey (2000) also noted that concentrations of cobalt, nickel, zinc and manganese in bed sediments were typically elevated by a factor of two or more in the active hyporheic zone compared to deeper sediments. The depth range of elevated

sediment metal concentrations (less than 15 cm) coincided with the zone where reactive metal uptake was calculated. This is consistent with metal uptake occurring within the streambed. On a drainage basin scale (in this case, the basin studied by the authors was on the order of 500 km^2 in area), attenuation of metals was found to be limited by the exchange rate of surface water into the streambed and the dimensions of the hyporheic zone, which controls the availability of sorption sites. Fuller and Harvey (2000) point out that the factors contributing to the observed variability in metal uptake include manganese oxide content, population of manganese oxidising bacteria, residence time of water in the hyporheic zone and pH. Harvey and Fuller (1998) also recognise a key process to be advection of dissolved oxygen into the hyporheic zone, which stimulates the activity of aerobic micro-organisms on sediments when dissolved organic carbon is readily available.

Harvey and Fuller (1998) looked at the rate of manganese oxidation within the hyporheic zone of the same mine water-contaminated creek in Arizona as studied by Fuller and Harvey (2000). They suggest that stream water entering the hyporheic zone enhances oxidation of dissolved manganese to form manganese oxide precipitates, by increasing the contact of stream water with sediment and microbes which act as reaction catalysts. 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 (Figure 3.2). It appears most likely 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.
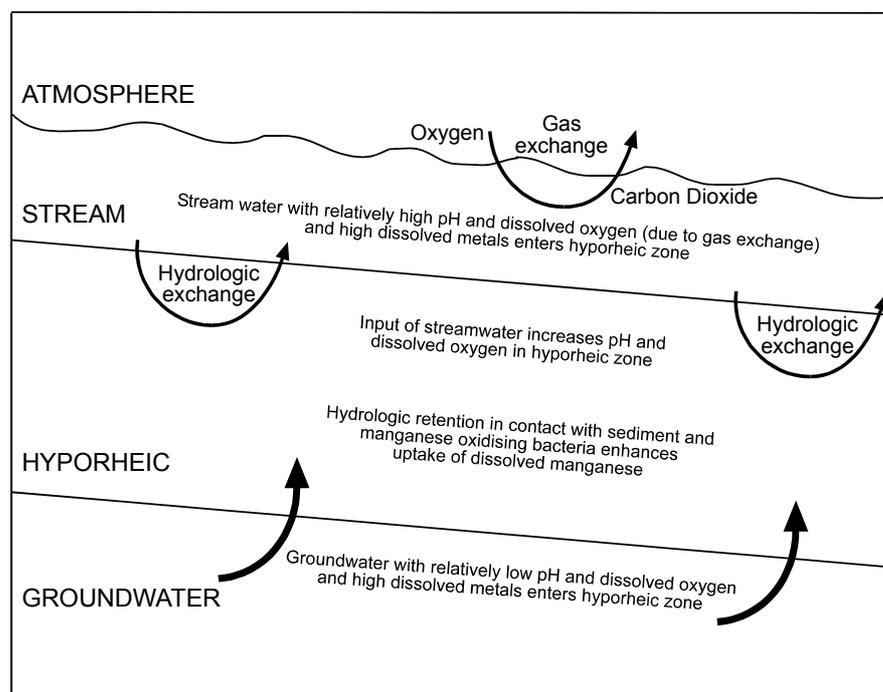
Figure 3.2: Schematic diagram showing factors that enhance oxidation of manganese within the hyporheic zone (adapted from Harvey and Fuller, 1998)

Laboratory experiments using sediment from the aforementioned creek in Arizona were conducted and the results compared to field data to determine the overall rate of dissolved manganese uptake by stream sediments, which occurs by reversible and irreversible processes. Reversible uptake of dissolved manganese (in the form of Mn^{2+})

includes uptake by adsorption and cation exchange because these processes should respond rapidly and reversibly to changes in dissolved manganese concentration or solution chemistry. Irreversible uptake is due to oxidation of Mn^{2+} to Mn^{3+} or Mn^{4+}, which is catalysed by 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 is favoured rather than reductive dissolution. The results confirmed that the rate of manganese oxidation in the hyporheic zone is significantly enhanced compared to that in groundwater and surface water because of the stimulation of microbial activity, likely a result of the increase in pH and dissolved oxygen due to stream water ingress to the hyporheic zone. This enhanced attenuation of manganese in the hyporheic zone represents an interesting passive remediation study. Manganese is notoriously difficult to remove by existing passive treatments. Characterising and then harnessing the microbial and geochemical conditions of the hyporheic zone, in constructed reactors, may therefore be an effective approach to remediation of manganese-polluted waters.

Manganese is usually not the most toxic metal in mine water discharges, but its importance within the hyporheic zone can be seen from the work carried out by Harvey and Fuller (1998) and Fuller and Harvey (2000). Changes in redox conditions when contaminated river water infiltrates an alluvial aquifer can lead to the reductive dissolution of manganese oxides in reduced zones and subsequent manganese oxidation and precipitation, under oxidising conditions, further along the flow path as observed by Bourg and Bertin (1993). From the latter's work, it appears that biological activity in the sediments can encourage both oxidation reactions and dissolution of iron and manganese oxides. In the study, chloride was used as a natural tracer of water mixing in a well field where a chloride-rich aquifer is recharged with a chloride-poor river water. A number of processes occurred as water infiltrated from the river through its bottom and bank sediments into the aquifer and mixed with groundwater. The most significant changes were found to occur within the first few metres of infiltration and were related to microbial degradation of organic matter. Further changes along the flow path were attributed to solubility adjustments controlled by calco-carbonic equilibria and to mixing with a deeper aquifer of different chemical composition. Respiration by micro-organisms and oxidative degradation of organic molecules led to the creation of a reduced zone, within which some species were consumed, such as dissolved oxygen, and others were produced, such as dissolved manganese.

The chloride tracer was used to help quantify the processes taking place, of which two types were observed. The first type involved irreversible reactions, where weathering produced enriched calcium, magnesium, bicarbonate and silica concentrations, and reductive reactions led to denitrification and adsorption reactions, removing zinc from solution. The second type comprised processes leading to the formation of the so-called reduced zone, most of which were reversible. As long as microbial activity, which is very intense in the river sediments, consumes more oxygen than is replenished from river water, the environment becomes reduced and leads to dissolution of manganese oxides. Further along the pathway, when microbial action decreases and when additional oxygen can be supplied by the permeable unsaturated zone, the water environment becomes oxidised again and manganese is removed from solution by a combination of adsorption and surface oxidation reactions, as described by Harvey and Fuller (1998) and Fuller and Harvey (2000).

Further work by Bourg and Bertin (1994) revealed seasonal trends in manganese solubility in the same river-aquifer system. The increase in dissolved manganese in the groundwater at various times of year was not caused by an input of manganese from the river, but was produced concurrently with the consumption of dissolved organic carbon and oxygen. This indicated that oxidation of organic matter, which appears to

be controlled by microbiological activity, led to dissolution of manganese oxides from the river bank and aquifer solids (hyporheic zone). A threshold temperature of $10^{o}C$ was found to be necessary in this study (located in south west France) to trigger bacterial activity which then created the reduced conditions necessary for the dissolution of manganese oxides.

Benner *et al*. (1995) studied the geochemical character of the hyporheic zone of a small creek in western Montana underlain by acidic, metal-rich groundwater. They sampled both the solid phase chemistry and the water chemistry to build a more complete picture of the geochemistry during surface water-groundwater interaction. Like Bourg and Bertin (1993), they found that the mobility of many ions was altered at the interface between infiltrating surface water and groundwater and that microbial populations could affect the rate and nature of adsorption processes. Unlike the previous literature reviewed, the site studied by Benner *et al*. (1995) comprised the interface between acidic, metal-rich groundwater and relatively uncontaminated surface water. The near-surface aquifer at the site was locally contaminated with acidic, metal-rich water (365 mg/l iron, 28 mg/l manganese, 1487 mg/l sulphate), which resulted from the oxidation of sulphides in mine tailings and the subsequent transport of contaminated water into the aquifer. Although metal concentrations in the surface water were low, with high pH and dissolved oxygen levels, short periods of contamination occurred, particularly following periods of heavy rainfall and intense run-off, when an influx of acidic, metal-rich water was observed. This shows the high connectivity between the surface water and groundwater systems.

As described in Section 3.1, Benner *et al*. (1995) divided the hyporheic zone into the surface hyporheic and interactive hyporheic zones, where the latter is a mixing zone containing between 10 per cent and 98 per cent surface water; these zones were clearly visible from their results. The pH of the surface water fell in the range 7.8 to 9.1 while the surface hyporheic zone, extending to a depth of 15 cm, had a pH of between 7.8 and 7.9. The interactive hyporheic zone, extending from a depth of 15 cm to 80 cm, had a pH of 6.2 to 6.9 while the groundwater beneath the interactive hyporheic zone had a pH of between 4.4 and 4.9. The pore water chemistry in the interactive hyporheic zone was therefore significantly different to both the surface water and surrounding groundwater and represented an intermediate between the two. As well as an average pH of 6.5, this zone was found to have an average alkalinity of around 70 meq/l and an average dissolved oxygen concentration of around 5 mg/l. These observations suggest that the hyporheic zone water was a mix of surface water and contaminated groundwater.

Benner *et al*. (1995) used mixing ratios calculated from ion concentrations in the surface water and groundwater to identify potential conservative ions. Chloride was used as a tracer, and mixing ratios indicated that the interactive hyporheic zone water (15 cm to 80 cm depth) comprised approximately 6 per cent groundwater and 94 per cent surface water. Similar results were found for manganese concentrations, suggesting that manganese was behaving conservatively. The authors also calculated the degree to which a given constituent was depleted within the hyporheic zone relative to its expected concentration, given only conservative mixing, which reflects the degree of non-conservative behaviour for that constituent. From this, iron and copper showed a high degree of non-conservative behaviour (suggesting they were being precipitated or adsorbed within the hyporheic zone) while potassium and sodium appeared to be acting conservatively. Further investigations showed that calculated concentrations of iron, manganese, zinc, cadmium and copper in the groundwater were higher than in the interactive hyporheic zone, suggesting that these elements were being depleted from the groundwater portion, while calcium and magnesium were shown to be undergoing removal from the surface water.

Extensive orange, iron-rich coatings were observed on the stream bed as well as within the hyporheic zone, indicating precipitation of iron oxides occurring to a depth of 80 cm. Below this point, iron concentrations were high 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 (Figure 3.3). It is thought 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.

Manganese, on the other hand, was shown 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 (Figure 3.3). In addition, aqueous manganese concentrations were high in the groundwater and interactive hyporheic zone and low in the surface water and surface hyporheic zone. Cadmium, copper and zinc were found to be mostly partitioned into the solid phase in the hyporheic zone and the aqueous phase in the groundwater which, along with mixing zone ratios, suggests that these elements were being removed from solution within the interactive hyporheic zone. This may have been the result of precipitation of solid-phase minerals or adsorption onto iron oxyhydroxides at the pH range found in the interactive hyporheic zone.

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

Figure 3.3: 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)

Measurable concentrations of arsenic and lead were also found by Benner *et al.* (1995) within stream sediments and the interactive hyporheic zone, despite not being detected in solution. Alkalinity showed the same pattern with depth as pH, presumably caused by it being consumed by acid from the mixing with acidic groundwater. Oxygen and nitrate concentrations also decreased with depth, likely driven by the oxidation of iron and/or organic matter. Sulphides may have been forming at depth, given high metal

concentrations found at the base of the hyporheic zone, where a lack of oxygen precluded oxide formation. However, as the concentration of metals in solution was not significantly lower at this depth, the sulphides may have been forming, in the presence of sulphate-reducing bacteria, at rates that did not significantly reduce soluble concentrations.

The study by Benner *et al*. (1995) underlines the importance of the hyporheic zone in attenuating metal movement, particularly those derived from mining activity, from groundwater into surface water. High levels of metal accumulation observed within the hyporheic zone suggest that it may act as a sink for metals and that metal loading on the bed sediment of the creek may be significant. The likely processes responsible for metal attenuation are precipitation of both oxides and sulphides and adsorption onto previously precipitated minerals. Bencala *et al*. (1990) also observed adsorption of manganese and zinc onto previously precipitated hydrous oxides on the streambed of an acidic and metal-rich mountain stream in Colorado. This resulted in small losses of these solutes from the stream.

Nagorski and Moore (1999) progressed the work of Benner *et al*. (1995) by looking at arsenic mobility in the hyporheic zone of the same creek. They discovered that arsenic and iron concentrations in hyporheic zone samples were significantly higher than those in the surface water and groundwater, where arsenic was detected in very low concentrations. As found by Benner *et al*. (1995) the pH, dissolved oxygen and concentrations of other metals in the hyporheic zone were intermediate between the values obtained for surface water and groundwater. Arsenic concentrations in the hyporheic zone ranged from <65 to 2700 µg/l with a median of 200 µg/l and were clearly related to dissolved oxygen and pH, with arsenic only elevated in samples with a pH between 6 and 7 and dissolved oxygen less than 3.5 mg/l. Iron concentrations in the hyporheic zone ranged between 0.15 and 400 mg/l.

Columns of artificial substrate inserted into the hyporheic zone at the site exhibited a red-orange zone of precipitation at the streambed-surface water boundary, indicative of iron precipitation. These precipitation zones were elevated in metals and generally tens or hundreds of times more enriched in iron than the non-precipitation zones. On two-thirds of the columns, arsenic was also at a maximum along the precipitation zones where iron concentrations were at their highest. Since the dissolved arsenic concentrations were significantly lower in both the surface water and groundwater, the authors state that the elevated concentrations observed in the hyporheic zone cannot be generated by simple physical mixing. They suggest that the high levels arise from chemical reactions involving a third source, such as the contaminated hyporheic zone 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. Sorption onto iron oxyhydroxides is thought to transfer arsenic from the dissolved phase to the particulate phase, while manganese oxyhydroxides catalyse redox reactions transforming soluble arsenic (III) to the less toxic particulate arsenic (V) (Figure 3.4). 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 form particulates and pyrite can fix large amounts of arsenic in its crystal lattice.

Nagorski and Moore (1999) hypothesise that when iron oxyhydroxides in the streambed sediments become buried and subject to reducing conditions, as found in the shallow hyporheic zone, arsenic sorbed or co-precipitated to them may be released by reductive dissolution of the iron oxides, which increases total arsenic concentrations

and encourages the reduction of arsenic (V) to the more toxic arsenic (III) (Figure 3.4). The partitioning of iron species between solute and particulate phases is controlled by pH-induced changes in sorption equilibria, which also influences arsenic release and sorption since iron and arsenic are closely associated. Such processes within the hyporheic zone may also control arsenic concentrations and speciation in the surface water during surface water exchanges with the hyporheic zone. When surface water enters the hyporheic zone, the dissolved arsenic and iron generated by the reduction of iron oxyhydroxide minerals is flushed into the surface water. A portion of the dissolved iron then oxidises, precipitates and sorbs arsenic upon contact with the oxic, slightly basic, surface water, thus explaining the precipitation bands observed at the streambed-surface water interface. The authors believe, however, that not all of the arsenic (III) is immediately oxidised and sorbed by the iron oxyhydroxides with a portion remaining in the surface water for some period of time before it oxidises or flushes through the hyporheic zone again. Therefore, from this study, it is clear that pH and dissolved oxygen appear to be the main controllers of arsenic partitioning and together encourage elevated arsenic concentrations in the hyporheic zone.

OXIDISING

$As^{3+}_{(aq)} \rightarrow As^{5+}_{(s)}$

Sorption to
$Fe(OH)_3$

REDUCING

$As^{5+}_{(s)} \rightarrow As^{3+}_{(aq)}$

Dissolution
of $Fe(OH)_3$
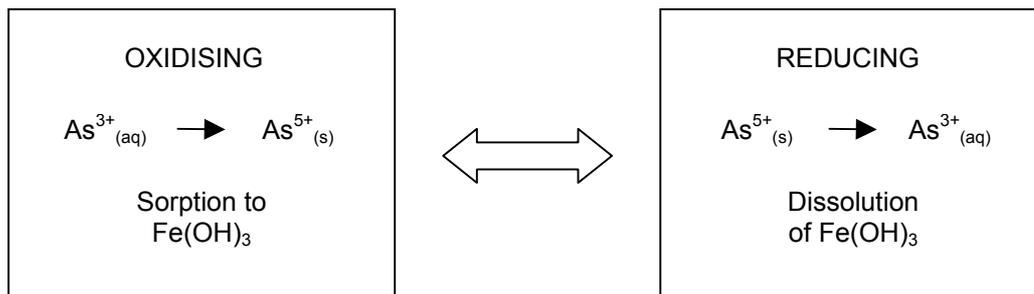
Figure 3.4: Effect of changes in redox conditions on arsenic mobility in the hyporheic zone.

Moser *et al*. (2003) investigated geochemical and microbiological parameters of sediment samples collected from the Colombia River hyporheic zone in Washington State. They found relatively large populations of sulphate-, nitrate-, and iron-reducing bacteria to be present, and significant concentrations of acid-volatile sulphide in some samples, indicating that anoxic regions existed within the hyporheic zone. Although interstitial waters tend to be oxidising, zones of small-scale anoxia can develop within sediments, even in areas of rapid infiltration. Cr(VI) was observed to be removed from a groundwater plume passing through the hyporheic zone by a combination of microbial activity and chemical reduction. The work by Moser *et al*. is reviewed in further detail in Section 3.3 (on microbiological processes), since the results reveal how microbes contribute to the natural attenuation of metals such as chromium in the hyporheic zone.

Winde and Van der Walt (2004) observed the attenuation of uranium in hyporheic sediments as it migrated, along with other heavy metals, from tailing deposits of gold mines via groundwater into rivers. They showed how retardation was triggered by either redox-initiated co-precipitation of uranium with iron and manganese oxides and hydroxides or by adsorption, although they suggest that co-precipitation dominated over adsorption. They also noticed distinct diurnal differences in contamination and were able to account for this. The high concentrations of uranium which they observed mainly occurred in salt crusts. The crusts were thought to be formed when capillary-ascending groundwater evaporated and dissolved sulphates, originating from pyrite oxidation and sulphuric acid leaching, precipitated, for example as gypsum. The high uranium content of these crusts was thought to be due to the formation of neutrally charged uranyl ion sulphate complexes which are often found in sulphate-dominated waters of such redox potential (-100 to -270 mV). Similarly, elevated concentrations of dissolved carbonates may allow aqueous uranyl carbonate complexes to form.

Winde and Van der Walt (2004) note 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, partly catalysed by bacteria, as hydrous oxides and hydroxides. They settle as amorphous gels in the sediment pores or form coatings on sediment particles, which eventually crystallise into water-free oxides such as hematite, thus attenuating the migration of these metals. A strong correlation between uranium concentrations in the solid samples and the iron and manganese contents suggest that these processes are also important mechanisms of uranium immobilisation. Uranium is either incorporated into precipitating oxyhydrates or adsorbed onto the large reactive surface area of freshly precipitated gels, with co-precipitation deemed to be the dominant process. Thus, as the interface between reducing groundwater and oxidising

surface water, the hyporheic zone can act as a geochemical barrier to remove uranium and other heavy metals from groundwater as it seeps into surface water. Given that the freshly precipitated gels are protected from fluvial erosion, being within sediment pores, the hyporheic zone acts as a long-term sink for these metals, thereby reducing stream pollution.

The distinct diurnal differences in stream contamination noted by Winde and van der Walt (2004) were based on the fact that, during dry conditions, contaminated groundwater only infiltrated the stream channel during high stream flow conditions at night, with the reverse occurring under low flow conditions during the day. This implied a daily cycle of contamination, with higher surface water concentrations of uranium and other heavy metals at night. The nightly high flow conditions arose from pumping-related flow conditions within the catchment.

Along with fluctuating groundwater levels, the redox potential of hyporheic sediments changes between reducing conditions (when submerged) and oxidising conditions (when dry). This alters the attenuation potential of the sediment, since it is the redox-initiated co-precipitation of uranium with insoluble iron hydroxides and manganese oxides which is the major mechanism for removal of uranium and other heavy metals within the hyporheic zone.

Winde and Van der Walt (2004) also regard varying pH and Eh conditions to be influential in the mobility of uranium. The pH affects precipitation of iron and manganese oxides and hydroxides, which is the major mechanism for uranium removal, as well as controlling the adsorption of uranium onto precipitated gels.

Brick and Moore (1996) also observed an increase in metal concentrations, particularly manganese and zinc, in a river at night and suggest that this arises from changes in biogeochemical processes within the hyporheic zone, resulting from variations in pH and dissolved oxygen concentration at night.

Wielinga *et al*. (1999) also looked at contamination from fluvially deposited mine tailings, and studied biogeochemical processes within the hyporheic zone in an attempt to characterise interactions which have an important effect on heavy metal contamination of shallow groundwater. They noticed that metal content decreased with depth to the water table and the presence of iron hydroxide layers, with a marked increase in zinc and manganese associated with these layers. As well as metal-oxidising bacteria, the authors discuss the activity of metal-reducing bacteria which, rather than attenuating metals, can provide a mechanism for metal mobilisation. The microbial reduction of iron and manganese oxides can result in the release of a wide variety of toxic metals previously sorbed to or co-precipitated with the oxides. The iron and manganese oxide layers were formed when acidic, metal-rich pore water came into contact with the circumneutral pH groundwater, encouraging the metals to precipitate as amorphous oxides and hydroxides. These poorly crystalline iron and manganese oxides were amenable to microbial reduction and the presence of iron-reducing bacteria was noted along with the precipitates (Wielinga *et al.*, 1999).

Nelson and Rioline (1999) used biota and chemistry from hyporheic samples to describe environmental changes, after treatment of mine water, in the shallow hyporheic zone. High concentrations of metals were found in the hyporheic zone (up to 910 µg/l zinc), compared to surface water (32 µg/l zinc), but were particularly high during spring run-off even several years after the start of treatment of the mine drainage. The hyporheic zone may have served as a sink for a number of metals during the years of exposure to pollution. Release of these stored pollutants is largely controlled by changes in the chemical characteristics of the hyporheic zone resulting

from the hydrological cycle. Snowmelt run-off was observed to lower pH, which may control chemical speciation and result in increased metals in the hyporheic zone. It is also possible that increased water volume from snowmelt could have displaced old groundwater that would be chemically different from surface water.

A black precipitate containing iron, manganese and zinc was found adhered to the sides of sampling pots, used by Nelson and Rioline (1999) for the collection of hyporheic samples, but only on the top third of the pots while the bottom portion remained clean. The authors suggest a change in conditions within the sediment which favoured precipitation, similar to that described by Benner *et al.* (1995), with metals in deep sediments in the aqueous phase and precipitated onto substrate near the surface. It is thought that a portion of the metals found in the interactive hyporheic zone were rapidly adsorbed as they upwelled into the surface water and, therefore, large increases in metal concentrations were not detected in surface water, although there was some evidence of depletion of hyporheic zone metals into the surface waters. Dilution was also thought to play a role in obscuring transfer of metals from the hyporheic zone to the surface, especially during spring run-off when large amounts of clean surface water are present. Nelson and Rioline (1999) also consider differences in substrate, pointing out that the larger surface areas associated with smaller particle sizes mean that finer substrates adsorb greater amounts of metal ions, which could have important implications during times of desorption.

Ren and Packman (2002, 2004a, 2004b) show how very fine sediments, such as colloids (with a diameter less than 10 μm), can have a significant effect on pollutant transport. While these sediments are normally assumed to be readily transported without deposition, Ren and Packman (2002) suggest that these particles will often be transported into and deposited within streambeds by a combination of physical and chemical mechanisms. Exchanges with the subsurface can result in bed sediment and pore water becoming a significant reservoir for storing pollutants within a stream system. Colloidal particles have a large reactive surface area which allows them to carry contaminants that would otherwise be transported primarily as dissolved species. Reactive colloids, such as clays, iron oxides and humic substances are common in streams and pollutants, including metals, have a high affinity for such particles under conditions commonly found in streams.

Ren and Packman (2004a) developed a model to predict the role of colloids in the exchange of pollutants between streams and the subsurface. Hyporheic exchange can carry both colloids and contaminants into streambeds, where extensive reactions can occur due to the increased contact of contaminants and colloids with streambed sediments and associated microbial communities. Such colloidal particles have extensive surface area per unit mass or volume due to their small size and are often strong sorbents for toxic contaminants such as heavy metals. According to Ren and Packman (2004a), in river systems metals such as copper, zinc and lead can associate with colloidal particles through either co-precipitation or adsorption. Model simulations indicated that, under conditions of low colloid filtration (interaction with bed sediments) and strong contaminant sorption to colloids, contaminants are mobilised by colloids and there is less retention of the latter within the streambed. Conversely, when colloid filtration is high, and contaminants still adsorb strongly to colloids, contaminant mobility decreases and there is greater contaminant retention, and thereby attenuation, in the streambed.

Ren and Packman (2004b) present experimental results which compare stream-subsurface exchange of zinc in the presence of colloidal silica and kaolinite. Zinc immobilisation in the bed was found to be significantly greater in the presence of kaolinite than colloidal silica, as the zinc sorbed more strongly to kaolinite, which also

deposited more readily in the streambed than the silica colloids. The results also showed that pH has a significant effect on zinc exchange in the presence of silica colloids, with zinc retention in the streambed increasing with increasing pH due to interaction between zinc and the bed sediments. Higher pH resulted in greater adsorption of zinc to the silica sand used in the experiments, with correspondingly more zinc immobilised in the streambed. These observations emphasise that reactive colloids can significantly affect the stream-subsurface exchange of contaminants, and that colloid deposition can provide a mechanism of contaminant immobilisation that, as pointed out by Ren and Packman (2004b), is not usually considered in field studies of contaminant transport.

Brunke and Gonser (1997) discuss hydrological exchange processes between rivers and groundwater, and show how the permeability of the hyporheic zone depends on the hydraulic conductivity of the sediment layers. Due to the heterogeneity of the sediment layers, they form many flowpath connections between the surface water and groundwater, from the small scale of a single microhabitat to the large scale of an entire alluvial aquifer. Local up- and down-wellings are determined by geomorphologic features such as streambed topography, whereas large-scale exchange processes are determined mainly by the geological properties of the catchment. Colmation - clogging of the top layer of the channel sediments - leads to a reduction of pore volume, consolidation of the sediment matrix and decreased permeability of the streambed. Consequently, colmation can hinder exchange processes between surface water and groundwater and may affect the passage of mining-derived metals through the hyporheic zone.

Younger *et al*. (1993), while not specifically looking at mine pollutants, studied attenuation of pollutants during river-groundwater interactions using integrated fieldwork and a three-dimensional model. They discovered that values of parameters describing the stream-aquifer interface, such as streambed thickness, roughness and hydraulic conductivity, had far more influence on the model output than values of aquifer transmissivity and storativity. The authors discuss the effects of the hydrogeology of streambed sediment, where a fine grain size provides a low hydraulic conductivity and a high clay and organic matter content makes the sediments highly sorptive. In fact, they state that the effect of organic matter on sorption is so strong that where the organic content of a sediment exceeds 1 per cent by weight, the contribution of mineral surfaces to the total sorption in the sediment is negligible. However, this is only likely to be the case for organic contaminants and not inorganic contaminants, such as those derived from mining. The authors also note that adsorption is likely to be the primary attenuation process operating in the streambed sediments, although the redox conditions of the streambed sediments, which are related to biological activity, can significantly affect the transport of pollutants, with heavy metals more mobile under reducing conditions. Upon encountering oxic conditions, however, metals will likely undergo precipitation or adsorption again (as proven by some of the other literature reviewed). According to the authors, sorptive capacity is a function of the mineralogy and organic content of the sediment ,with montmorillonite having the highest cation exchange capacity of any clay mineral.

Walling *et al*. (2003) compared metal fluxes in three rivers draining mining areas and non-mining areas in Yorkshire, UK. They investigated downstream changes in the storage and deposition of these heavy metals and found that distance from the pollution source was important in terms of sediment storage, with concentrations of lead and zinc in fine sediment stored within the channel bed of the River Swale decreasing downstream, reflecting the location of historic lead and zinc mines in the headwaters of the river. Similarly, in the other rivers studied, contaminants associated with the fine channel bed sediment exhibited both increases and decreases in

concentration downstream, which reflected geological controls as well as the effects of urban and industrial areas. The amount of sediment deposited, according to the study, 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 is offset by a downstream increase in the amounts of sediment stored. However, the authors conclude that, in terms of long-term transport of contaminants through a river system, storage is equivalent to only a relatively small proportion (less than 3 per cent) of the annual flux at the catchment outlets, while in the shorter term, gains and losses to channel storage can have a strong influence on contaminant fluxes. This work by Walling *et al.* (2003) also highlights the control of sediment grain size on retardation, storage and transport in different river catchments.

In their general review of the hyporheic zone, Biksey and Gross (2001) comment on the transition between anaerobic and aerobic conditions which takes place over short distances (as studied by Mermillod-Blondin *et al.* (2005) and noted by Boulton *et al.* (1998)) and which can lead to biodegradation and transformation of both organic and inorganic contaminants. The authors note how important these processes are for the natural attenuation and removal of contaminants. They also consider the differences between up-welling zones, where groundwater moves upward into the river, and down-welling zones where surface water enters the streambed. Up-welling zones are characterised by anoxic conditions and anaerobic processes, while down-welling zones are characterised by high oxygen levels and aerobic processes. Depending on the proportion of groundwater and surface water present within the hyporheic zone and whether up-welling or down-welling is occurring, the zones differ in oxygen content, acidity and temperature, factors that determine which biogeochemical processes will take place.

3.3   Microbiological processes

Bacterially mediated oxidation (and reduction) of iron and manganese is widely cited as a potentially significant mechanism 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. The first is the energy-yielding aerobic oxidation of ferrous iron, and the best-known bacteria in this category are *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*, which are both obligately acidophilic. The second mechanism involves sheathed bacteria, of which *Leptothrix* is the most commonly cited (Madigan and Martinko, 2006). Such organisms have the ability to precipitate iron oxides on their sheaths, and evidence of this can be seen at many mine water-impacted sites. This mechanism is particularly prevalent in locations where there is a rapid change from anoxic to oxic conditions (Emerson and Revsbech, 1994), and therefore the presence of such precipitates might be anticipated 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. The following paragraphs provide an overview of what little literature exists on the specific issue of microbial processes and metal mobility at the hyporheic zone.

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 looking 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 expected to be high (due to reduced groundwaters meeting aerobic surface waters, providing a range of environmental conditions for interstitial organisms - see Jones *et al.,* 1995; McClain *et al.*, 1994; Storey *et al.*, 1999).

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 (that is, 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 there is no literature that explicitly examines this hypothesis.

The most detailed investigations of the microbial dynamics of metal-impacted watercourses have been undertaken by Kevin Feris and co-workers at the University of Montana, USA (Feris *et al.*, 2004a, 2004b, 2003). This 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). Initially, Feris *et al.* (2003), using a range of methods including denaturing gradient gel electrophoresis and 16s RNA phylogeny, established that there was no correlation between sediment metal content and total microbial biomass across six study sites affected by heavy metal contamination. However, this first study revealed a significant relationship between microbial community structure and total metal loads in the hyporheic zone; heavy metal load was positively correlated with certain phylogenetic microbial groups, whilst being inversely correlated with other phylogenetic groups.

Feris *et al.* (2004a) subsequently determined, at the same suite of sites, that the correlations between metal load and phylogenetic group was strongly influenced by seasonality. In brief, correlations were evident only in autumn and early winter, when organic matter deposition to streams is greatest. The conclusion of Feris *et al.* (2004a) was that the abundance of organisms susceptible to heavy metals was at its greatest during the period of maximum bacterial growth.

In their most recent investigation of microbial communities of the hyporheic zone in metal-contaminated environments, Feris *et al.* (2004b) investigated the effect of varying metal load on community structure, and identified a strong positive correlation between heavy metal contamination and community structure. Communities responded rapidly to exposure to elevated metal loads (less than seven days). However, communities also recovered from these metal treatments, albeit different phylogenetic groups recovered to different degrees, and in a unique manner. Feris *et al.* (2004b) suggest that microbial communities may respond to metal loads an order of magnitude lower than those necessary to induce a measurable response from benthic macro-invertebrates, and therefore such organisms may be a very sensitive indicator of pollution. The disadvantage of such organisms as indicators of pollution, which Feris *et al.* (2004b) do not make clear, is that such an assessment requires costly, time-consuming laboratory techniques, whereas assessment by macro-invertebrate community abundance and diversity is a rapid, inexpensive, system that requires relatively limited expertise.

3.4 Methods for characterising biogeochemical processes in the hyporheic zone

A number of methods have been employed to characterise biogeochemical processes taking place within the hyporheic zone (Bridge, 2005), some involving the collection of samples of hyporheic zone sediment or pore water, and others involving simulations in the form of laboratory experiments or computer models. Perhaps the most unique method was that used by Benner *et al*. (1995), in which the solid phase chemistry of the hyporheic zone was sampled *in situ* and compared with water chemistry data. Tubes containing ceramic beads (composed of aluminium silicate) were installed vertically into the bed of the studied creek to collect mineral coatings. The authors state that the use of an artificial solid matrix has the potential to eliminate problems of sample collection and history as it can be easily removed from the bed and reflects the geochemical conditions only during the period in which it is emplaced. However, it has the disadvantage of not being able to exactly mimic the physical and chemical characteristics of the natural solid matrix, the mineralogy of which can affect adsorption processes, along with the lack of microbial populations which can affect the rate and nature of coating formation. Despite these limitations, Benner *et al*. (1995) believe that coating accumulations on the artificial solid matrix approximate and reflect the solid phase in equilibrium with the aqueous species present. By combining this solid-phase sampling technique with the analysis of water samples, they were able to show the behaviour of different mining-derived constituents during surface-groundwater interaction.

Moser *et al*. (2003), on the other hand, employed a 'freeze core' technique to collect intact cobble-bed samples from the hyporheic zone of the Colombia River in Washington State, in order to obtain information on the geochemistry and microbiology of hyporheic zone sediments. The method involved the installation of tubes, driven into the river bed, which were filled with liquid nitrogen in order to freeze the sediment and interstitial waters. The resulting frozen cores were then removed and transported to the laboratory where they could be analysed. This technique has the advantage of enabling the collection of samples to extended depths while preserving the vertical structure of the substrate and interstitial water, but it also has the disadvantages of the cores being difficult to remove and handle (due to the large size of sample recovered); they are also only suitable for use in shallow streams.

Wielinga *et al*. (1999) extracted sediment cores from a hyporheic zone contaminated by metals from fluvially deposited mine tailings. Cores were collected by mechanically driving sterile polycarbonate tubes through the tailings and were then fractionated based on sediment stratigraphy. The cores were processed on return to the laboratory and underwent geochemical and microbial analysis. As with Benner *et al*. (1995), the results were compared with water chemistry data from samples collected during the same time period.

Nelson and Rioline (1999) used hyporheic pot samplers built of polyvinyl chloride piping which were installed vertically into the substrate and filled with natural substrate. These samplers were perforated to allow the collection of invertebrates. Hyporheic zone pore water samples were also collected, both before the placement of pot samplers and whilst they were in position. Water samples were collected before pot placement using an air stone and tubing attached to the end of a wooden pole. This pole was inserted into the substrate and a sample was withdrawn using a hand-operated pump. In addition, a fused glass air stone was attached inside the bottom of each hyporheic pot sampler before its placement; plastic tubing, connected to the air

stone, led to the surface and allowed for collection of pore water samples *in situ*. The air stone was used to prevent clogging of the tubing by sand particles during sample collection. The authors believe that the collection of hyporheic pore water samples using this technique should minimise changes in the *in situ* chemical characteristics of the water. Piezometers were also used to monitor changes in groundwater level and compare these with river water level, to identify periods of up-welling of groundwater into surface water and down-welling of river water into the substrate.

Several authors have attempted to study hyporheic zone processes using tracer tests (for example, Bencala *et al*., 1990; Bourg and Bertin, 1993). However, as pointed out by Harvey and Fuller (1998), stream tracer tests can not always reliably isolate or distinguish hyporheic zone processes from other processes. Harvey and Fuller (1998) and Fuller and Harvey (2000) used an alternative technique of stream tracer tests that did not alter natural levels of the reactive constituent within the system; they also estimated hyporheic reactions at finer scales (within hyporheic flow paths and in laboratory experiments) and compared these to the tracer tests. Surface water and pore water samples from the hyporheic zone were also collected for chemical analysis. Sediment characterisation was carried out by coring the streambed, in a similar manner to that described by other authors, and the samples were then analysed for metal content. Laboratory batch experiments were conducted with hyporheic zone sediment to establish the overall rate of dissolved manganese uptake, for comparison with estimates from field data.

Some authors (such as Bourg and Bertin, 1994; Nagorski and Moore, 1999) have simply observed the hydrogeochemistry of river water and groundwater during their interaction. Others, such as Ren and Packman (2002) have set up laboratory experiments to investigate stream-subsurface exchange. The experiment undertaken by Ren and Packman (2002) involved a re-circulating flume which provided good control of the physical and chemical conditions in the stream and sediment bed. They also carried out column experiments in order to obtain certain parameters required for the flume experiments.

Mermillod-Blondin *et al*. (2005) used slow filtration columns, composed of sand and gravel, to quantify at a small scale (on the order of centimetres) biogeochemical processes and associated microbial activity within the hyporheic zone. The columns were shown to accurately recreate the aerobic-anaerobic gradient often observed in the hyporheic zone (Biksey and Gross, 2001). They also reproduced the high heterogeneity of the hyporheic zone, with anaerobic portions in sediments where denitrification and fermentation processes occurred. Overall, slow filtration columns were shown to be an appropriate tool to quantify *in situ* rates of biogeochemical processes and determine the relationship between microbial activity and the physicochemical environment in hyporheic sediments.

An intensive literature search revealed very few modelling studies covering the fate of pollutants in the hyporheic zone. However, Ren and Packman (2004a) developed a theoretical model to predict the role of colloids in assisting the advective exchange of contaminants between streams and the subsurface; this involved the simulation of physical transport as well as processes such as sorption-desorption and filtration by bed sediments. Ren and Packman (2004b) then applied this model to interpret observed stream-subsurface exchanges in laboratory experiments. As discussed in Section 3.2, Younger *et al*. (1993) integrated a three-dimensional model with fieldwork to study attenuation of pollutants during river-groundwater interactions. The model was developed to simulate solute transport in stream-aquifer systems using a particle tracking technique. The fieldwork involved the collection of samples of streambed sediment by dredging. Another modelling study was undertaken by Broshears *et al*.

(1996), who simulated physical transport and geochemical processes in the water column and at the sediment-water interface of a stream affected by acid mine drainage. Geochemical processes modelled included precipitation-dissolution and sorption-desorption, along with oxidation and reduction reactions under equilibrium conditions. Kimball *et al*. (1994) had previously carried out some solute transport modelling of the same acid mine drainage-affected stream.

Grimaldi and Chaplot (2000) used a novel method for collecting hyporheic zone water samples. 'Collectors' comprising a polyethylene bottle riddled with holes, wrapped in nylon tulle and fitted with a rigid plastic tube were placed in the soil and water was sucked with a syringe through the rigid plastic pipe which sheltered the sample from contact with air. The pipe was only open during the sampling period and the collectors were emptied before each sampling. These collectors enabled a spatial characterisation of the groundwater composition.

4 Biological impacts

The hyporheic zone has been increasingly recognised as a distinct biogeochemical environment in recent years. Ecologists have established the importance of this zone, not only as a biologically rich ecotone but also as an interface important to the entire river's ecology. The zone has its own resident biota called 'hyperheos', composed of surface and subsurface species (Hancock, 2002). The hyporheic zone is ecologically important for a number of reasons, principally because 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 zone provides a food base for small organisms, which in turn provide food for benthic macroinvertebrates, while the zone also offers a refuge from predators. In addition, advection and diffusion-driven cycling of nutrients and carbon from the groundwater to the 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). According to Nagorski and Moore (1999), studies of biological communities in hyporheic zones have shown that they are important sites of refuge, dwelling and development for many freshwater fauna.

The flux of acidic, metal-rich waters into the hyporheic zone can have an adverse impact not only on the zone itself, but on the ecology of the entire river. As pointed out by Biksey and Gross (2001), the hyporheic zone is particularly vulnerable since it is exposed to groundwater contaminants before the surface water ecosystem. The sudden influx of toxic metals can be fatal to hyporheic organisms, and can have a detrimental effect on the life cycle of benthic invertebrates (Brunke and Gonser, 1997). Nelson and Rioline (1999) studied the recovery of a hyporheic invertebrate river community structure following metal contamination, and found that sampling of this zone was important for monitoring the recovery of polluted streams. The authors studied the relationship of hyporheic macroinvertebrates to declining metal concentrations and also noted how biogeochemical processes taking place within the hyporheic zone, including adsorption and precipitation (as discussed in Section 3.2), had an impact on aquatic macroinvertebrates by coating substrate materials. The overall conclusion of their work was 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. 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.

According to Hancock (2002), hyporheic fauna have been suggested as biological indicators, since relatively short food webs and a low diversity of food sources makes these organisms sensitive to environmental change. Poisoning of hyporheic invertebrates and microbes can affect the attenuation potential of the hyporheic zone, given that microbes play an important role in the attenuation of mine-released metals (Section 3). Changes in pH caused by the influx of acidic water can alter redox conditions, which may also affect the attenuation potential (by inhibiting precipitation and adsorption reactions, for example).

Most authors who have studied the biogeochemical processes within the hyporheic zone of mine-polluted streams have observed high concentrations of metals. In fact, Nagorski and Moore (1999) found arsenic and iron in higher concentrations in the hyporheic zone than in the surface and groundwater. In addition, dissolved arsenic existed as arsenic (III) (mobilised during reductive dissolution of iron oxides) which is more toxic to invertebrates than arsenic (V). The physical and chemical conditions of the hyporheic zone, with a pH between six and seven and a dissolved oxygen

concentration of 0-3 mg/l, appeared to allow sediment-bound arsenic to occur in its dissolved form of arsenic (III), which then re-entered the stream. Thus, the hyporheic zone acted as a toxic source to the stream. Losses in the invertebrate fauna within the hyporheic zone can impair processes, as the fauna would not be present to stimulate bacterial activity (by grazing) and maintain interstitial porosity (by bioturbation) (Hancock, 2002).

Apart from the poisoning of biota by toxic metals, one of the biggest impacts of mine pollutants on the biology of the hyporheic zone is the blocking of interstitial spaces by precipitates. These blockages can create anaerobic conditions in areas which were previously oxic, thus inhibiting faunal and microbial activity (Hancock, 2002). However, if fluctuations occur within hydrological and chemical conditions that favour the precipitation of metals, sediments are at a lower risk of being clogged. If precipitates are distributed over a wider spatial scale, more time is available for microbial breakdown.

5 Research gaps

As can be seen from our literature review, a number of authors have studied the fate of mine pollutants as they pass through the hyporheic zone but, in general, the amount of published information is limited. As such, there appears to be opportunities for further research based on apparent gaps in the literature. Gaps may be due, to some extent, to the difficulty in accessing the hyporheic zone to retrieve sediment samples which portray the full range of processes taking place within the zone. Although a wide range of methods are available to extract sediment samples (Section 3.4), no comparative research appears to have been undertaken to establish any differences in the efficiency of extractions (Boulton *et al.*, 1998).

Suitable sampling methods depend upon the sediment type present. Furthermore, as pointed out by Benner *et al.* (1995), once a sample is collected, difficulties arise in its transport and analysis, particularly in the extraction of many layers of coatings which may no longer be in equilibrium with the water present. Benner *et al.* (1995) propose the alternative use of an artificial matrix to collect solid phase data, but this has its own problems of failing to exactly mimic the physical and chemical characteristics of the natural solid matrix. However, it does help to eliminate problems of sample collection and history and allows the solid phase chemistry of the hyporheic zone to be sampled *in situ* and compared with water chemistry data.

Although most studies of the physical and chemical dynamics of the hyporheic zone have generally concluded that surface and groundwater interact extensively, and that the zone plays a major role in storing and attenuating metals, little progress appears to have been made in fully understanding these dynamics. In particular, there are many unanswered questions about the role of the zone in the storage of metals, and the release of metals to surface water or groundwater. Although manganese has been studied quite extensively (for example, Harvey and Fuller, 1998; Fuller and Harvey, 2000; Bourg and Bertin, 1993, 1994), few authors appear to have investigated the role of iron, which is typically the more dominant mining-derived metal researched. To date the literature does not appear to address how iron behaves in the hyporheic zone, what processes control its mobility, and the effects of those processes on surface water and groundwater concentrations of iron. The extensively studied geochemistry of iron, particularly its presence in mine water, has not seemingly been applied to understanding its mobility in the hyporheic zone. The same goes for other metals such as aluminium, copper and zinc which, although mentioned in the literature, do not appear to have been studied in such great detail.

Research is also needed to establish how relationships observed at the sediment scale translate to the river-reach scale (Boulton *et al.*, 1998). Although many studies have explored the connection between the surface stream and the hyporheic zone at the reach scale, very little appears to have been carried out on the effects of hyporheic zone biogeochemical processes on a larger scale. Small-scale investigations are essential to identify such processes and a limited amount of literature does exist, but the results appear too variable between different sites to establish the cumulative effects on an entire river system. Harvey and Fuller (1998) explored this to some degree with manganese, but no studies appear to have done the same for other mining-derived metals.

The hyporheic zone is an extremely dynamic environment, not only in terms of its hydrology and physicochemical characteristics, but also its microbial ecology and function. Studies of specific microbial processes are few, however, with many

investigating the overall mineralisation of organic carbon or overall respiration rates. There may be practical difficulties in designing experiments which would deliver results that relate to real environments. Some work has focused on the reaction of microbial communities to heavy metal contamination, and it has been suggested that these communities could act as indicators of pollution events, either directly or through the cumulative effect of heavy metal transfer to macroinvertebrates.

Clearly there is scope for more work on the microbial ecology of these systems, if appropriate experiments can be designed. Very little literature appears to exist on microbiological processes, such as sulphide oxidation, taking place within the zone, including reaction rates and limiting factors. One particularly interesting opportunity for research would appear to be the potential to recreate conditions of the hyporheic zone in a reactor vessel, since the zone's microbial community appears to be highly effective at immobilising manganese, a task that has hitherto proved difficult in passive mine water treatment.

6 Conclusions and recommendations

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 focus on its role in mobilising and/or attenuating metal pollutants. Existing literature suggests that the hyporheic zone may be an important sink for metal pollutants, but investigations have not been sufficiently detailed to date to fully understand how zone processes vary spatially and temporally and, more significantly, how this environment might be used to tackle mine water pollution (if indeed this is feasible).

There has 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 appears to be in large part due to the difficulty of physically measuring the volumes of water transferred across the zone (under differing hydrological conditions) and the metal loads associated with these fluxes. The 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, although this may be revealed by ongoing research recently published by Mayes *et al*. (2005) at least for one catchment in the north-east of England.

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. Interestingly, this immobilisation of manganese appears to occur rapidly, which raises the question of whether such conditions could be imitated in a water treatment system for manganese remediation?

The major pollutant of most mine waters - iron - 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 mine waters, 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 rates of these reactions are not yet clear.

Our literature review reveals a set of generic conditions for the attenuation or release of mine pollutants within the hyporheic zone (Figure 6.1). 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 or copper are co-precipitated (or adsorbed) along with the iron and manganese oxides. Alternatively, respiration by micro-organisms and oxidative breakdown of organic matter may deplete dissolved oxygen, generating reducing conditions within the hyporheic zone. This encourages the dissolution of iron and manganese oxides and 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. As a general rule, metals are more mobile under reducing conditions and less mobile under oxidising conditions (Younger *et al*. 1993).

```
                    ┌─────────────────────────┐
                    │     HYPORHEIC ZONE      │
                    └─────────────────────────┘
                       ↙                   ↘
        ┌──────────────┐              ┌──────────────┐
        │   High DO    │              │    Low DO    │
        │   High pH    │              │    Low pH    │
        └──────────────┘              └──────────────┘
               ↓                             ↓
        ┌──────────────┐              ┌──────────────┐
        │  Oxidising   │              │   Reducing   │
        │  conditions  │              │  conditions  │
        └──────────────┘              └──────────────┘
               ↓                             ↓
        ┌──────────────┐              ┌──────────────┐
        │ Fe oxide and │              │  Reductive   │
        │   Mn oxide   │              │ dissolution  │
        │ precipitation│              │ of Fe oxide  │
        │              │              │ and Mn oxide │
        └──────────────┘              └──────────────┘
               ↓                             ↓
        ┌──────────────┐              ┌──────────────┐
        │Co-precipitation│            │  Associated  │
        │ or adsorption │              │ dissolution  │
        │ of other metals│            │ of other     │
        │              │              │ metals       │
        │              │              │ adsorbed or  │
        │              │              │ co-precipitated│
        └──────────────┘              └──────────────┘
               ↓                             ↓
        ┌──────────────┐              ┌──────────────┐
        │   Metal      │              │  Release of  │
        │ attenuation  │              │ metals into  │
        │              │              │  solution    │
        └──────────────┘              └──────────────┘
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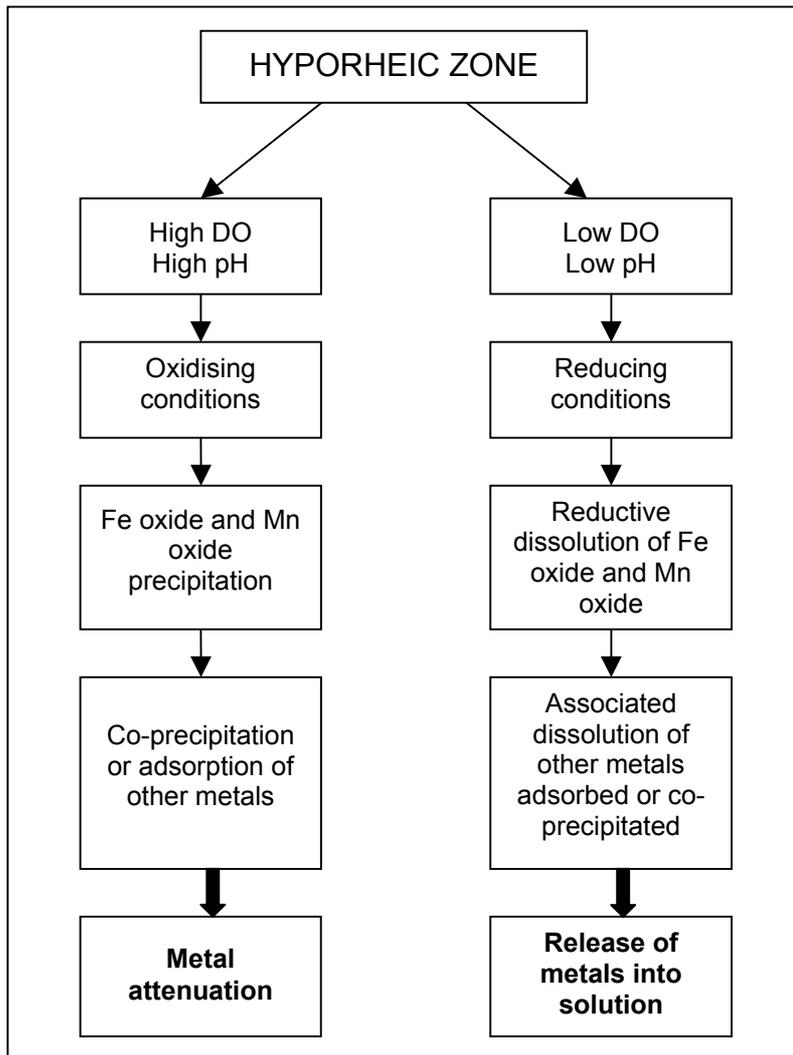
Figure 6.1: Generic redox and pH conditions for attenuation or release of metal pollutants within hyporheic zone (where DO is dissolved oxygen).

It is clear from the brief discussion above that there are a number of research gaps in the field of mining water-derived pollutants in the hyporheic zone, and the main areas for potential projects are summarised in the questions posed below:

- How important, quantitatively, is the hyporheic zone in governing the overall loading of metal contaminants to rivers, and how does it affect the proportions of mine water pollution arising as point sources or diffuse sources?
- What are the key biogeochemical processes, and associated rates, that result in the attenuation of metals in the hyporheic zone, and could these processes be recreated in a passive treatment system to remove some of the 'problematic' metals such as manganese (Mn), zinc (Zn) and lead (Pb)?
- What is the most appropriate, and accurate, method for monitoring the hyporheic zone to answer these questions?
- Is it feasible to resolve the scale-dependence of these biogeochemical processes, such that we can understand the role of the hyporheic zone in mine water-affected freshwaters for entire catchments?

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