

ABSTRACT

Introduction of the Water Framework Directive has put greater emphasis on the remediation of polluting minewater discharges. However, the net effect of these remediation schemes upon catchment scale pollutant fluxes is poorly understood. Diffuse sources of inorganic pollution derived from historical mining activity in post-industrial catchments often represent a considerable obstacle in achieving Water Framework Directive targets. This investigation presents data from the Rivers Tyne and Wear catchments in the north of England, which are heavily affected by metal and coal minewater discharges. In-stream metal fluxes were measured throughout the catchments during high flow and low flow conditions. The importance of minewater discharges and seepages to total metal loading appears to be overridden by diffuse sources lower in the catchment, far from heavily mined headwaters. These diffuse sources may arise from re-suspension of contaminated streambed sediments, contaminated groundwater input via the hyporheic zone or non-mine related sources (for example, sewage works). A high particulate contribution to total loading seen in the lower reaches is likely to have little direct ecological effect due to lowered bioavailability. On the other hand, the fluxes of particulate material through the catchment may provide a mechanism for pollutant transport, which may subsequently become more bioavailable. Remedial measures targeted at highly contaminated discharges may have a marked short-term impact on dissolved, bioavailable metals in the immediate waters. However, the considerable contribution of diffuse sources to total loadings throughout the catchments is likely to be a significant obstacle in attaining quantified good ecological and chemical status within the study catchments.

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1.0 INTRODUCTION

The Rivers Tyne and Wear in the north east of England are generally accepted to be contaminated as a result of historical mining activities. This project aims to address the fluxes of metaliferous pollution in the post-industrial catchments of these rivers by systematically quantifying and spatially mapping problematic in-stream metals, that is those which are present within the water column.

1.1 Background

Anthropogenic extraction of metals from immobile reserves within the geosphere, and subsequent dispersion into the surface environment via poor management within the mining and minerals industry, is causing a worldwide pollution problem.

Prior to the 18th century, England was generally a rural society, where the aqueous environment remained relatively unpolluted, and where the chemistry of that environment was influenced almost entirely by natural processes. Following the Industrial Revolution, England became known as the workshop of the world, where mining for fuel and raw materials went to great lengths, with little or no concern for the environment.

Changes in environmental sensitivity in the late 19th, early 20th century occurred in Britain and much of western Europe, where wastewater treatment systems began to be developed in industrialised areas, and discharge consents were imposed as a response to the dire state of rivers and groundwater. Further development of environmental sensitivities and understanding subsequently led to a movement towards cleaner rivers. Recently, the long-term sustainability of water resources has become a priority of the Environment Agency (See: www.environment-agency.gov.uk) as well as the European Commission, via the Water Framework Directive, which is probably the most important piece of European legislation with regards to the aqueous environment.

Minewater contamination of water resources has been suggested as a significant threat to compliance with the developing targets of the Water Framework Directive. (Jarvis et al. 2007).

1.2 European Union Directives

The European Commission has set a number of Directives to regulate the pollution of the aqueous environment by certain defined substances to maintain ecological balance. Directives of particular relevance are the Dangerous Substances Framework Directive (76/464/EC), the Freshwater Fish Directive (78/658/EC), and the recent Water Framework Directive (2000/60/EC) (See: http://europa.eu/index_en.htm). Environmental Quality Standards (EQS) have been developed in the UK to quantify the objectives by, for example, providing threshold limits for certain polluting substances in a particular environment. The EQS controlled substances are listed within the Directive. Despite these Directives and considerable progress in water pollution treatment systems, there still remains a gap in the remediation of polluting minewater discharges.

1.2.1 Dangerous Substances Directive

The Dangerous Substances Directive (76/464/EC) was designed to protect the aqueous environment from certain dangerous substances, with a two-tiered approach: Black List substances, which must be eliminated from discharges into the aqueous environment, and Grey List substances, which must be reduced within discharges into the aqueous environment within member states (see annex A for substances).

1.2.2 Freshwater Fish Directive

The Freshwater Fish Directive (78/659/EEC) seeks to protect freshwater bodies that are suitable for sustaining fish populations by setting chemical and physical quality objectives. This Directive will be superceded in 2013 by expansion of the Water Framework Directive. Both the rivers Tyne and Wear and their tributaries are included within the directive and are regulated as 'salmonid waters'.

1.2.3 Water Framework Directive

The recently introduced Water Framework Directive (2000/60/EC) was developed as a response to the growing necessity to protect both freshwater resources and the natural environment by avoiding long-term deterioration of quality and quantity. The combined

approach, specifics of which are still in a state of flux, targets individual river basins and the requirements within them in order to develop methods of mitigation and remediation where pollution is an issue. The summative objective of the Directive is to achieve a quantified good ecological and chemical status in surface waters and good chemical and quantitative status in groundwaters by 2015. The most environmentally damaging chemicals will be regulated at European levels (including lead, cadmium etc which are priority/ priority-hazardous substances respectively) as a follow-on from the Black and Grey List substances in Directive 76/464/EC. The regulation of other specific substances will be undertaken by member states under guidance of the Directive. The ecological status will be classified upon floral/ faunal diversity in comparison to a reference condition, below which is poor status, and above which is good status. In addition to this, the ecological status will also be classified with respect to specific pollutants that may cause ecological impoverishment (Environment Agency 2007a).

Jarvis et al. (IN PRESS) discuss the potential implications of the new EQS, which are currently being reviewed, on sustainable management issues within the mining sector. Frequent EQS breaches for a range of metals (notably the ecotoxin zinc, priority substance lead and priority hazardous substance cadmium) continue to occur in reaches of the Rivers Wear and Tyne (Mayes and Jarvis 2007 Pers. Comm.). Early indications suggest that the new EQS threshold limits will be more stringent than the existing standards mainly due to the ecological targets of the Directive (Jarvis et al. IN PRESS).

This situation raises potential issues with remedial measures: the catchment-based approach defined by the Directive relies upon total remediation to set standards. In many circumstances, the background concentrations are likely to exceed EQS, in particular those in heavily-mined catchments where remedial measures targeted at point sources are already in place. Mayes et al. (2007) discuss the significance of diffuse minewater pollution to total in-stream metal fluxes through the catchment, highlighting the problem that conventional remediation measures targeted at point sources are insufficient in meeting the new EQS.

Before a strategy for catchment-based remediation of minewater pollution can be developed, the fluxes and sources of contamination must be defined.

1.3 Aims and Objectives

- To locate potential sources of contamination in the upper reaches of the Tyne and Wear catchments.
- To quantify the in-stream metal fluxes and critically evaluate mobility trends.
- To evaluate the long-term environmental implications of pollutant fluxes through the catchment.
- To propose remedial measures to mitigate the pollutant fluxes proposed in accordance with EQS set by 2000/60/EC, to meet a quantified good ecological and chemical status in surface waters of the Rivers Tyne and Wear by 2015.

2.0 The Site

Located in the north east of England, the Tyne and Wear catchments are particularly shaped by historical industries which relied heavily upon metal mining in the upper catchment, and coal mining in the lowlands.

2.1 The River Tyne

The River Tyne lies in the North Pennines, passing eastwards through the lowlands of the Newcastle conurbation before meeting the North Sea at Tynemouth. It is heavily affected by elevated in-stream metals as a result of historical mining activities (see figure 1).

The River Tyne does not appear in the LOIS study literature, but elevated metal concentrations can be inferred from independent studies (e.g. Hall et al. 1996). The Environment Agency for England and Wales monitor the bulk chemistry of major rivers including the Tyne; and these data are readily available under the Freedom of Information Act (OPSI 2000).

2.2 The River Wear

The River Wear lies to the south of the Tyne, and also runs through the North Pennines, with its source formally at Wearhead, and passing north eastwards through Durham before meeting the North Sea at Sunderland (see figure 1). Like the Tyne it is heavily affected by elevated in-stream metals as a result of historical mining activities.

Neal and Robson (2000) present a compiled report of core data for rivers draining into the North Sea obtained during the Land-Ocean Interactive Survey (LOIS), highlighting the issue of pollutant fluxes through river catchments. The River Wear, included in this study, showed marginal elevation of concentrations of in-stream metals at Sunderland Bridge, notably, zinc ($\sim 22\mu\text{g/l}$), lead ($\sim 2.7\mu\text{g/l}$), lithium ($81\mu\text{g/l}$), iron ($201\mu\text{g/l}$) and copper ($3.7\mu\text{g/l}$) which were attributed to minewater discharges in the upper reaches

2.3 Topography

Both study catchments extend from the meandering lowlands of Durham and Northumberland into the steep valleys within the uplands of the North Pennines, reaching 893m A.O.D. at Cross Fell in east Cumbria (Tables 1 and 2, Figure 2).

Table 1. Maximum altitude of Tyne and major tributaries

River	Max Altitude (M.O.D.)
Tyne	893
North Tyne	600
South Tyne	893
West Allen	673
East Allen	673
Derwent	560

Table 2. Maximum altitude of Wear and major tributaries

River	Max Altitude (M.O.D.)
Wear	747
Brownay	380
Gaunless	461
Wear	747
Bedburn Beck	535
Rookhope	611

(Data obtained From: NWA, Centre for Ecology and Hydrology 2007)

2.4 Geological History and Orefield Formation

The geology in and around the catchments has been extensively documented, due primarily to the wealth of ores and minerals in the region, and the historical mining activities which have taken place (e.g. Patrick and Polya 1993; Dunham 1990; Dunham 1949).

The Caledonian Orogeny, which ended in early Devonian times, caused a mountain belt to develop across northern England of which the Pennines form the easternmost part (Woodcock and Stracan 2002, 187; Taylor 1971). During this time, a plutonic intrusion caused regional metamorphism and the development of dykes and sills, which were subsequently offset by the formation of the Buttreford Disturbance, which runs north –

south across the centre of the orefield (Dunham 1990). The Weardale Granite lies below the North Pennines, entirely concealed below more recent Carboniferous rocks, it was located during a geophysical survey, and proved by the Rookhope Borehole (Dunham 1965). The age of the Weardale Granite has been radiometrically dated to 364MyrBP - during the Devonian Period (Burgess 1971; Holland 1970).

During the period of the Caledonian Orogeny, climatic warming in conjunction with uplifted sediments formed a barren desert; this lasted for approximately 50MA and was known as the Old Red Sandstone era after the great thickness of red aeolian sandstone beds which remain.

2.4.1 Carboniferous Cyclothsems

Rhythmic fluctuations in sea level and isostatic response of uplifted rock resulted in abrupt changes in depositional environments between marine, deltaic and non-marine (see figure 3). As sediments built up within the newly formed shallow, sea level was eventually reached. Coal forming forests flourished on the new land, which later subsided, burying the forests under further sediment deposition. Sandstones formed extensively within periodic deltaic conditions (Guion et al. 2002, 231; Land 1971).

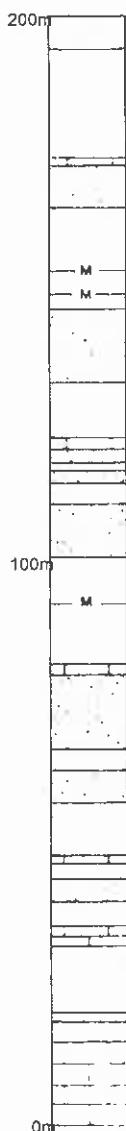
Deleted: seas that had newly formed

The resulting cyclothemic sequences consist of rhythmic sandstone, shale, coal and limestone beds, laterally interspersed and rarely complete. Large scale uplift and deformation, and the intrusions of igneous bodies occurred during the late Carboniferous, most notable of which is the Great Whin Sill and associated Dykes, which extends from Cumberland, Northumberland, along the Pennine Escarpment and to Teesdale (Eastwood 1971).

The carboniferous system can be subdivided into the following major series:

- Carboniferous Limestone Series (Dinantian)
- Millstone Grit Series (Namurian)
- Coal Measures (Westphalian)

The heavily faulted block and trough structure of the Dinantian Limestone resulted from rapid deposition and subsidence in basins compared to the more stable massifs (Mills 1971).



*Figure 3. Allenheads
Borehole (No2.)
showing Namurian
strata Redrawn after
Dunham 1990*

The Millstone Grit Series, which developed during the Namurian exhibits many similarities with the carboniferous limestone series of the Dinantian, including the cyclothsems: deltaic sandstones, limestones and coal measures. The Namurian can be seen as a change between the dominance of the Dinantian shallow seas and the deltaic swamps of the Westphalian. Aranaceous facies and coarse sandstones dominate the Millstone Grit Series (Land 1971).

Deposition of the coal measures of the Westphalian were, again, subsidence controlled. Sediment influx from higher ground continued to the north-east, with the resultant cyclothem taking the form: marine shale bed, overlain by non-marine shale/ mudstone, sandstone, seatearth and a coal seam, the latter of which resulting from sediment build-up above sea level. Since the sedimentation kept pace with the subsidence, the depositional material from marine incursion is relatively minimal, dominated by mudstones rather than the earlier great thickness of limestone (Taylor 1971). The great concentrations of decaying organic matter within the stagnant sediments consumed all available oxygen. The reducing conditions that ensued allowed dissolution of metals, primarily iron derived

from weathered material influx from the northern landmass, forming minerals in the ferrous (II) oxidation state. Siderite and Pyrite were two common minerals that formed within coal measures, iron oxide and sulphide respectively.

2.4.2 Orefield Formation

Faults and fissures, which formed during the structural deformation of the Upper Carboniferous, allowed hydrothermal circulation of NaCl – CaCl₂-rich brines at initial

temperatures of 220°C within the newly formed sedimentary rocks (Patrick and Polya 1993, 372-375). The convection that occurred was due to the remnant heat and uranium/thorium decay from the intruded Weardale Granite, which still provides a high heat-flow anomaly (Evans et al. 1988; Gebski et al. 1987). The circulating pore fluids became enriched with trace elements, leached from the country rocks. As the fluids migrated radially from the heat source along fractures and faults, fractional precipitation of dissolved minerals occurred. This behaviour first proposed by Dunham (1934) forms a 'zoning' pattern within the orefield, where concentric bands of a range of minerals are found dependent upon temperature (See Figure 4).

The exact age of the deposits has been subject to much controversy (Patrick and Polya 1993; Shepherd et al. 1982; Hirst and Smith 1974; Kanasewich and Slawson 1964; Moorbat 1962). Veins of the North Pennine cross-cut the dykes and sills of the Whin Suite, dated 293MA, and therefore are certainly no earlier than this (Dunham 1990). A number of attempts have been made using isotope dating, the most reliable of which is based on Rb-Sr ratios of mineralisation from the great sulphur vein, placing the origin of mineralisation at approximately 206MA (Patrick and Polya 1993; Shepherd et al. 1982). Due to the zoning of the mineralisation, the ore field exists only in the upper reaches of the Tyne and Wear in the North Pennines.

2.4.3 Permian and Triassic Systems

Uplift occurred at the close of the Carboniferous period, the resultant continental phase saw the erosion and deposition of red sands in deserts and red/green mottled muds, evaporates and rock salt within closed seas. These Lower Permian sands thin to the east where little erosion occurred. Rhaetic sea transgression followed, with the deposition of the massive magnesian limestones which still dominate the southeast of the site (Woodcock 1993).

No Jurassic rocks remain in the area; it is probable that any geological evidence was rapidly eroded following uplift in the Tertiary.

2.4.4 Tertiary Uplift

Generally, little is known about the Tertiary in Northern England. What is known is that gentle uplift of the previously deposited sediments into a vast dome occurred, centred around the Lake District. The faulting and erosion which followed is responsible for the present day arrangement of beds and outcrops (see figure 5).

2.4.5 Quaternary

Climatic chance and subsequent glaciation caused a highly erosive environment that shaped the present day landscape. Glacial erosion caused the removal of rock debris, grinding, polishing, striation and plucking of bare rock with the resulting formation of steep sided valleys and moraines

It is thought that as many as four or more successive glaciations, varying in severity, occurred during the middle and upper Pleistocene, namely: Anglian, Wolstonian and Devensian (Woodcock 2002, 401).

Deposition of glacial till within the Team valley is thought to have obstructed and diverted flow of the Wear, originally a tributary of the Tyne (Eastwood 1963).

2.5 Local Geology See figures 6, 7 and 8 (BGS Sheets E13 – E27)

2.5.1 Solid Geology

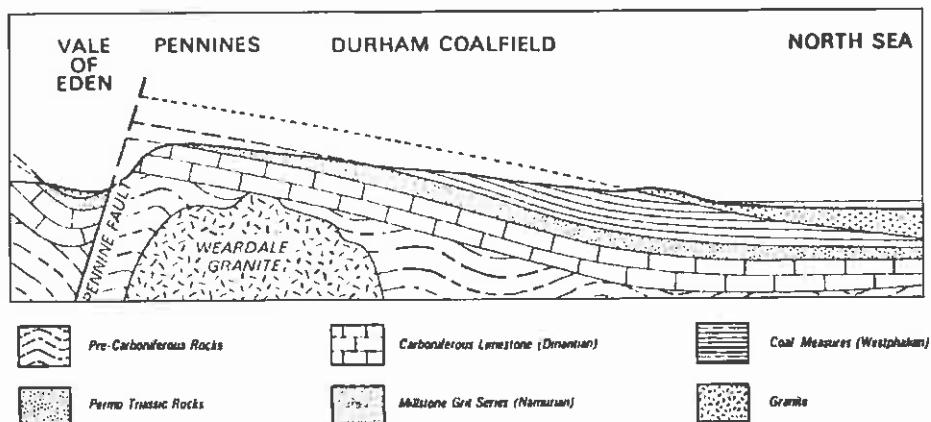
In the upper catchment of the North Pennines, the geology comprises Namurian Millstone grit series (Sandstone), underlain by the Carboniferous Limestone Series. The Great Whin Sill is of early Permian age and of doleritic composition, located within the Carboniferous Limestone at variable depth, it is offset by faulting and exposed in the South Tyne gorge at Cocklacke (Johnson and Dunham 2001; BGS Sheet 25 1973; Holmes and Harwood 1928). To the east, the unexposed Weardale Granite has been proved at depth. Between this and the Carboniferous Limestone Series are the Basement Conglomerates (Fitch and Miller 1967).

Generally, the upper reaches of the Tyne and Wear exist in Middle Carboniferous limestone-bottomed valleys with only smaller streams extending into the Millstone Grit sandstones within which occasional coal seams crop out (See Figure 7).

The lower reaches of the Tyne and Wear bisect the Westphalian Coal Measures of the Durham Coal Field, which lie conformably on the Millstone Grit Series. The middle/upper Coal Measures dip eastward at a shallow angle, and have been extensively eroded in the uplifted areas west of Consett/ Stanhope (see figure 5).

Figure 5. Sketch section of geology from Vale of Eden (west) to North Sea (east)

Adapted from: Eastwood 1971 (*Not to scale*)



The Alston Block See Figure 9.

The northern, western and eastern margins of the North Pennine Orefield are bounded by the Stublick fault system, the so-confined region is commonly known as the Alston Block after Trotter and Hollingworth (1928) (Dunham 1990; 1949). The Stublick fault system comprises a belt of east - west to east - north east faults extending from Castle Carrock east to Thirlbrough. A continuation of the Stublick fault system occurs en-echelon as the Ninety Fathom Dyke, which runs from Acton Fell to the coast at Tynemouth (Dunham 1990).

2.5.2 Mineral Deposits

Extensive zoned mineralisation occurs as fissure-veins within country rocks of Carboniferous age, located primarily within the Dinantian strata of the Alston Block (see figure 9), but also extending into the Westphalian rocks of the Durham Coalfield (Forbes et al. 2003; Dunham 1990. See figure 4).

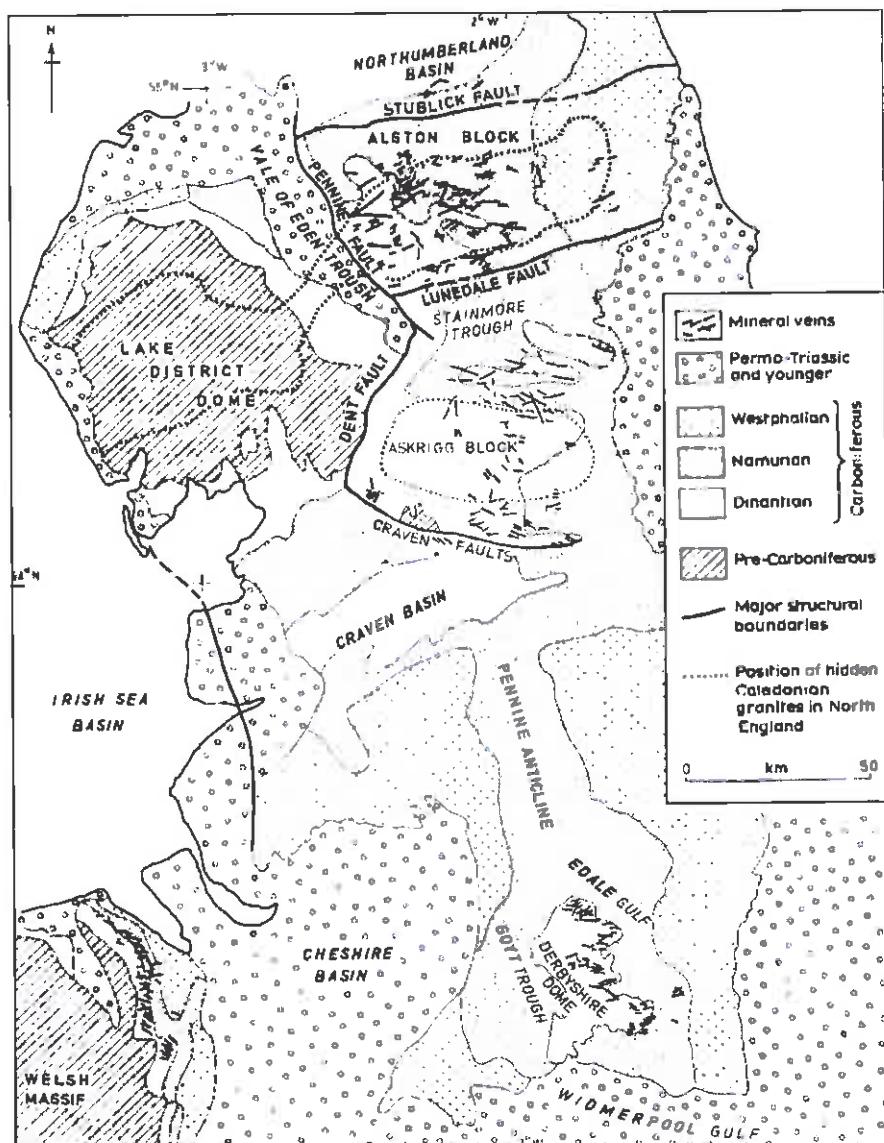


Figure 9. The Alston Block in Relation to the Askrikk and Peak District Orefields and Major Stratigraphical Features. (Adapted from Dunham 1983)

The workable oreshoots in the North Pennines are present within vertical fractures or veins, and bedding orientated flats. They primarily include:

Mineral	Chemical Formulae	Appearance and Occurrence
Galena	(PbS)	Cubic crystal system, metallic. Found commonly within hydrothermal veins. The primary lead ore of the North Pennines, often small amounts of silver were contained within the deposits.
Sphalerite	(ZnS)	Cubic crystal system, resinous. Often associated with galena deposits in hydrothermal veins. Commonly known as Zinc Blende
Pyrite	(FeS ₂)	Cubic crystal system, metallic brassy yellow. Hydrothermal deposits and sedimentary rocks often contain pyrite. Small amounts found in mineral veins as replacement deposits.
Chalcopyrite	(CuFeS ₂)	Tetragonal crystal system, deeper yellow than pyrite. Most finds are of massive crystal association, rarely workable amounts found in the North Pennine Orefield.
Witherite	(BaCO ₃)	Orthorhombic crystal system, white to pale yellow. A rare mineral, yet common in the North Pennines, a unique feature of the Orefield.
Baryte	(BaSO ₄)	Orthorhombic crystal system, transparent to opaque depending upon impurities. A common gangue mineral in the Orefield.
Flourite	(CaF ₂)	Cubic crystal system, transparent to opaque depending upon impurities. Crystal masses commonly found with lead deposits. Probably the most abundant mineral in the Orefield.

Table 3. Common Minerals found in the North Pennine Orefield. *Information from Dunham 1949, 84 – 98; Curtis 1997, 12 – 28.*

A number of rarer sulphides and arsenides also exist within the Orefield (Dunham 1949).

Examples of galena, sphalerite and chalcopyrite are common within Dinantian Limestone outcrops, spoil heaps, river flood deposits (respectively) in the Nenthead area – see Plates 1, 2, 3 and 4.

2.5.3 Drift

Glacial deposits were once clearly visible on the Durham coastline, however these are now widely obscured by colliery spoil dumped from coastal mines (Mills and Holliday 1998).

Tertiary drift deposits cover much of the survey area, consisting predominantly of boulder clay; material to the east of the catchments is derived from the Cheviots to the north (Eastwood 1971), and some outcrops on the coast are thought to derive from Scandinavia (Bridgeland et al. 1999).

Flood plain terrace gravels and alluvium exist in present day river channels (see figure 8).

2.6 Hydrogeology

The geological setting of the Tyne and Wear catchments varies significantly from west to east as a result of the generalised eastward dip of strata; consequently, the hydrogeology of the region varies in accordance with lithology (see figure 10).

The North Pennine headwaters are set within sedimentary aquifers, classed as minor by the Environment Agency (Groundwater Vulnerability Sheet 4), of variable permeability, with large areas covered in low-permeability drift deposits. Despite being of relatively low permeability, minor aquifers are important for providing baseflow to rivers and local (farm/village) supplies (Downing 1998, 31).

Modification of groundwater regimes within the North Pennines by historical mining activity, primarily the driving of levels and shafts within the fells, has caused increased permeability and hence lateral flow of groundwater, which then can spectacularly burst out of the hillside (See plate 5). Adams and Younger (2001) appropriately termed the increased permeability of mined strata as an ‘anthropogenic aquifer’, the long-term hydrological impacts of which are yet to be realised. In addition, hydrogeochemical changes within the disused workings, including the oxidation and dissolution of metal sulphides (See Section 3.1), can result in highly contaminated seepages and discharges (see plates 6 and 7).

The non-aquifer of the cyclothemic Westphalian Coal Measures of the eastern lowlands, is unconformably overlain further east by a Permian Magnesian Limestone Aquifer (See figure 7), extending seaward from Sunderland (Smith 1971, 70–72). The Magnesian Limestone Aquifer of south east Durham is the most important aquifer in the north east of England, almost entirely covered with impermeable glacial till, so that vulnerability to contamination is generally low (Cairney 1972). However, Neymeyer et al. (2007) documents the migration of polluted minewater, from the underlying worked coal measures, into the confined public supply aquifer: a result of a rebounding water table following the cessation of local mine dewatering in 1974.

2.7 Hydrology

The River Tyne drains an area of approximately 2,920km² (Kneale et al. 2001), and the Wear an area of approximately 1,315km² (Environment Agency 2006b).

The upland areas of the North Pennines are dominated by peat moorland with steep topographical gradients and lack of substantial vegetation, providing rapid discharge to headwaters following heavy rainfall. The permeability of surface geology is generally high where aquifer material is exposed; this decreases in areas covered by substantial drift deposits (See: Figure 8). Groundwater contributions to river flow are highly significant within the catchments, particularly during low flow conditions (Neymeyer et al. 2007).

A number of reservoirs have been constructed within the catchments to provide an additional water supply to groundwater and river abstractions, notably the Kielder Reservoir on the North Tyne, the Derwent Reservoir on the River Derwent; and the Burnhope Reservoir on Burnhope Burn. Release from the reservoirs is controlled in order to maintain statutory regulations of Minimum Maintained Flow (MMF), often supplementing summer dry spells; and also to minimise ‘flash’ type discharges from the headwaters, which have the potential to cause flooding downstream (Marsh et al. 2000 109). Despite this, the beneficial hydro-ecological effects on the native ecosystems have reportedly been variable (Gibbins et al. 2001).

Changes in land-use and modification of river channels has had a great impact upon the drainage and flow regimes within UK catchments. In addition to a probable increase in

intense rainfall events due to climate change (Acreman, 2000; Environment Agency 2006; Shenan 2006), modified drainage within urbanised areas magnifies surface run-off events, increasing the peak flow rates within UK rivers. Towards the lowlands of the Tyne and Wear, greater thickness of drift, in conjunction with extensive urbanisation, is likely to have increased the susceptibility of lower reaches to flash flood type responses to rainfall (Marsh et al. 2000, 109 – 123).

Recent work has been carried out to assess the impacts of climate change on river basins (See: Environment Agency 2006), and even the impacts of climate change on water pollution (Shenan 2006).

2.8 Climate

The climate of the Tyne and Wear basins varies significantly between the upper and lower catchments. The average minimum and maximum temperatures between the years 1971 and 2000 in the Pennines were -0.8°C and 10.3°C respectively, whereas in the lowlands of Durham and Northumberland, the average temperatures ranged between 6.4°C and 12.2°C (Met Office 2007).

The upland areas are subject to much greater annual precipitation (up to $\sim 2500\text{mm}$ in the Pennines) in comparison to the lower reaches ($\sim 600\text{mm}$ Smith 1972) The lowlands of the Wear at Chester-le-Street, for example, received 855mm of rain during 2006, whereas further up the valley at Stanhope, an average of 1280mm of rainfall fell (NWA, Centre for Ecology and Hydrology 2007).

2.9 Climate Change

The widely accepted phenomenon of 'global warming' commonly refers to anthropogenic climate change, primarily caused by the emission of carbon dioxide through fossil fuel combustion (e.g.: Pepper et al. 1996, 183-184). An increase in average global temperature of 0.5°C has been recorded over the last 50 years (IPCC 2007).

From the geological record, climatic fluctuations can be seen to have occurred on a variable scale throughout earth's history, from rapid cooling in the Miocene (Holburn et al. 2005), to more recent warming at the end of the last glaciation (Brooks 1949). Climate change archives, both short-term meteorological records and long-term ice and sediment cores, have been used to infer future climatic trends (See: Frakes et al. 1992; Brooks 1949). However, due to the complexity of the interlinked factors controlling global climate, potentially great error could be generated when modelling future trends, especially when predicting the effect of carbon emissions (see Ruddiman 2003).

Despite this, recent increasing extremes within UK weather, including prolonged droughts of the 1980s and 1990s and more recent severe flooding events, have drawn attention to the probable effects of global warming (e.g. Arnell and Reynard 2000, 3 - 29).

Climate has always dominated the control of surface water hydrology, and during the current period of change, the implications for flow regimes within major rivers is likely to be highly significant.

2.10 Land use

Land use in the upper reaches is predominantly rough grazing (sheep farming) over the moorlands, with many relics of historical metal mining activities, including spoil heaps, adits and disused shafts (particularly around Nenthead and Killhope). There is little visible current industrial activity within the once heavily industrial Alston – Allendale – Killhope area in the North Pennines.

Towards the lower reaches, land use is predominantly arable farming and with a greater concentration of urbanised areas. The geology of the lower reaches gave rise to extensive coal mining. Many settlements sprang up around the coalfields in the 19th and 20th centuries, and whilst mining has ceased in the area, light industry remains.

3.0 LITERATURE REVIEW

The legacy of contaminated land and consequent pollution of the aqueous environment as a result of industrial activity is an ongoing problem in many parts of the world. Scientific literature covers many aspects of the subject, in particular, the common cause of metaliferous pollution of watercourses, Acid Mine Drainage (AMD).

Historical mining activities in the UK have caused a vast potential for metal mobility, with an estimated 1800 km of streams and rivers contaminated to an extent where they are at risk of failing to meet the EC Water Framework Directive (2000/60/EC) objectives (www.environment-agency.gov.uk).

The continual flux of metals through rivers and dispersion into the seas and oceans is of significant environmental concern in terms of water resources, aquatic ecology (and hence fishery resources) and general amenity value.

3.1 Historical Mining Activities

The reportedly acute metal contamination of the rivers Tyne and Wear is thought predominantly to have occurred, and continues to occur, as a result of the legacy of extensive historical mining activities within the catchments (e.g.: Lakey and Steele 2006; Neal et al. 2000b; Younger 1994).

3.1.1 Mining in the North Pennines

The North Pennine Orefield was one of the most productive lead and zinc mining areas of Britain (Macklin et al 1997). Archaeological evidence suggests that the lead ores of the North Pennine Orefield have been exploited since the Roman Conquest (Dunham 1949). However, Wallace (1890) concluded that no extensive mining had been undertaken in the more mineral rich Alston District prior to 1650.

The construction of bell pits (Dunham 1949) and the processes of 'hushing' (Lord and Morgan 2003) have been utilised since the 12th century. Bell pits comprise a pit to expose mineral formation, followed by radial excavation along the vein to obtain valuable lead

ores. This practice continued until the roof of the pit became unstable or collapsed. Hushing involved the construction of a temporary dam in a stream, which was subsequently breached, allowing a surge of water to erode the upper sediments and expose the underlying mineral veins (Lord and Morgan 2003; Forbes et al 2003). This process was immensely damaging to the environment, particularly because of the amount of debris dumped into the rivers and washed downstream, causing significant contamination.

Large-scale pollution from metal mining did not arise until the 'heyday of mining' in the 19th century. A initial boom in lead mining and smelting occurred in the 18th century, brought about by investment from the London Lead Company, and the Beaumont Company (Dunham 1949), and sustained by the developing supply of pit and sea coal from the nearby coalfields. A number of deep shafts, and drainage/ exploratory levels were engineered, including the Nentforce and Blackett Levels, allowing more than 20,000 tonnes of lead concentrates to be produced during the 19th century (Dunham 1949).

In Alston moor, zinc mining was established by the London Lead Company following the decline of the lead industry. This was continued by its successor the Nenthead and Tynedale Zinc Company until 1921 at which time it is believed that the key veins were exhausted to the depth of the Four Fathom Limestones (Dunham 1990). Meanwhile, fluorspar was established as the principal product of the Northern part of the orefield until 1952 (Dunham 1990).

3.1.2 Mining of the Durham Coalfield

The principal workable coal seams within the Durham Coalfield exist within the lower coal measures of Westphalian age, located between the second and third grits of the Millstone Grit Series and lying north east of the main mineral field (Dunham 1990).

Coal mining in the Durham coalfields started approximately in the 13th century, with the construction of shallow working bell pits. However, the shaft and adit system was first recorded by the Prince Bishops of Durham in the 14th century (Victoria History of the Counties of England - Durham 1907). Workings below the water table were undertaken during the late 15th Century, with the installation of a horse-drawn pump (a practice used extensively in the 16th and 17th Centuries). The first steam-driven dewatering pump was

erected in 1712 at the Washington Fell, revolutionising the ability to mine at greater depths (Victoria History of the Counties of England - Durham 1907) During this time, coal was used extensively in the smelting of iron ores on the west coast, a mutually beneficial practice, as the production of cheap iron allowed further development of mine shafts and pumps (Whellan 1894).

Although some workable coal seams occur within the carboniferous limestone, over 95% of past production is derived from the coal measures of Durham, the easternmost part of which are overlain by a major magnesian limestone aquifer. It was not until the 19th century that mineshafts were first sunk through the Permian cover, primarily due to the technical difficulties of mining far below the water table (Warren 1970). The peak production of coal was reached in 1911, with an annual turnover of 41.7 million tonnes. (Warren 1970)

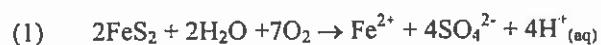
Cessation of mining in the north east of England came about at a time of both increased international competition for coal, and a switch to cleaner fuels, primarily North Sea gas (Banks 1997)

3.2 AMD (Acid Mine Drainage)

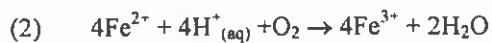
Acid Mine Drainage (AMD) is a term given to the acidic discharge with high levels of total dissolved solids (TDS) emanating from active and disused mine workings as a result of sulphide oxidation, commonly pyrite (FeS_2). Sulphides remain stable under in-situ geological conditions, but when excavated and exposed to the atmosphere, the solid phases become chemically unstable, and percolating water can readily cause oxidative dissolution and leaching (e.g. Younger et al. 2002).

The oxidation of pyrite involves a complex series of reactions which are often bacterially catalysed. The simplified net equations are as follows:

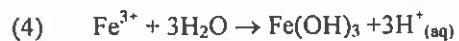
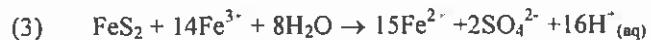
Pyrite Oxidation:



Ferric iron from ferrous consumes $\frac{1}{4}$ of protons:



Ferric iron may accept electrons during further pyrite oxidation, converting back to ferrous iron (3), or hydrolysis may occur (4), both processes producing more acidity.



(After Banks et al. 1997)

However, discharges often have a circum-neutral pH, indicative of water-rock interaction; usually alkaline carbonate buffering from the carboniferous limestone host rock (Nuttall and Younger 1999; Worrall and Pearson 2000). In the absence of the carbonate minerals such as calcite and dolomite, the dissolution of alumino-silicate minerals or sulphate reducing conditions can make a significant contribution to neutralising capacity (Iribar et al. 1999; Banks et al. 1997). This buffering capacity can be overcome giving discharges of very low pH values where high proton acidities exist, particularly when evaporation occurs to further concentrate surface discharges (España et al. 2005). The importance of pH is emphasised by Younger et al (2002, 88-90), as it has control on the solubility and mobility of metals. A lack of buffering capacity can have catastrophic consequences on the polluting nature of discharges: a significant drop in the pH of minewaters can cause large-scale dissolution of solutes such as metal ions from within the workings and host bedrock, which may subsequently be discharged into the aqueous environment.

Discharge of metal rich acid mine waters into rivers and groundwater can result in severe environmental damage and loss of valuable water resources, both from precipitation of metal oxy-hydroxides and elevated in-stream metal concentrations (e.g. Younger et al. 2002; Armitage 1979). In some regions, discharge from abandoned mine workings are the single greatest cause of freshwater river pollution (Younger 1997).

Long-term trends in contaminated minewater discharges have been studied by Wood et al. (1999) in the Midland Valley of Scotland, the findings of which document a high severity of pollution within the first few decades of discharge ('first flush'), decreasing to lower levels with time as the most available sulphide minerals are oxidised. A modelled prediction and laboratory study undertaken by Gandy and Evans (2002) for a colliery spoil heap in County Durham shows an exponential type decay in pyrite oxidative dissolution with time, with greater severity of pollution occurring in the short term. However, the study concludes a half-life in the region of 40-years for the oxidative depletion of pyrite within spoil heap conditions, emphasising the potential for severe pollution for many centuries.

The long term severity of a specific discharge depends on a considerable array of geological and hydrological factors, in addition to the nature and extent of mine workings. Often post 'first flush' discharges are highly polluting and their longevity uncertain.

Coal Mine Discharge

Most coal measures exploited in Britain occur within sandstone beds with variable pyrite and little carbonate content (Mills 1971; Dunham 1949). Subsequent generation of acid mine waters from a fluctuating water table can be extremely proton rich due to the iron sulphide oxidation, and insufficiently buffered due to relatively low anion contribution (Younger et al. 2002).

Discharges from coal mines and spoil tips can consequently have a very low pH and large amounts of dissolved metals (predominantly iron(II) and manganese(II)), which precipitate only when either the pH or oxidation potential is raised. This usually occurs upon discharge to rivers and streams, where oxygen is introduced, and the heavy iron loading is deposited as ochre (iron(III)oxy-hydroxide). This is a common occurrence in the Durham Coalfields, exacerbated by the cessation of mine dewatering: the minewater related degradation of reaches of the River Wear and tributaries is highly significant (Younger 1996; Jarvis and Younger 1997). However, where consistent mine water pumping is undertaken, the water table can be kept stable: little pyrite below the water level is oxidised and few metals are leached from above (Banks et al. 1997).

Metaliferous Mine Discharge

Unlike coal mine discharge, that from metal mines can often leave no precipitate or discolouration of watercourses. There are some major exceptions, in particular those mines with iron or aluminium rich deposits where a red ochre (as at Wheal Jane, a Cornish tin mine) or a white sludge can be precipitated, respectively (see Younger 1996). Assessment of the extent of water pollution from disused metal mines is often difficult due to the lack of visible indicator parameters, and an extensive programme of water sampling is often required (see Lakey and Steele, 2006).

Mining in the North Pennine Orefield for lead and silver (and later zinc) during the 18th, 19th and early 20th centuries (Dunham 1949) continues to discharge waters rich in zinc, lead and cadmium (Nuttall and Younger 1999; 2002) which are buffered to the pH range 8 – 10 by calcium carbonate. Despite a lack of visible precipitate in the discharge from the workings in this region, Armitage (1980), amongst others, has discussed the severe detrimental effect on river benthos seen to extend into the lower reaches of the River Tyne. The effect on the aquatic ecosystem was attributed to the elevated zinc concentrations: although zinc is a necessary trace element for mammals, it can be highly toxic to fish at very low levels (Nuttall and Younger 1999).

Zinc pollution of the North Pennine headwaters has been most comprehensively documented (e.g.: Armatige 1979; Nuttall and Younger 1999; 2002), primarily due to its more prevalent nature within riverine environments and elevated solubility in oxidising conditions.

Remediation of AMD sources has conventionally focused on point sources such as mine adits and drains, where the poorest water quality can be seen. However, it has been suggested that the net contribution of point source pollution to in - stream metal concentrations is far outweighed by diffuse sources and dispersed subsurface contributors (Kimball et al. 2002). Mayes et al., (2007a) finds that typically 50% of in-stream metals are derived from diffuse sources in low flow, escalating to values as high as 98% in high flow, seen within a heavily mined catchment in the north east of England (River Allen). The biggest diffuse contributor is generally spoil tips, where mildly acidic rainwater and oxidising conditions cause sulphide oxidation within the spoil and where pH in the

immediate area can be in the region of 2.5 resulting in extensive leaching of metals. This is exacerbated by the lack of carbonate buffering capacity in the spoil heaps which usually exists in groundwaters (Banks et al. 1997).

The longevity of acid minewater pollution is discussed by Younger (1997) using a number of case studies in the UK. It is suggested that the time frame of most poor water discharge (acidity and elevated TDS) is dependent not only upon the supply of source material (such as pyrite) but also the degree of interconnection between underground workings, rainfall, groundwater table fluctuations and mobility (which is most commonly inhibited by carbonate buffering and oxidation). As a rule, the discharge stabilises after several decades to a manageable level, with iron concentrations falling to <30mg/l with an increasing pH after 40 years (Wood et al. 1999).

The effective remediation of the deleterious effects of historical industrial activities within a developed country such as Britain is a challenging task. Indeed Younger et al. (1997b) acknowledge that although Britain leads the way in minewater remediation, many watercourses still fall outside legislative guideline values for in-stream metals (Mayes et al. 2007a). The adverse implications of large-scale minewater discharges in less economically developed countries, in particular those that are heavily industrialised, are potentially great in terms of regional and global sustainability.

Espana et al. (2005) suggest that several thousand tonnes of metals per annum (including Mn, Zn, Cd and Cu) are exported to the Atlantic Ocean by local rivers as a result of metal mining in the Iberian Pyrite Belt. Such a large contribution from a single orefield raises concerns about both the environment impact of current and historical mining on a global scale, and the buffering capacity of natural systems.

3.3 Mobility of Metals in Surface Waters Affected by Mining

The input of minewater into the riverine environment is not the only source of pollution. Greatly elevated metal concentrations have been found to occur in contaminated sediments of rivers draining the North Pennine Orefield, derived from historical mining activities in the headwaters (Neal et al. 2000; Macklin et al. 1997). It is therefore important to consider the potential for re-mobilisation of deposited material, both as suspended sediments and

dissolved species, to be a major contributor to the metal flux within the aqueous environment. Indeed, during high flow conditions, it has been suggested that the greatest contribution to total flux could be from re-suspended material (Macklin et al. 1997).

Often, however, the dissolved fraction originally derived from minewater discharges is subject to a range of attenuating processes. These may involve adsorption/ complexation with stream bed sediments (Gandy et al. 2006) or biotic uptake.

The zinc tolerant green algae taxa *Mugeotia* sp., *Hormidium rivulare* Kutz and *Stigeoclonium tenue* have been found in abundance within Pennine Headwaters (Say and Whitton 1981; Harding and Whitton 1976; Hargreaves and Whitton 1976), and have been shown to take up zinc from contaminated surface waters during the growing season (Pawlik-Skowronska 2003). The recession of algae following the growing season is a probable source of net zinc export from such headwaters (Mayes et al. 2007; Kalin 1998). The feasibility of the algae *Mugeotia* sp., *Hormidium rivulare* Kutz and *Stigeoclonium tenue* amongst others as a short term sink for mine-related zinc pollution is of particular significance.

The hyporheic zone: The interface between surface and ground waters

In a review of the literature, Jarvis and Gandy (2006) and Gandy et al. (2006) present a compiled report on the work to date with regards to hyporeic zone chemistry and its applicability to minewater pollution. Their findings document a general lack of research in the field, attributed to the practicalities of successfully defining and investigating the zone. The greatest body of research focuses on biogeochemical processes, especially in relation to manganese.

Hyporheic zone groundwater influx, chemically altered by minewater contamination, is likely to be under acid reducing conditions and rich in dissolved metals (Coyne et al. 2007; Gandy et al. 2007). The boundary of the hyporheic zone and groundwater has also been suggested as the geochemical boundary between reducing and oxidising conditions, and thus the stability of contaminants (Benner et al 1999; Nelson and Roline 1999); see figure 11. However, this boundary occupies a non-steady state as environmental and biochemical conditions fluctuate (Van Den Berg et al. 1998).

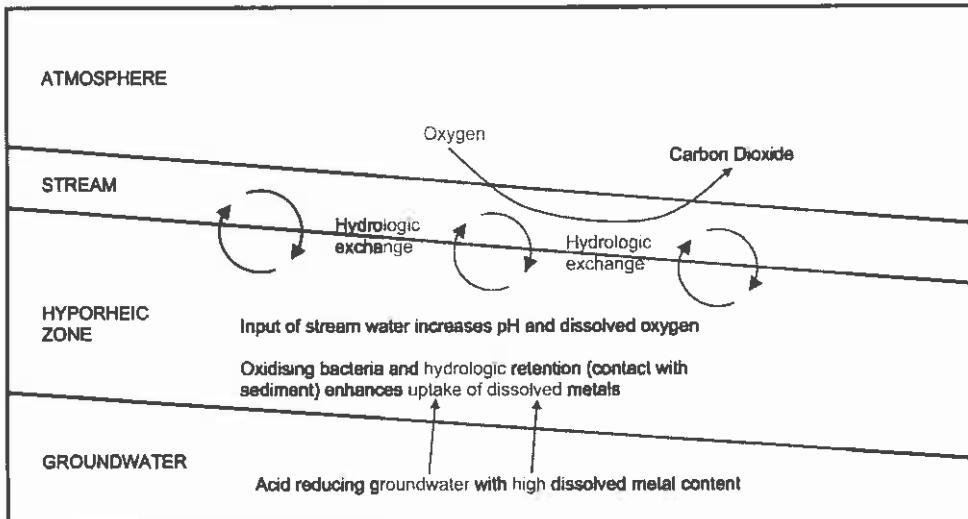


Figure 11. Schematic Diagram of the Hyporheic Zone. Re-drawn after Gandy et al. (2007)

Investigations into trace metal uptake in the hyporheic zone by Fuller and Harvey (2000), found that the formation of manganese oxides in the Mn^{3+} , Mn^{4+} valances commonly caused co-precipitation of minewater contaminants, notably zinc and cadmium. Input of groundwaters with elevated dissolved Mn^{2+} concentrations have been found to undergo microbially mediated oxidation within sediments of the hyporheic zone, precipitating onto oxide surfaces. Trace metal co-precipitation and adsorption of soluble metals derived both from groundwater and surface waters with manganese has been suggested as a major sink for minewater pollution (Harvey and Fuller 1998). Similar behaviour is probable for iron, indeed Benner et al (1995) found iron rich precipitates to a depth of 800mm within hyporheic material on the streambed of a creek in western Montana, underlain by acidic reducing conditions rich in dissolved iron. In addition, Fe(III) precipitates are renowned for their highly adsorptive structure; Mayes (2007c) investigates the use of waste Fe(III) precipitates from coal mine treatment in the removal of zinc from circum-neutral minewaters, finding a mean removal of 37%. Despite the moderate success of this pilot treatment method, it was noted that seasonal algae cycles caused great variability in results. This highlights the significance of biogeochemical interactions on the mobility of minewater pollution.

3.4 LOIS (Land Ocean Interaction Study)

In recent years there have been great developments in understanding of the quality of water discharging from rivers of the eastern UK into the North Sea, conventionally a convenient sink for industrial and urban wastes (Neal et al 2000a).

The most important recent project is the Land Ocean Interaction Study (LOIS), a collation of work undertaken by British universities, the Natural Environmental Research Council, the Environment Agency and the Scottish Environmental Protection Agency, amongst others (Neal et al. 2000a; Neal and Robson 2000) The study spanned the period 1993 – 1999, examining the fluxes of sediments and pollution in eastern UK rivers draining approximately one-fifth of the UK, from agricultural land, urban and industrial centres to rural areas of outstanding natural beauty (see: Neal et al. 2000c).

The significance of the study was quantification of exchange, transformation and storage of materials at the land – ocean boundary of the North Sea and determination of temporal and spatial variability (Neal et al. 2000a).

Nutrient and major, minor and trace element concentrations have been measured within rivers from the Tweed on the Scottish border, to the Ouse and Thames in the south of England (Jarvie et al. 2000a; 2000b; Neal and Robson 2000; House and Denison. 1997; and Neal et al 1997). The information derived from the study is of great European and potentially global value as a resource for managing pollutant inputs to estuarine, coastal and open sea environments (Neal and Robson 2000).

Lead and zinc pollution of the Tyne and Wear catchments is an ongoing problem in terms of Directive 2000/60/EC compliance, but the impact upon groundwater resources is generally poorly documented. Younger (1997) suggests that the buffering of minewater seepages into carbonate bedrock causes significant retardation of the dissolved metal content, thus preventing extensive pollution. Beamish and Klinck (2006), on the other hand, note the potential significance of a groundwater plume in the Nottingham coalfield, which is located within the Sherwood Sandstone aquifer. It has been suggested (Younger et al. 2007; Younger 1994) that the increasing head (due to discontinued pumping) in similar workings may lead to greater contamination of supply aquifers. Nonetheless, weathering

and dissolution of spoil heaps, and discharge from adits is known as a major problem in terms of metal flux through the rivers of the region.

Despite the well-documented metal contamination of the Rivers Tyne and Wear (for example, Hudson-Edwards et al. 1998; Younger 1997), the true behaviour of such contamination is ill defined. Periodic in-stream sampling for regulatory purposes is often limited to 'choice' days: pleasant weather intervals where the flows are typically low. Rarely is sampling undertaken during the very occasional torrential rainfall weather events, where flow rates typically take the form of storm surge type discharges (Mayes 2007 Pers. Comm.). Macklin et al. (1997a, b) point out the significance of the often underestimated 'pulse or slug' type contributions to total in-stream metal loading, via sediment disturbance from flood type events. It is probable that these contaminated river sediments will behave as highly significant pollutant contributors, defining the in-stream fluxes for hundreds if not thousands of years after the cessation of mining in the upper catchment.

It is therefore important that the processes controlling the transport of metals throughout the catchment are more thoroughly understood, and the bulk contributors and sinks are quantitatively defined.

3.5 Environment Agency Metal Mine Project

The Metal Mine Project was developed as an Environment Agency project to investigate the impacts of metal mine discharges in the Northumbria area with a view to identifying the sites of greatest impact (see Lakey and Steele 2006). The site itself spans Northumberland, Co. Durham and Cumbria, areas most heavily affected by metal mining. The project conforms to a phased site investigation and a phase three remediation strategy is eventually intended to mitigate the impact of the minewater discharges on the predefined environmental receptors.

Historical information dating back to the 1970's has been collated by the Agency, with in-stream measurements of flow and chemical parameters. Consultation and compilation of these historical data, specifically for seasonal variation of in-stream metal fluxes, may be a useful tool in modelling the future trends of metaliferous pollution.

At present, no strategy exists for remediation of the mines listed in the Metal Mine Project. A lack of financial backing and uncertainties as to legal responsibilities for environmental damage inevitably hinders the development of extensive investigation with an aim to long-term mitigation.

3.6 Effects of Minewater Pollution on Aquatic Fauna and Flora

It is widely accepted that metaliferous minewater discharges have a negative impact on the aquatic environment by both oxyhydroxide precipitates and elevated levels of eco-toxin metals such as zinc and cadmium (e.g. Banks et al. 1997; Younger 1997; Armitage 1980; O'Grady 1976) This negative impact has been best documented for the riverine environment (for example, DeNicola and Stapleton 2003; O'Grady 1975), but has also been shown to have a significant impact upon the estuarine and coastal environment. Giusti et al. (1999) and Gusti (2001) found that high concentrations of metals (especially zinc, lead, and copper) persisted in sediments of the UK coastline between the rivers Wear and Tees, and bio-accumulated within the native brown seaweed and mussels. The results were compared to a control site unaffected by industry, and a clear correlation emerged between locations of elevated trace metals and historical coal mining sites and associated industries throughout the coastal and river catchments.

The best-known environmental problem associated with coal and metal mine discharges is the formation of ferric oxyhydroxides and hydroxides, which can spectacularly stain the stream beds into which they discharge (Younger et al. 2002). These precipitates cause smothering of benthic habitats, reducing light penetration to photosynthetic producers and inhibiting the circulation of oxygen through the streambed (Mayes et al. 2007a). In addition to iron, manganese, an essential nutrient in much lower concentrations to iron, is often present at elevated levels within minewaters. Due to its greater solubility under more slightly more oxidising conditions, persistence of dissolved manganese is seen throughout watercourses where iron has generally precipitated (Green et al. 2003). However, despite the smothering and mild toxicological implications of oxyhydroxide precipitates, the sorption of minewater-associated trace metals significantly reduces their mobility and bioavailability (Vuori 1995).

A study by Armitage (1980) into the heavily-mined catchment of the River Nent (a tributary of the Tyne) found that elevated in-stream zinc levels caused a severe reduction in benthic diversity. It was also found that, contrary to other studies by O'Grady (1981) and Solbe (1977), there were no signs of recovery of fauna downstream of the discharge over time, with just a few zinc tolerant species remaining. The susceptibility to metal toxicity varies greatly between species. O'Grady (1981) found that within a heavily metal-mined basin in Wales, there was a severe and persistent reduction in brown trout colonies, whereas invertebrate colonies recovered rapidly following the closure of mine workings. The effect on brown trout was attributed to acute zinc toxicity and chronic lead toxicity. It would be sensible to suggest that toxicity pathways vary between different fauna in the benthic environment, and at higher trophic levels bio-magnification of metals would occur, thus species towards the lower end of the food chain will be affected to a lesser extent. In addition, some species may be more zinc tolerant (O'Grady 1981) and thus acute zinc toxicity may affect that species during pulse-type pollutant fluxes at high flow. However, the free Zn²⁺ ion, most prevalent within low-flow riverine conditions, is the most toxic species to fish and invertebrates (Alabaster and Lloyd 1980), with heavily mined catchments such as the Nent being generally devoid of life except for the filamentous green algae (Nuttall and Younger 2002).

Metal pollution of surface waters has a significant impact upon the benthic ecosystem, but varying significantly depending upon the nature of the pollution and the contaminants present. The toxicity of specific contaminants is, however, controlled by a number of factors including metal speciation, pH, hardness and susceptibility (Gerhardt 1993).

4.0 EXPERIMENTAL RATIONALE

In order to develop a methodology to best fulfil the aims and objectives set out in part 1.3, a strategy had to be developed. This section deals with the decision making process in selecting the experimental approach, by evaluating historical water-column chemistry data and undertaking a site reconnaissance survey.

4.1 Outcomes

Following from the aims and objectives section (1.3), experimentation was undertaken to reach the following outcomes:

- Definition of probable metaliferous pollution sources within the Tyne and Wear catchments.
- Quantification of metal fluxes through the catchment.
- Critical evaluation of mobility patterns and chemical behaviour.

4.2 Proposed Strategy

In order to meet the aims and objectives set out in part 1.3, the following sequential strategy was adopted:

- High-resolution site reconnaissance to define probable sources of contamination within the catchment.
- Consultation of historical chemical monitoring data from Environment Agency archives.
- Systematic water sampling and flow gauging to define the metal fluxes through the catchment.

4.3 Site Reconnaissance

The site reconnaissance was carried out in order to:

- Confirm the existence and extent of pollutant sources in the catchment
- Facilitate collection of preliminary samples
- Examine the geology to aid understanding of descriptions in the literature
- To select sampling locations, based upon accessibility, flow rate and likelihood of contamination

4.3.1 Pollutant Sources and Geology

Metal Mining

An extensive site walkover was carried out in the historically heavily metal mined Nent catchment, a tributary of the River Tyne, on the 7th, 9th and 10th of June 2007. Water samples were taken from a number of reaches of the River Nent and tributaries for preliminary purposes. During this survey, the weather was good and the rivers were representative of low-flow conditions.

The cyclothem sequence of sandstones, shales and limestones (discussed in section 2.2) was confirmed (see plates 8, 9, 10 and 11)

Mineralised deposits could be found in the 'Nenthead Mines' area, erosion of the Nent gorge revealed some significant mineralised flats within the Carboniferous Limestone.

Vast amounts of spoil, and numerous shafts and levels could be seen in the area. Many of the level adits (including Hagg and Nenthead, plate 12 and 13) were discharging water, with a high pH (~8 - 9), which increased downstream of discharge (~ 9 – 10) suggesting extensive carbonate buffering of any sulphide oxidation products (see Younger 2006, 90). Ochreous deposits existed in only a handful of reaches and seepages (e.g. Blagill Burn, plate 14), yet aquatic fauna and flora appeared extremely suppressed throughout the Nent (see plate 15). Conductivity (EC) measurements in the lower reaches of the Nent were much greater than those in the headwaters, from 58µs/cm near the source in the fells south

of Nenthead, to 588 μ s/cm in the main channel. Total Dissolved Solids (TDS) can be calculated from EC values using a conversion factor, typically 0.65 (Walton, 1989). Higher TDS values could be attributed to carbonate dissolution from the streambed or, more likely, an increased groundwater contribution to flow via the hyporheic zone (Pretty et al. 2006; Mayes et al. 2007). In addition, elevated TDS values were inferred from conductivity measurements taken at minewater point discharges; further investigation is required to confirm major ionic species.

Coal Mining

A site walkover of historical coal mining sites in the Gaunless catchment, a tributary of the River Wear, was undertaken on the 7th July 2007. The weather was poor during this time, and recent heavy rain continued to cause prolonged high flow conditions.

A number of coal mining shafts were seen (plate 16); in addition to large spoil heaps which are now heavily overgrown. The River Gaunless has been reported as heavily polluted by ferric oxyhydroxide deposits which have caused smothering of the streambed (for example, Mayes et al. 2007). However such degradation was not seen, a probable result of the exceptionally high flow at the time of visit and the implementation of numerous remediation schemes (see plates 18 and 19). Dewatering of workings was confirmed at a number of locations: pumping could be heard from within the shafts, and surface discharges were seen.

4.4 Historical Chemistry Data

The Environment Agency carries out periodical sampling of the Tyne and Wear and major tributaries for monitoring and regulatory purposes, at approximately monthly intervals. Historical archives of in-stream chemistry data can be obtained upon request, and have been used as a useful tool in setting experimental parameters for this investigation. This data covers a range of environmental parameters, including concentrations of the metals: zinc, lead, arsenic, chromium, iron, manganese, cadmium, copper and vanadium.

Tables 4 and 5 summarise the chemical analyses taken from tributaries of the Tyne and Wear between 1996 and 2006.

Table 4. Historical Chemical Data for the River Tyne (Adapted from Environment Agency archives 2007)

	Mean concentrations in parts per billion (ppb) – (max conc. in brackets)								
	Zn	Pb	As	Cr	Fe	Mn	Cd	Cu	V
70/464/EC EQS	40*	25	50	15*	1000		5	5*	100
* Hardness Related									
S-Tyne at Alston	58.6 (127)	48.5 (87.0)	< 1.0 (1.6)	< 1.0 (1.8)	360.7 (1240)	13.9 (13.9)	0.2 (0.2)	1.4 (4.5)	< 1.0 (1.1)
East Allen	87.9 (216.0)	10.1 (67.0)	< 1.0 (1.4)	< 1.0 (2.7)	475.2 (3680)			1.66 (8.5)	< 1.0 (2.5)
Tyne D/S Lambley Bridge	118.0 (163.0)	10.9 (31.6)		< 0.5 (0.8)	1236 (4400)	151.9 (652.0)		1.5 (2.4)	
Tyne at Bywell	58.7 (362.0)							1.7 (16.1)	
Derwent at Linzford Bridge	25.5 (123.0)	4.4 (57.7)	1.5 (2.9)	1.4 (9.5)	766.0 (4630)			3.2 (19.3)	1.34 (2.9)
Derwent at Eddys Bridge	31.1 (81.2)	4.9 (29.6)	< 1.0 (1.0)	< 0.5 (1.1)	556.7 (3770)			1.8 (16.4)	< 1.0 (2.1)
Team at Western Bypass	101.2 (730.0)	5.2 (51.4)			1182 (4040)		0.2 (0.8)	7.2 (34.3)	

Table 5. Historical Chemical Data for the River Wear (Adapted from Environment Agency archives 2007)

	Mean concentrations in parts per billion (ppb) ~ (max conc. In brackets)								
	Zn	Pb	As	Cr	Fe	Mn	Cd	Cu	V
70/464/EC EQS	40*	25	50	15*	1000		5	5*	100
* Hardness Related									
Wear at Sunderland Br.	46.2 (1020)	28.0 (886)	1.2 (1.6)	4.6 (77.7)			0.3 (0.9)	4.1 (35)	
Wear at Stanhope	81.7 (556)	18.9 (235)	1.4 (2.46)	1.3 (4.3)	334.7 (2320)		0.26 (1.36)	3.6 (87)	1.74 (1.74)
Rookhope	253.3 (3950)	39.1 (890.7)		0.9 (1.7)	451.0 (1580)		0.5 (3.1)	3.6 (10.6)	1.8 (6.9)
Wear at Westmills	53.2 (471)	27 (510)			563.2 (4850)		0.24 (1.17)	2.9 (7.3)	
Wear at Lumley Br	27.3 (142.7)	14.5 (162)			599.4 (3040)	111.2 (356)			

4.5 Systematic Water Sampling

Following the consultation of literature, the review of historical in-stream chemical data and site reconnaissance, an approach to catchment-scale water sampling was developed.

The sample locations were distributed to most effectively cover the entirety of the catchment, with individual localities targeting the most heavily mined tributaries.

4.6 Selection of Experimental Parameters

Analysis of collected samples included identification of a range of metals, listed as priority or priority hazardous substances in directive 76/464/EC, and commonly associated with acid mine discharges of the North Pennines and Durham Coalfield. In addition, the historical monitoring information summarised in tables 4 and 5 was consulted in order to set expected chemical parameters.

For example, the ecotoxin zinc is listed as a priority substance, and is found within minewater discharges in the South Tyne catchment (Nuttall and Younger 1999; Armitage 1979). In addition, historical records for the Nent at Alston show an in - stream average of 58.6ppb total zinc with 81.8ppm hardness (band 50 – 100 ppm CaCO₃) for the 10-year sampling period of 1996 – 2006. This breaches the 50ppb EQS threshold limit given in directive 76/464/EC for salmonid waters, under which the Nent is classified.

Arsenic, an ecotoxin that has been associated with mine discharges into the River Nent (Younger and Nuttall 1999) is also classified as a priority substance within directive 76/464/EC. However, arsenic contamination is reportedly minimal (1.93ppb max. in the River Wear (Neal and Robson 2000),) and historical data sets of the Tyne show a maximum of 2.9ppb in the Nent at Alston, a value far lower than the EQS average threshold for arsenic: 50ppb.

On the other hand, cadmium, despite no actual record of a breach above the 5ppb EQS threshold (greatest value recorded 3.1ppb at Rookhope, a tributary of the Wear), the association with lead and zinc ores (Jarup 2003; Patrick and Polya 1993), and lead/zinc rich minewater discharges (Nuttall and Younger 2002), in addition to an elevated status under EU directives (a priority hazardous/ list 1 substance) increase both the hazard and likelihood of significant contamination.

Similar scrutiny has been applied to all potential contaminants, and those which have elevated concentrations and the potential to cause harm will be selected for investigation (see Table 6).

Table 6. Pollutants Selected for Analysis

Metal:	Detection range:	Classification in directive /	
		76/464/EE	2000/60/EC
Zn	ppb	List 1	Priority Hazardous Substance
Pb	ppb	List 2 (Hardness Related)	Priority Substance
Fe	ppb	List 2	Priority Substance
Mn	ppb	Na	na
Cd	ppb	List 2 (Hardness Related)	Priority Substance
Cu	ppb	List 2 (Hardness Related)	Priority Substance

Concentrations of major cations and anionic species were determined both for quality assurance purposes (charge balancing) and for contaminant source fingerprinting. For example, influx of pyrite (FeS_2) oxidation products can be traced using the SO_4^{2-} anion, when oxidising conditions have caused precipitation of ferric iron upstream, greatly reducing in-stream iron concentrations.

4.7 Flow Gauging

In order to determine the total fluxes of in-stream metals through the catchment, both the concentration of metals must be determined, and the flow volume. This was achieved by flow gauging, and measuring of the stream cross-section, from which the volume of flow could be calculated.

Environment Agency flow gauges are located throughout the major reaches of the Tyne and Wear, and the data is readily available on request. The sample locations were based upon accessibility for sample taking and practicalities for manual flow gauging where this was required. Tables 7 and 8 list the chosen sample locations, and state the flow gauging requirements.

Table 7. Wear Sampling Locations

Ref.	Eastings	Northings	Location	Gauging
1	428304	551226	Wear at Chester le Street	EA Station
2	426520	537734	Wear at Sunderland Bridge	EA Station
3	425904	538688	Browney at Burn Hall	EA Station
4	421155	528044	Gaunless at Dovecot Hill	EA Station
5	417280	530900	Wear at Witton	EA Station
6	411799	532192	Bedburn Beck	EA Station
7	402662	535990	Bollihope Burn at Frosterley	Manual Gauging
8	399010	539284	Stanhope Burn	Manual Gauging
9	398366	539040	Wear at Stanhope	EA Station
10	395246	539739	Rookhope at Eastgate	Manual Gauging
11	393480	537819	Westernhope Burn	Manual Gauging
12	390698	538050	Middlehope Burn	Manual Gauging
13	386593	538658	Ireshope Burn	Manual Gauging
14	385584	539487	Burnhope downstream reservoir	EA Station
15	383541	541716	Killhope Burn	Manual Gauging
16	383536	541618	Wellhope Burn	Manual Gauging

Table 8. Tyne Sampling Locations

Ref.	Eastings	Northings	Location	Gauging
17	424964	558471	Team at Coalhouse	EA Station
18	426557	555587	Rowlech Burn at Birtley	Manual Gauging
19	425758	557023	Team upstream of Lamesley	Manual Gauging
20	416815	558094	Rowlands Gill	EA Station
21	404107	550791	Eddys Bridge	EA Station
22	395501	561669	Devils Water	Manual Gauging
23	383043	556646	East Allen	EA Station
24	378217	557046	West Allen at Blueback	EA Station
25	378041	543659	Nent at Nenthead	Manual Gauging
26	374535	541616	Garrigill Burn	Manual Gauging
27	370785	543564	Black Burn	Manual Gauging
28	371635	546767	Nent at Alston	Manual Gauging
29	371543	546530	South Tyne at Alston	EA Station
30	367216	561064	South Tyne at Featherstone	EA Station
31	385656	564671	South Tyne at Haydon Bridge	EA Station
32	390555	573231	North Tyne at Reaverhill	EA Station
33	403858	561700	Tyne at Bywell	EA Station

5.0 MATERIALS AND METHODS

5.1 Determination of Contaminant Fluxes

Systematic sampling of flow and water chemistry was undertaken throughout the rivers Tyne and Wear and their tributaries.

A number of field measurements were made, in addition to sample taking, to enable laboratory analysis for specified anions and cations:

- Eh, pH, conductivity and temperature were measured using a Myron 6P Ultrameter
- Total alkalinity was measured using a Hach Digital Titrator
- Flow velocities (see part 5.3)

Sampling sites progressed up – catchment, working from the lower reaches up into the headwaters as opposed to working down the catchment, following the hydrograph's peak flow. This technique was used because the highly complex hydrology and weather patterns of the North Pennines prevent a simple and even discharge pattern, invalidating the latter technique. The benefit of the chosen strategy is that it prevents retrieving water samples contaminated with suspended material, disturbed whilst gauging flow at upstream locations.

5.2 Sample Locations See figure 12

The sampling points were located to give the most representative cross section of metal fluxes through the catchment.

A number of sampling points were targeted at heavily metal mined tributaries of the North Pennines such as the River Nent – a tributary of the Tyne, and Killhope Burn – a tributary of the Wear. Coal mining to the east of the catchment is a probable source of in-stream iron and manganese as well as a range of trace metals (Mayes et al. 2006; Worrall and Pearson 2001). A sampling point was thus located on the heavily coal mined Gaunless (See: Mayes et al. 2007). Rivers potentially affected by other industrial activities were included: Rowletch Burn sampling location at Birtley, for example, was downstream of an

operational galvanising works and adjacent to a landfill site (located during site reconnaissance). The locations of mineralised deposits can be seen on figures 7 and 8 (annex A).

Additional sampling at major intervals into the lower reaches was undertaken at Environment Agency monitoring stations, where accurate continuous flow monitoring is recorded using a variety of methods. This also overcame the logistical problems of gauging flow velocity in larger reaches of the rivers.

5.3 Gauging Flow and Sampling

5.3.1 Flow Gauge

Manual flow gauging was required in the upper reaches where no accessible monitoring stations or weirs existed. The flow velocity gauge chosen for this task (Valeport 301) was an electromagnetic induction type, which consists of an electromagnet and pair of receiving electrodes housed in a resinous body (see figure 13). The principle behind the electromagnetic flow gauge relies upon the extent to which the flow of water cuts the lines of electromagnetic flux, inducing an electromotive force (e.m.f.) in the surrounding water. (Herschy 1999) This e.m.f. is then received by the electrodes, which is converted into a velocity reading, with additional statistical error provided by this particular model (standard deviation).

This device was chosen due to its increased accuracy and reliability over mechanical types such as the cup or propeller flow gauges, which require frequent calibration. (Herschy 1999) Another advantage of this type is that it remains relatively unaffected by suspended material, particularly important during high flow.

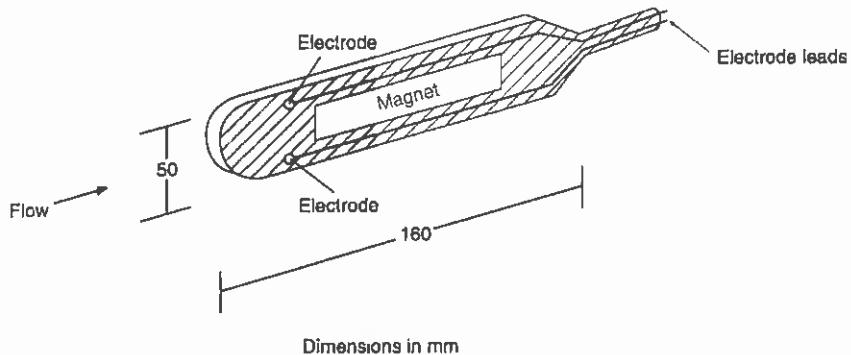


Figure 13. Electromagnetic Flow Gauge. Adapted from Herschy 1999, Figure 3.25, 111.

EA Flow Gauges

In the time between obtaining the list of operational flow gauges from the Environment Agency, and requesting the gauged data, the gauges on the River Allen became unserviceable and subsequently no flow data exists. Whilst sampling from the Team at Coalhouses on the 24th July, the Environment Agency were seen to be working on the flow gauge. No flow data exists for this date at Coalhouses. In addition, the gauge on the River Gaunless records flow data only at extremely high discharges, the threshold of which was not reached during sampling.

Due to these unforeseen circumstances, the inorganic pollutant fluxes could not be plotted for some areas of the catchment.

5.3.2 Gauging Flow

In order to determine the total rate of discharge using water velocity values, the stream cross section was divided into a number of smaller segments of equal width. The cross sectional area of each individual segment was calculated from depth and distance measurements, and the mean flow of each segment computed from flow measurements. The flow rates in meters per second (m/s) were then multiplied by the cross sectional area of the corresponding segment, and added together to get a total volumetric flow rate for the river at the time of sampling.

Care was taken to select a clear reach of river with an even and level streambed, ensuring that the gauge was located in an area of greatest uniform flow, for example, not behind a rock in the stream.

5.3.3 Sampling

Samples were collected from the centre of the river, where greatest flow rates occurred. This best represents the material in flux throughout the catchment as opposed to more stagnant areas towards the edge of the river which may be subject to more anoxic conditions and settlement of sediment out of suspension.

It was ensured that the samples were simultaneously collected just upstream of the gauging location in order to prevent any contamination from sediments disturbed whilst gauging activities were undertaken. At gauged localities, the monitoring station was located and sample taken from an adjacent position (see plate 20).

Three samples were taken at every sampling point:

1. Unfiltered for total anion content
2. Unfiltered for total metal content (acidified to prevent precipitation during transit)
3. Filtered for total dissolved metals (acidified to prevent precipitation during transit)

See section 4.7 for sampling locations and gauging requirement

Additional Sampling

Flow conditions on the 12 June were variable due to intermittent heavy showers in certain areas of the Wear catchment giving discrepancies between flow data. For example, the lower reaches of the River Wear at Chester le Street had a flow rate of less than 4.5 cumecs at 0915, whereas 30 minutes later at 0945 just upstream at Sunderland Bridge, the flow had increased to ~18 cumecs. Following the completion of the sampling programme, additional samples were taken in the lower reaches of the Wear to account for the intermediate high discharges seen in the headwaters.

5.3.4 Sampling Materials

Filtration of samples was conducted using $0.2\mu\text{m}$ cellulose acetate syringe filters, the threshold of which is generally accepted as the limit of colloidal material. In addition, finely dispersed iron oxyhydroxide particulates can pass through the more ubiquitous $0.45\mu\text{m}$ filters (Appelo and Postma 1993).

Acidification of the samples for cation analysis was undertaken in accordance with sample preparation guidelines given in the Agilent handbook (Agilent ICPMS used for sample analysis). Before sample collection, the sample tubes were pre-acidified in the HERO labs with 0.25ml of concentrated nitric acid. This ensured consistency of pH (≤ 2) in collected samples, preventing any precipitation of dissolved metals during transit. (see figures 14-19 for pourbaix diagrams (annex B))

Samples were stored in 25ml polyurethane sample tubes and were refrigerated to below 5°C prior to analysis to minimise any biotic metabolism which might change the oxidation states of species present.

5.4 Laboratory Analysis

Laboratory analysis of the collected samples was undertaken at the School of Earth and Environmental Sciences, Portsmouth University and at the Department of Natural Sciences, University of Gloucestershire.

5.4.1 Cation Analysis

Analysis of samples for both the total and dissolved metals was undertaken using a Agilent 7500CS ICP-MS (Inductively Coupled Plasma Mass Spectrometer, see plate 21) using helium mode for improved consistency.

The ICP-MS was calibrated to detect major ions: magnesium, calcium, sodium and potassium for charge balancing purposes, in conjunction with zinc, lead, cadmium, copper,

iron and manganese, which have been attributed to minewater pollution issues in the Tyne and Wear catchments (Mayes et al. 2007; Neal et al. 2000b,c; Nuttall and Younger 1999).

Settlement of suspended material in-transit occurred within unfiltered samples; this sediment could not be effectively analysed for metals using the ICP-MS. In order to ensure accuracy of total metal quantification, without changing the concentrations significantly, additional concentrated nitric acid was added (0.25ml) to displace the metals bound to colloids into solution. The samples were then filtered using a 0.7µm glass fibre membrane filter to remove larger particulates, which may cause blockage of the injection system or nebulizor within the ICP-MS. However, subsequent perusal of the 'total metal' results revealed abnormally high concentrations of zinc at some localities. The only possible source of contamination of samples was the glass fibre filters; to resolve this, a re-run of the samples was undertaken using an alternative method (centrifugation), which produced more consistent results.

5.4.2 Anion Analysis

The unacidified samples were analysed for major anion concentrations (sulphate and chloride) using an ion chromatograph (Bran and Luebbe Autoanalyser 3) at the Department of Natural Sciences, University of Gloucestershire.

5.5 Quality Assurance

In order to ensure consistency and accuracy of results, a number of quality assurance procedures were undertaken:

Triplicate samples

Triplicate samples were taken at convenient points for sample collection quality assurance. The triplicates were taken individually at the sampling location and analysed in sequence within the batch run. A tolerance of within ±5% provided assurance of sampling consistency.

Calibration Standards

Calibration standards (SLRS4 and TMDA-54.3) and a blank sample (twice distilled water) were incorporated respectively into each batch of samples in the ICP-MS autosampler at 10 sample intervals. For quality assurance of the anion analyses, drift standards prepared in the laboratory were incorporated within the program at 10 sample intervals. The calibration standards and drifts were checked for analytical consistency.

Mass balance calculations

Concentrations of major anions and cations, widely occurring at high concentrations in the aqueous environment, were determined in addition to the range of environmentally damaging metals. Charge balance calculations were undertaken, accounting for all present species in order to determine the charge imbalance (C.I.) using expression (5), after Ball and Nordstrom (1991). An electro-neutrality within $\pm 10\%$ is generally accepted as an adequate assurance of combined sampling and analytical accuracy.

$$(5) \quad C.I. = 100((\sum \text{cations} - \sum \text{anions}) / (\sum \text{cations} + \sum \text{anions})/2)$$

Where Cation values are in meq/l and C.I. is given as a percentage error. See annex F

Despite careful observation of good experimental practice, numerous C.I. values were given in excess of the 10% electro-neutrality threshold. Further consideration of the results for consistency, and a review of analytical procedures revealed areas for potential error.

Data provided by the LOIS study covers a great range of contaminants present within the riverine environment, including the Wear, the parameters of which are far beyond the limitations of this investigation. From this data, there are a significant number of ionic species which have not been accounted for in this investigation, particularly those arising from non-industrial sources, yet are generally present in small concentrations (for example, from agriculture).

The discrepancy in charge balance could simply be a result of additional ions not having been accounted for during the analysis, for example trace metals (see Neal and Robson 2000).

Another potential source of this charge imbalance could be the analytical procedures themselves. Quality control procedures undertaken during cation analysis (ICP-MS) used two separate certified reference materials (SLRS4 and TMDA-54.3), covering the multitude of concentrations likely to be experienced throughout the Tyne and Wear catchments. In addition, due to trace contamination of the 'total metal' samples during sample preparation, two sets of data existed for major ion concentrations. The major ion results for both sample analyses correspond (with an error of $\leq 5\%$), and the data for the certified reference materials fell within the provided tolerances. A simple technique which can be used to check cation accuracy is based upon the relationship of electrical conductivity (EC) with the ions present in solution. At 25°C, the EC is approximately 100x the total cation or anion concentration for major species (see Appelo and Posta 1993, 17-18) and thus, using the following expression, the total cation/ anion concentrations can be estimated:

$$(6) \quad \Sigma \text{anions} = \Sigma \text{cations (meq/l)} = \text{EC}/100 (\mu\text{S/cm})$$

Estimated values for cation concentrations showed a good correlation to the analytical data and thus it would be reasonable to assume that the cation results obtained are representative of the samples taken.

The only quality assurance measures taken during anion analysis were the incorporation of drift samples to check for machine consistency. Nevertheless, these involved numerous dilutions of a salt solution to achieve a concentration in the correct range. These drift samples relied upon extrapolated concentrations with great margin for error. Despite a probable true relativity of anion concentrations (useful for hydrogeochemical fingerprinting), absolute values may be erroneous. A brief comparison to estimated values derived using the above expression (6) confirms that the results may indeed be erroneous.

It is likely that the high C.I. value is a result of a combination of factors, both errors with accounting procedures and with the analyses themselves. However, the validity of absolute cation values and relative anion values is sufficient to support the investigation.

6.0 RESULTS AND DISCUSSION

Evolution of metal mine pollution and contamination through the Tyne and Wear has led to a highly complex pattern of metal fluxes through the catchments.

See annex F for data

6.1 Overview of Field Conditions

Low pressures brought particularly unsettled weather patterns with abnormally high rainfall for the time of year, generally in the form of heavy showers (Metcheck 2007). During the time of sampling (June and July 2007), the weather was characterised by heavy rain at frequent intervals giving consistently moderate to high flow conditions.

Typically, the annual pattern of metal content within stream flow will include a period of low flow with a high dissolved content during summer months, when perennial contaminated groundwater discharges from former mine workings contribute a relatively high volume to in-stream flow. This will be interspersed by infrequent high flow conditions which dilute the baseflow dissolved metals, but increase suspended contribution to total in-stream metal loading from re-suspension of contaminated streambed and overbank sediments (e.g.: Masson et al. 2006; Neal et al. 1997). The prolonged high flow conditions during the sampling period would have caused not only a significant dilution of the perennial mine waters during sampling, but also would have washed large amounts of metal rich sediments through the catchment. It is also possible that the mine workings and groundwater conditions would have been repetitively ‘flushed’ through, which may have lead to early stage episodic increases in the flux of metals from adits as mineral veins in the vadose zone are weathered and the products mobilised (see Younger 1997). Therefore, despite sampling in both high and low flow conditions, the sampling profile is unlikely to be wholly representative of typical circumstances.

During sampling of the River Wear on the 12 June, conditions became high to extremely high flow through the day, following several days of low flow conditions. The River Tyne was sampled on the 5th July as river levels were receding following several days of high flow.

The River Wear was sampled at medium – low flow conditions on the 10th July, and the River Tyne on the 24th July, both sampling days following several weeks of heavy rain and the river levels were generally in recession. During the week preceding the 24th July, the mean flow rate on the Tyne at Bywell was ~162cumecs, decreasing to ~77cumecs on the day of sampling. An average flow rate of 20cumecs was recorded for Wear at Sunderland Bridge the week proceeding the 10th July, and 8cumecs was recorded on the day.

6.2 Hydrochemical Facies

Clear variability between water signatures can be seen throughout the catchments (see figure 20). The River Team, for example, has relatively high pH and alkalinity values, indicative of a significant groundwater contribution via the hyporheic zone and input of point mine water discharges (Battin et al. 2003; Sear et al. 1999). Similar facies can also be seen in the lower reaches of the River Wear, in particular at Chester le Street. During low flow conditions; elevated alkalinity concentrations reflect the greater contribution of groundwater sources to baseflow

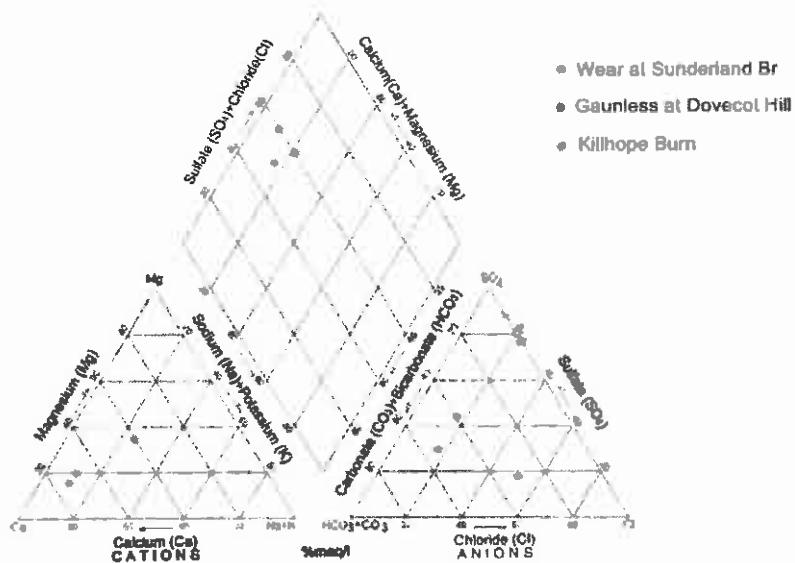


Figure 20. Piper diagram of a heavily coal mined catchment (Gaunless), a heavily metal mined catchment (Killhope), and a composite location downstream on the River Wear (Sunderland Bridge after confluence of Killhope Burn and the River Gaunless, amongst others) on the 12 June. It should be noted that corrected anion values have been used).

Further up the catchment, the pH generally falls, with the Nent at Nenthead (one of the smallest headwaters sampled) having both the lowest pH and total alkalinity value for the low-flow sampling (24th July), and the lowest total alkalinity during high flow (5th July). These facies typically occur in the upper reaches during and after medium – high flow, where steep topography and more intense rainfall cause rapid run-off. Devils Water and the River Allen also appear to be dominated by surface water run-off. This was evidenced by the notable rich red-brown colour of the waters at the time of sampling and is characteristic of rivers draining peat-moorland, which lowers the pH (organic acids) and causes leaching of some metals, particularly iron (Ritchie and Postner 1982). In addition, rainwater itself is mildly acidic (carbonic acid). During particularly high flow, an increase in pH of headwaters was seen (Ireshope Burn, Middlehope Burn, Westernhope Burn), a probable result of aggravated carbonate dissolution within the streambed (total alkalinity values were unobtainable/unreliable due to muddied water).

During sampling on the 12th June, torrential rainfall was experienced at some localities, resulting in abnormally localised high flow in a number of headwaters, particularly Middlehope Burn (see plates 22 and 23). The dilution of groundwater input in the lower reaches can be seen by a reduction in total alkalinity concentrations of the additional samples, which was undertaken later in the day. See pourbaix diagrams for conditions at sampling points and dominant species of selected metals (annex B).

Metal	Species
Manganese	Mn ²⁺
Iron	Fe(OH) ₃ , Fe ²⁺
Copper	Cu ₂ O, CuO
Zinc	Zn ²⁺ , ZnCO ₃
Cadmium	Cd ²⁺ , CdCO ₃
Lead	PbCO ₃

Table 9. Dominant metal species in a mildly oxidising (0 – 250mV), circum – neutral environment (pH 6– 8)

6.3 Contaminant Concentrations

Contaminant concentration data (see figure 21-32, annex D) reveals numerous EQS breaches with reference to values given by Directive 76/464/EC. It must be noted, however, that these spot breaches do not necessarily constitute an effective breach under the terms of the Directive, which is based upon annual averages.

Dissolved iron and manganese concentrations are normally low. Marginal elevation to levels in excess of Directive 76/464/EC occurs in reaches which drain peat moorland (Devil's Water is a prime example of this, an indicative rich red-brown colour could be seen during sampling). Peak total iron concentrations of up to 21630 μ g/l (Westernhope Burn) were seen in the peat draining headwaters during high flow, but low bioavailability of particulate iron and abundant natural sources renders regulation based upon EQS unsuitable (Nagai et al. 2006). Possible sources include iron yielding minerals in the North Pennine Orefield, minor coal seams in the region and the peat moorlands in the headwaters. Colliery workings, a common culprit of iron rich discharges (e.g.: Younger et al. 2002), appear to currently have little effect on elevated iron concentrations in major tributaries of the Tyne and Wear. In recent years there has been a vast improvement from the worst offenders in the Durham coalfield by a range of passive and active treatment systems, as well as continued dewatering (Younger 2000; 1997b). The impact of colliery minewater discharges on the Rivers Gaunless, Browney and Team remains prevalent (Mayes et al. 2007), and the precipitation of oxyhydroxide deposits near the source can be re-mobilised during high-flow.

Copper concentrations remain consistently low, the greatest value for dissolved copper being obtained on the North Tyne (~3 μ g/l), which drains a generally un-mineralised catchment (see figure 7). In addition, the River Team at Lamesley contains elevated particulate copper concentrations in excess of 400 μ g/l. In-stream copper concentrations have commonly been attributed to metal mine discharges (for example, Brown 1974), and agricultural sources (Masson et al. 2006; Jongbloed and Lenis 1998), the latter being a probable source of the contamination in the North Tyne due to the lack of metal mining in the area. The source of copper in the River Team is likely to be of current industrial origin,

from sewage works or highway run-off, rather than mining related discharges owing to the current land-use setting of the catchment.

Zinc concentrations are persistently high in the historically heavily mined headwaters of the North Pennines (e.g.: Nent, Killhope, Wellhope, Allen), typically in the 50 – 1500 $\mu\text{g/l}$ range, in excess of the annual average 8 – 50 $\mu\text{g/l}$ threshold limit set by the Directive for the hardness category 0 – 100mg/l CaCO₃. This is consistent with the historical data obtained from the Environment Agency where the mean concentrations over a ten-year period for heavily mined headwaters are in the range 87.9 $\mu\text{g/l}$ and 58.6 $\mu\text{g/l}$ for the East Allen and South Tyne at Alston respectively. During low flow conditions; the concentrations of dissolved zinc remain high relative to the total zinc concentrations. During high flow, however, the dissolved species are generally reduced in concentration and the particulate contribution increases giving greater total in-stream zinc concentrations. The effect of dilution is apparent, however; the balance between dissolution and dilution cannot be quantified solely on concentration data.

Towards the lower reaches, greater total hardness values occur due to a more significant groundwater input, shifting the EQS categorisation to a more tolerable level (see Annex G). On the 12th June, the Wear at Chester-le-Street, for example, has a hardness value of 233mg/l, increasing the threshold EQS value of zinc to 75 $\mu\text{g/l}$. Despite dilution and a less stringent EQS, the zinc concentration was 901 $\mu\text{g/l}$ and still far in excess of the limits. Zinc, unlike the aforementioned metals, is generally present in the dissolved species Zn²⁺, as the complex ZnCO₃⁰(aq) or ZnOH⁻ within circum – neutral surface waters. (Mayes et al. 2007; Younger 2002, 112; Brown 1974) (See Figure 17, Table 9).

The cadmium concentration profile down catchment generally followed that of zinc, but at a far lower magnitude, reaching a maximum of 8.1 $\mu\text{g/l}$ at Middlehope Burn, but otherwise remaining below the 5 $\mu\text{g/l}$ annual average limit set by Directive 76/464/EC. However, it should be noted that the regulation of cadmium is based upon Maximum Admissible Concentrations (MAC's) and therefore a single breach represents an EQS failure.

Particulate lead values were found in many instances far in excess of dissolved species, with particularly large concentrations existing in the heavily mined headwaters of the

Nenthead to Killhope area. Lead concentrations reached a maximum concentration of $7259\mu\text{g/l}$ in Middlehope Burn on the 12th June; this was during extremely high flow conditions. This behaviour would suggest a strong particulate contribution from lead compounds, both primary and secondary minerals derived from sources such as streambed sediments and spoil heap run – off, particularly significant during high – flow conditions (Masson et al. 2006; Mayes et al. 2006). The EQS standard for Directive 76/464/EC regulates the dissolved species only at $10\mu\text{g/l}$ (within the hardness categories found in these waters), primarily due to its elevated bioavailability over particulate material. Breaches of this threshold for dissolved lead occur widely in the upper catchment of the Wear and Tyne, the greatest of which are in the River Nent and Killhope Burn ($39\mu\text{g/l}$ and $34\mu\text{g/l}$ respectively), with concentrations above $10\mu\text{g/l}$ extending to the South Tyne at Haydon Bridge. Little change in this pattern of dissolved concentrations was seen during high flow conditions, except for Middlehope Burn and the Wear at Stanhope, which were subject to very high flow conditions. In the riverine environment (pH 6 – 10, Eh ~100), the dominant lead species is PbCO_3 (See Figure 19).

6.4 Catchment Scale Fluxes and Mobility

Spatial mapping of quantified contaminant fluxes through the catchment is a useful tool in understanding the mobility patterns of metals. Annex E contains graphical representations of the fluxes of the inorganic pollutants subject to investigation.

6.4.1 High Flow Conditions

During high flow conditions, there appeared to be a notable disparity between the findings between the Tyne and Wear. The balance of bulk metal contribution for the Tyne during high – flow is weighted towards dissolved species in almost all cases, whereas in the Wear the contribution is from particulate material (lead fluxes show this clearly in Figure 44). This discrepancy is a probable result of the difference in temporal flow regimes: the extremely high – flow of the Wear following a dry spell had disturbed sediments, whereas the relatively lower conditions experienced whilst sampling the Tyne are likely to have resulted in a more immobile and stable condition of any contaminated sediments. Macklin et al. (1997) discusses the significance of short-term pulse fluxes or ‘slugs’ of

contaminated sediments through post-industrial catchments as a bulk contributor of metals from headwaters to lower reaches. These 'slug' contributions occur during particularly high flow conditions, and it appears that the sampling of the Wear on the 12 June clearly reflects this.

In addition, unexpectedly high results for total zinc, lead and cadmium were obtained from the North Tyne at Reaverhill, which passes through a non – mineralised area of the catchment, and appears to remain generally unaffected by other sources of contamination (for example, sewage works, industry or intensive agriculture). These results are not consistent with either the dissolved metals (which show no significant contamination), or to the results obtained during low – flow conditions. Further data from the site to corroborate, or otherwise, the patterns seen here would be beneficial to ascertain whether these elevated metal concentrations are truly reflective of the quality of the waters at Reaverhill.

6.4.2 Low Flow Conditions

During the low flow condition of the Wear, it can be seen that the contributions of metals from heavily mined headwaters is of great significance. Wellhope Burn and Killhope Burn contribute 17.1mg/s and 31.5mg/s of zinc respectively, with a value of 177.8mg/s total in stream zinc found in the Wear at Sunderland Bridge. The total contribution to in-stream zinc loading from these headwaters is 27% of that found downstream at Sunderland Bridge, a significantly greater proportion than that at high-flow (18%). This pattern can also be seen in the River Tyne: The Nent at Alston contributes 15% zinc found downstream at Bywell during high flow, which increases to 17% of loading during low flow conditions. This behaviour suggests additional/elevated inputs to downstream fluxes during high flow, most likely to be re-suspension of metal laden sediments which are widely dispersed through the catchment.

This pattern, however, appears to occur only for zinc. Lead and Iron show the opposite trend, with a greater contribution to loading from headwaters occurring during high flow, a trend which could be attributed to the lower mobility of these contaminants (e.g. Macklin et al. 1997).

6.4.3 Discrepancy between Metal Fluxes

In numerous instances, the quantity of total metal influx from headwaters, and the subsequent export further downstream is marginally imbalanced during low flow. A good example of this is in the Tyne headwaters, where the input of zinc from the three major tributaries: South Tyne at Garrigill, Black Burn and the River Nent was 1.54 g/s; whereas further downstream at Featherstone on the South Tyne, 1.63 g/s was exported from the catchment. This pattern can also be seen on the Wear during low flow: the major headwaters of Rookhope Burn, Westernhope Burn, Middlehope Burn, Ireshope Burn, Burnhope Burn, Killhope Burn and Wellhope Burn together contribute 0.006g/s of lead and 0.065g/s of zinc to total loading. However, downstream at Stanhope on the Wear, the values of lead and zinc were 0.04g/s and 0.203g/s respectively.

Solid Phase Mobility

A general pattern of increasing zinc fluxes down catchment can be seen during low flow (figure 39), yet with a greater proportion of particulate species to dissolved species in the lower reaches than in the headwaters. This pattern is contrary to the generally accepted model of decreasing fluvial energy downstream leading to settlement of suspended material (Coynel et al. 2007; Rodrigues et al. 2007; Macklin et al. 1997). To try and explain this phenomenon, the interaction between individual hydrogeochemical components must be considered.

The cation complexation potential of organic acids, specifically humics, has long been recognised and thus their control of metal pollutants within the environment. Additional inorganic ligands include iron, manganese and aluminium oxyhydroxides, carbonate, chloride and sulphate which can bind to metals instream, decreasing their mobility and bioavailability (Cappuyns and Swennen 2004; Logan et al. 1997).

The headwaters of a heavily mined catchment such as the North Pennine Orefield are generally dominated by hydrochemical facies comprising minewater discharges/ seepages and organic rich peatland drainage. In general, minewaters and associated seepages are of a low organic content, with a high content of dissolved sulphide oxidation products and associated minerals (Younger et al. 2002). Conversely, peatland drainage is rich in organic

material, particularly dissolved organic acids (Neal et al. 2001) which often form Fe(III) complexes (Geraldine et al., 1982). Thus, in the headwaters, a balance exists between dissolved species (Cd, Cu, Mn, Zn) due to the low pH, and metal rich particulates (bound to organic acids). Further downstream, contaminated groundwater input to flow via the hyporheic zone could increase metal loading but also total alkalinity values. In addition, an increase in biological activity is likely, largely attributed to nutrient input in the lower reaches from agriculture. Therefore, precipitation and/or complexation of metals re-released into the water column from sediments and contaminated groundwater input may be occurring.

The exception to this pattern is seen between the headwaters of the South Tyne which contain 0.27 g/s particulate zinc, and downstream at Featherstone, 0.19 g/s particulate zinc. In this case, the loss of particulate contribution can be attributed to simple settling of material from suspension as the fluvial energy decreases.

6.5 Catchment Scale Export

By dividing the mass lost at the bottom of a catchment by the surface area of the catchment, the quantity of metal exported per km^2 of land can be inferred.

During high flow, the most heavily mined headwaters such as the River Nent, Wellhope Burn and Ireshope Burn contributed relatively large amounts of metal, notably zinc, iron and lead per km^2 . However, samples taken in the main river channels of the Wear at Chester-le-Street and the Tyne at Bywell also show greatly elevated concentrations. Furthermore, the overall greatest flux of metals per km^2 during high flow is found in the Wear at Stanhope, producing $\sim 24\text{kg}/\text{km}^2/\text{d}$ of iron, $\sim 10\text{kg}/\text{km}^2/\text{d}$ of lead and $2\text{kg}/\text{km}^2/\text{d}$ of zinc.

These exceptionally high results do not reflect the presumption of greatest pollution per unit area of land occurring in the heavily-mined headwaters, which run through large amounts of riparian spoil material, and are greatly affected by minewater discharges and seepages.

Contrary to the results discussed above, the low flow conditions conform almost perfectly to the simplified hypothesis: heavily mined catchments export more metal per km² than non-mining catchments; and metal concentrations in the lower reaches form a composite of the smaller catchments upstream, including dilution from less polluted tributaries. The River Nent and East Allen both show pronounced in-stream zinc fluxes of ~5kg/km²/d and ~0.5kg/km²/d respectively, whereas the un-mineralised River North Tyne exports ~0.03g/km²/d; further downstream at Bywell, a value of ~0.3kg/km²/d of zinc was recorded (*note units*). A similar situation was seen in the Wear catchment: greatest exports per unit area were seen in Killhope Burn and Wellhope Burn

6.6 Re-mobilisation of stream bed and bank sediments

Material derived from the heavily mined North Pennine Orefield that has been deposited in overbank and streambed sediments during high flow conditions is often highly contaminated (Macklin et al. 1997) and therefore represents a considerable and persistent source of metals which can be remobilised to the water column (see figures 24 and 25 which show sediment deposition following high flow).

Furthermore, precipitation and binding of dissolved metals to minerals has been well documented (e.g. Donahoe 2004; Brown et al. 1999; Zachara 1999), potentially representing a significant sink for minewater pollution (Gandy et al. 2007; Wielinga et al. 1999). However, a net loss of in-stream metals through the catchment was not seen during the investigation. To the contrary, an increase in total fluxes was seen both during high and low-flow, suggesting an additional source of contamination to headwater influx.

The mobility of metals within the catchments varies considerably with environmental conditions. Anoxic reducing conditions in the streambed are likely to cause re-mobilisation of metals such as iron and manganese, originally deposited during high flow conditions (Gandy et al. 2007). Other metals, notably zinc and lead, form secondary sulphide minerals during such conditions (see pourbaix diagrams, annex B).

The elevated particulate concentrations of metals seen downstream, particularly during low-flow are likely to be derived from re-mobilised in-stream sediments (given that flows were not sufficient to entrain overbank sediments) as well as potential sources related to

the hyporheic zone. The re-mobilisation of dissolved species in the lower reaches of the Tyne and Wear may be subject to in-stream ligands (e.g. DOC's, carbonates), or taken up by bacteria or algae, thus increasing the particulate fraction (Dawson and Macklin 1998). The potential hyporheic related sources may involve the input of contaminated groundwater or re-mobilised metals from localised changes in geochemistry. Additional sources of metals could include highway run-off, sewage discharges and industrial discharges, but the impact of these is likely to be minor upstream of the urban lowlands where such sources exist. The provenance of the in-stream metals cannot be categorically determined without more detailed sediment characterisation exercises. However, the greater exports from, for example, the upper Wear in high-flow conditions (where there is a disparity between exports of particulate metal per land surface area in downstream locations, and the combined headwater contribution) does suggest that re-suspension of bed sediments is likely to be the dominant source of metals in the water column during high-flow.

Attenuation of metals from the water column is likely to occur in various reaches given the documented fall in loadings at certain locations (for example, lead fluxes through the Wear during low-flow). This may be due to a number of processes including: sediment settles out of suspension, sorption/ complexation within streambed sediments, organic acids and biota, and through hyporheic cycling. Again, it is not possible from a basin scale characterisation exercise such as this to determine the relevant importance of these processes in attenuating metals, and this could be a subject for future research to gain a better understanding of natural attenuation processes of mining derived contaminants in surface waters.

Findings from a study by Van den Berg et al. (1998) suggest a distinct peak in mobile metal concentrations on the sediment – water interface, and the formation of sulphide secondary minerals at a small depth. During times of increased flow, it is likely that the reducing environment may be disturbed, causing release of physically trapped dissolved species, and oxidative dissolution of secondary sulphate minerals at depth. Conversely, during low-flow, reductive dissolution of metals within the upper oxide zone may cause additional re-mobilisation. Subsequent complexation by carbonates, DOC's and microbiotic uptake within the water column, in addition to contaminated sediments in

suspension, may well have caused the elevated contribution of particulate material seen in this investigation.

6.7 Persistence of Metal Mine Pollution

The diffuse pollution of historical metal mining in the North Pennines is a product of the large-scale land disturbances associated with the winning of metal ores from the host rock. Open cast mining, hushing and construction of tailing dams have resulted in extensive contaminated land in riparian areas, particularly within realms of the North Pennine headwaters of the Tyne and Wear, which causes subsequent inorganic pollution to surface waters. Mayes et al. (2006) found this diffuse nature of pollution contributed between 48 and 90% of total in-stream metal loading dependent upon flow, the primary contaminant studied in the catchment being zinc. These figures were comparable to a co-study of the Gaunless, a heavily coal mined catchment (50 – 98% total Fe load). These high diffuse contributors put into context the applicability of point source minewater remediation schemes, which may mitigate the most heavily polluting discharges and lead to considerable localised improvements in water quality, but are likely to have little effect on the long-term net export of metal from the catchment due to the prevalence and persistence of diffuse sources. The results of this study have similarly indicated that large sources of in-stream metals are not directly associated with point minewater discharges. This is particularly the case under high-flow conditions when re-suspension of secondary sources of contamination, notably metal-rich bed sediments which are gradually transported and dispersed through the larger watershed downstream of mineralised and mined areas.

6.8 The Effectiveness of Minewater Remediation Schemes on Long Term Water Quality Sustainability

The target of the Water Framework Directive (2000/60/EC) to achieve a quantified good ecological and chemical status within surface waters is dependent upon a sustainable approach to catchment based remediation in historically heavily mined regions where a legacy of extensive contamination and numerous polluting discharges exist. The demands of Directive 2000/60/EC require a programme of measures to improve the water quality and ecology of river systems.

Minewater remediation schemes in the UK have conventionally focused on coal mine discharges which often produce unsightly ferric iron precipitates on contact with the surface environment (Jarvis et al. 2007). The formation of the UK governments Coal Authority in 1994 gave the coal minewater treatment programme substantial momentum in terms of site prioritisation, funds for remedial measures and the construction (to date) of over 40 full-scale treatment or preventative schemes (for example, wetland treatment works and continual pumping of contaminated groundwater.) (see www.coal.gov.uk). Precipitation of iron from acidic discharges begins to occur above pH 3.2, and the equilibrium threshold level is reached at neutral (Younger et al. 2002), conditions easily attainable using passive treatment methods. More soluble trace metals found within the iron rich discharges easily bind to the ferric iron oxyhydroxide precipitates as a result of their open structure and high specific surface area (see Younger et al. 2002).

Discharges from metal mines, particularly those rich in zinc which occur throughout the North Pennine Orefield, receive little funding for remediation schemes due to disputed liability (Jarvis et al. 2007). Whilst there have been recent national initiatives for an integrated programme of prioritisation for abandoned metal mine sites for remedial work (Jarvis et al. 2007), there are still major issues with regards to legal liabilities, stakeholder issues (such as mine heritage issues and the colonisation of mine spoils with rare biota increasing conservation value (see Batty 2005; Bradshaw 1983; Ratcliffe 1974) and technical issues with regards to metal removal that need to be resolved (e.g. Nuttall and Younger 1999; Johnston et al. 2007). During normal conditions (pH 6 – 8 in an oxidising environment), the mobility of zinc far exceeds that of iron, with a prevalence of the dissolved species throughout the catchments during the sampling period (see pourbaix diagrams, annex B). A pH of more than 8.2 must be maintained for zinc precipitation to occur at a level suitable for significant aqueous-phase reduction during remediation (Younger et al. 2002). Passive treatment techniques including Anoxic Lime Drains (ALD's) have been implemented on a trial based scale, with relatively unsuccessful results (Nuttall and Younger 1999). Similarly, passive treatment with wetlands only yields minimal removal (Younger et al. 2002) particularly for mobile elements such as zinc, and is not necessarily suited to the steep sided valleys where metal mining was mainly focused in the UK, due to minimal availability of suitably low-gradient land for wetland construction.

Figure 14. Manganese Pourbaix Diagram

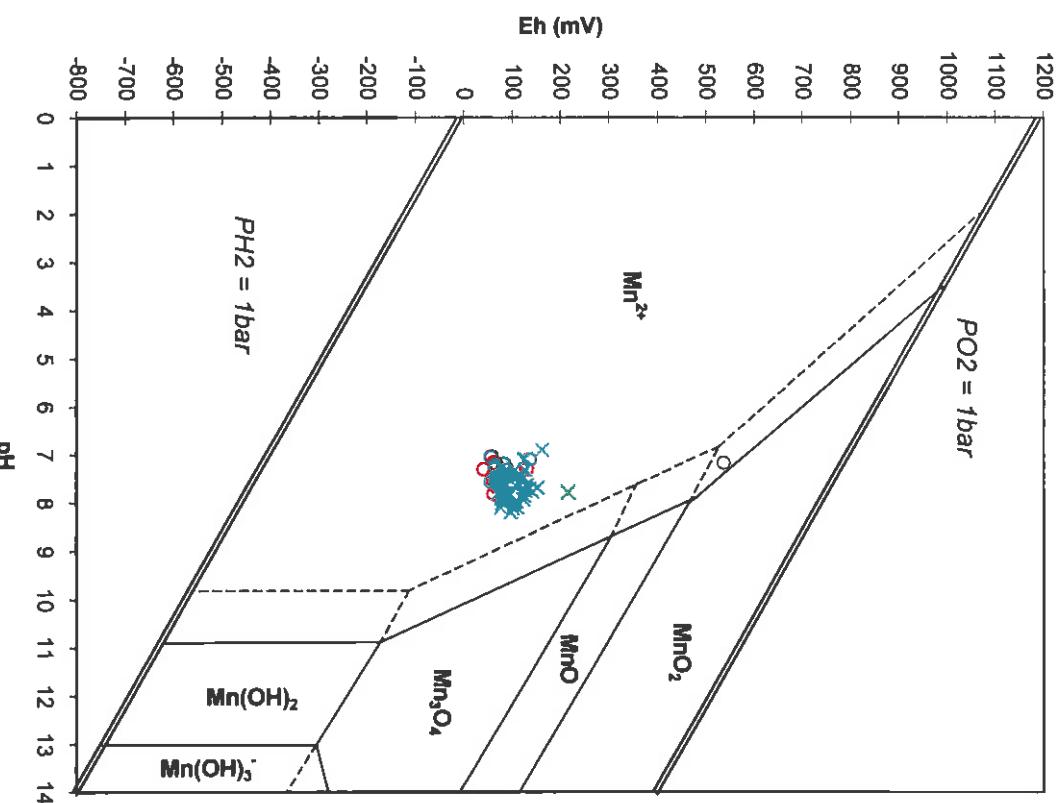
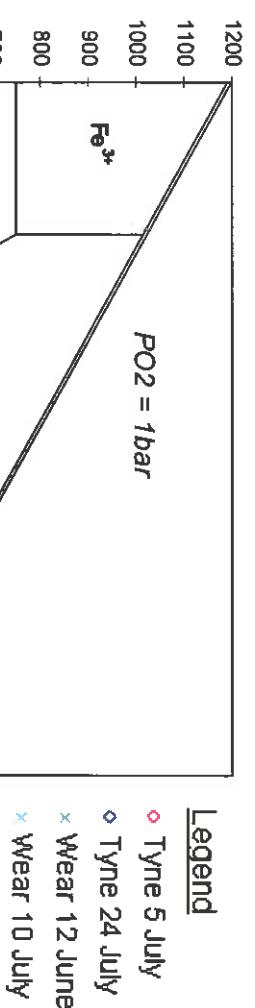


Figure 15. Iron Pourbaix Diagram



Eh - pH diagram for the system: Mn - O - H
(Adapted from Wagman et al., 1982)

Eh - pH diagram for the system: Fe - O - H
(Adapted from Wagman et al., 1982)

B

The catchment-scale modelling of inorganic pollutants undertaken during this study reveals complex behaviour of contaminants during different weather conditions. The study indicates that a strong contribution to in-stream fluxes occurs from diffuse sources, such as stream-bed sediments and potential hyporheic interaction, including the possibility of contaminated groundwater input. Most conventional remediation schemes, as discussed above, cannot be applied to diffuse sources in the way that they can to point sources due to the technical problems associated with identifying, quantifying and isolating the sources (e.g. Mayes et al. 2007). Despite a significant contribution to in-stream metal loading from highly polluted headwaters, there are large fluxes of metals which arise from parts of the Tyne and Wear downstream of the heavily-mined, mineralised upland areas. The most likely source of these metals in the lower catchments is from re-suspended, contaminated streambed sediments. These sediment related metal sources have been shown elsewhere to be a long standing source of aquatic pollution (see Macklin et al. 1997) although the specific ecological impacts of such sources at different trophic levels are not entirely understood.

7.0 CONCLUSIONS

7.1 General Patterns of Metal Pollution

Iron and manganese concentrations, which are generally problematic in coal mine discharge affected waters, are generally low throughout the catchment with greatest iron concentrations seen in the headwaters, a possible result of peat land drainage rather than mine-related contamination.

Copper concentrations, despite being above the EQS threshold limit in many instances, cannot be directly attributed to minewater discharges, i.e. the fluxes of copper through the catchments do not correspond to areas impacted by a legacy of historical mining. Therefore the bulk copper contamination is likely to arise from non-mining sources such as agriculture.

Cadmium concentrations are consistently low with just a single EQS threshold breach occurring during high-flow. However, the MAC status of this substance means that a single breach constitutes a failure under directive 2000/60/EC.

Lead and zinc contamination frequently occurs in excess of the guideline values set by the Directive both in the historically heavily mined headwaters and far downstream. In the headwaters, this contamination is a probable result of the discharges and seepages from historical metal-mining. However, in the lower reaches, significant additional contributions to in-stream fluxes can be seen.

The difference in patterns of zinc and lead fluxes through the catchments reflect the difference in the metal's mobility. PbCO_3 is likely to be the dominant in-stream lead species, fluxes of which are controlled primarily by suspension of particulate material during high flow. Zinc is either present as Zn^{2+} ions or the ZnCO_3^0 complex, and thus generally behaves as a dissolved species, having a greater mobility than lead, iron and manganese.

7.2 EQS Status at Sampling Points

Table 10. The levels of metal contamination within the Rivers Tyne and Wear frequently breach EQS thresholds under Directive 2000/60/EC

	P – EQS Pass F – EQS Fail	Low Flow					High Flow				
		Fe	Cu	Zn	Cd	Pb	Fe	Cu	Zn	Cd	Pb
Wear Catchment	Wear at Chester le Street	P	P	P	P	P	P	P	P	P	P
	Wear at Sunderland Bridge	P	P	P	P	P	P	P	P	P	P
	Browney at Burn Hall	P	P	P	P	P	P	P	F	P	P
	Gaunless at Dovecot Hill	P	P	P	P	P	P	P	P	P	P
	Wear at Witton	P	P	P	P	P	P	F	F	P	F
	Bedburn Beck	P	F	F	P	F	P	P	F	P	P
	Bollhope Burn	P	F	F	P	F	P	P	F	P	F
	Stanhope Burn	P	P	P	P	F	P	P	P	P	F
	Wear at Stanhope	P	P	F	P	F	P	F	F	P	F
	Rookhope Burn	P	P	F	P	F	P	P	F	P	F
	Westernhope Burn	P	P	F	P	F	P	P	F	P	P
	Middlehope Burn	P	P	F	P	F	P	F	F	F	F
	Ireshope Burn	P	P	P	P	P	P	F	F	P	F
	Burnhope Burn	P	F	F	P	F	P	F	F	P	F
Tyne Catchment	Killhope Burn	P	F	F	P	F	P	F	F	P	F
	Wellhope Burn	P	P	F	P	P	P	F	F	P	F
	Team at Coalhouse	P	P	P	P	P	P	P	P	P	P
	Birtley	P	P	P	P	P	P	P	P	P	P
	Team upstream of Lamesley	P	P	P	P	P	P	P	P	P	P
	Rowlands Gill	P	P	P	P	P	P	P	P	P	P
	Eddys Bridge	P	P	F	P	F	P	F	F	P	F
	Devils Water	F	F	F	P	F	P	F	F	P	P
	East Allen	F	F	F	P	F	P	F	F	P	F
	West Allen at Blueback	F	F	F	P	F	P	P	F	P	F
	Nent at Nenthead	P	F	F	P	F	P	F	F	P	F
	Garrigill	P	F	F	P	F	P	P	P	P	P
	Black Burn	P	P	F	P	F	P	F	F	P	F
	Nent at Alston	P	F	F	P	F	P	P	P	P	F
	South Tyne at Alston	P	F	F	P	F	P	P	P	P	F
	South Tyne at Featherstone	P	F	F	P	F	P	P	F	P	F
	South Tyne at Haydon Bridge	P	F	F	P	F	P	P	F	P	F
	North Tyne at Reaverhill	P	F	F	P	P	P	F	P	P	P
	Tyne at Bywell	P	F	F	P	F	P	F	F	P	F

7.3 Catchment Scale Fluxes

The catchment based approach to this study revealed the importance of metal input from diffuse sources, either by secondary mobilisation of flood sediments, input of contaminated groundwater via the hyporheic zone or external non-mining related sources.

The highly contaminated headwaters contribute a small but significant percentage of in-stream metals to downstream fluxes. However, the greatest input to total metal loading comes from diffuse sources further down the catchment.

Catchment scale mapping and calculations of metal export per km² area reveal disproportionately high fluxes in the middle to lower reaches of the rivers, particularly during high flow. For example, the greatest total export of zinc, lead and iron was found in the Wear at Stanhope. The major source of this contamination can be attributed to re-suspended, contaminated streambed sediment fluxes or 'slugs' (see Macklin et al. 1997). Bulk export calculations suggest a *greater* contribution to flux per km² in the lower reaches. This unexpected behaviour occurs during both high and low flow, and suggests that additional sources of contamination exist: probably in the form of streambed sediments, input of contaminated groundwater and/ or external sources (sewage works, industrial discharges, highway run-off etc).

A pattern of greater colloidal metal loading is seen in the lower reaches than in the headwaters. This suggests that in-stream dissolved metals could be precipitating/ forming complexes or accumulating in microbiota, either derived upstream or via contaminated groundwater influx from the hyporheic zone. The downstream location of this behaviour would suggest either contamination with agriculturally derived ligands, or biotic uptake driving the precipitation process.

The findings of this investigation suggest that targeted minewater remediation of point sources in the historically heavily headwaters could potentially have a marked impact upon the immediate bioavailable inorganic pollution. However, particulate fluxes, less critical in terms of first order bioavailability, may provide a mechanism for pollutant transport and future mobilisation of bioavailable species.

Thus, diffuse sources of inorganic pollutants within the post-industrial Tyne and Wear catchments could represent a significant obstacle in achieving the latest EQS targets to be introduced under the Water Framework Directive 2000/60/EC.

7.4 Limitations

The scale of the survey area and short time frame available for sampling limited the resolution of this investigation.

The anion results obtained using the ion chromatograph did not appear to conform to the expected values. This suspicion was confirmed by cross-referencing a select number of samples, duplicates of which were analysed at Newcastle University using a similar technique. The duplicate samples gave readings that were in-range and gave only marginal error when inserted into the charge balancing expression.

Weather conditions of sample taking did not conform wholly to typical circumstances, the flow conditions were elevated throughout the sampling period.

7.5 Suggested Further Work

This investigation provides an insight into the patterns of inorganic pollution through a post – industrial catchment. Future research may quantify the input of metals not only from headwater sources, but also from streambed/overbank sediments and the hyporheic zone. This could be achieved using higher resolution techniques such as longitudinal water sampling at short intervals of the river, thus ruling out external controls on metal loading.

Investigation involving systematic co-sampling of sediments and hyporheic material during a range of flow conditions could be undertaken. This would provide information on the behaviour of the streambed and hyporheic zone as both a sink and source of contamination.

Additionally, analysis of water samples for organic material, particularly on a perennial basis, may give insight into the reason for pronounced colloidal fluxes of metal in the lower reaches.

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GLOSSARY OF TERMS AND ABBREVIATIONS

ALD	-	Anoxic Limedrain
AMD	-	Acid Mine Discharge
AOD	-	Above Ordnance Datum
BGS	-	British Geological Survey
C.I.	-	Charge Imbalance
DOC	-	Dissolved Organic Carbon
E.C.	-	Electrical Conductivity
Eh	-	Voltage Potential
E.M.F.	-	Electro-Motive Force
EQS	-	Environmental Quality Standard
g/s	-	grams per second
HERO	-	Hydrogeochemical Engineering and Outreach Group
ICP-MS	-	Inductively Coupled Plasma Mass Spectrometer
IC	-	Ion Chromatograph
km	-	kilometers
LOIS	-	Land-Ocean Interaction Study
Meq	-	Milliequivalents
Mg/l	-	milligrams per litre
mV	-	milliVolts
ppb	-	Parts per Billion
TDS	-	Total Dissolved Solids
µg/l	-	micrograms per litre
µs/cm	-	microSeimens per Cm
Σ	-	sum
~	-	approximately

Figure 21. River Wear (Fe, Mn Concentrations High Flow)
 Showing the concentrations of total and dissolved manganese and iron during High Flow Conditions

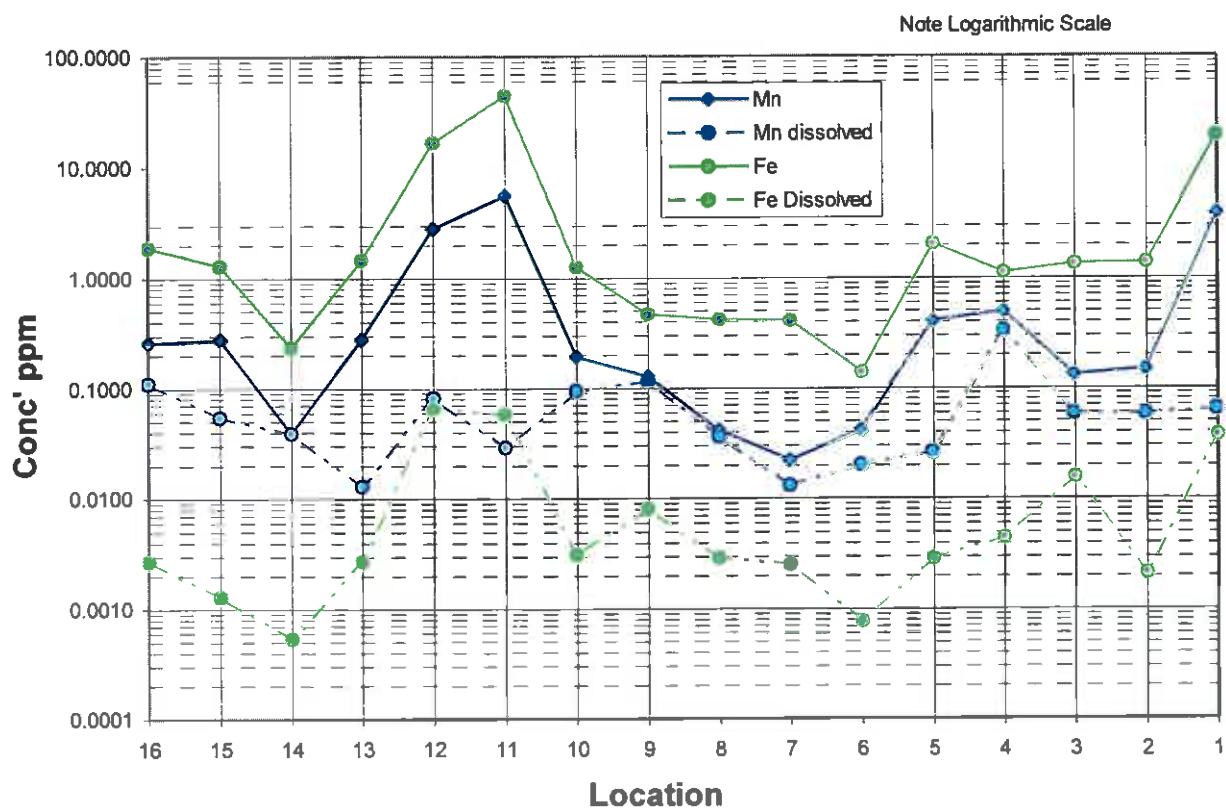


Figure 22. River Wear (Fe, Mn Concentrations Low – Flow)
 Showing the concentrations of total and dissolved manganese and iron during Low Flow Conditions

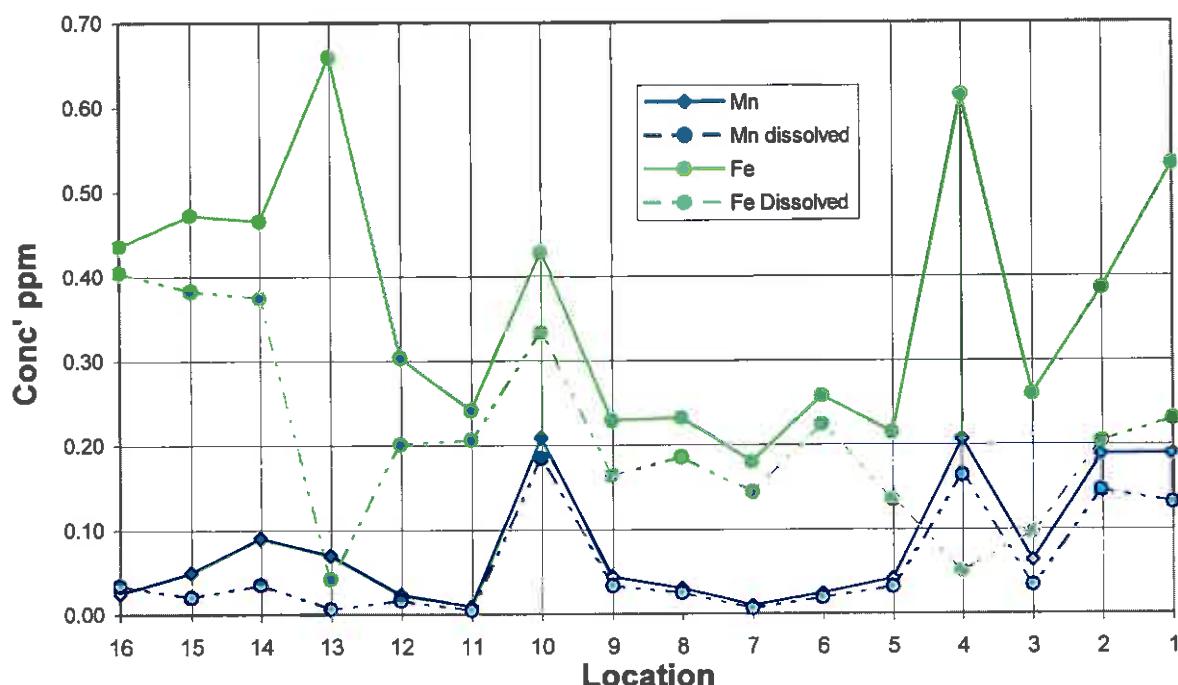
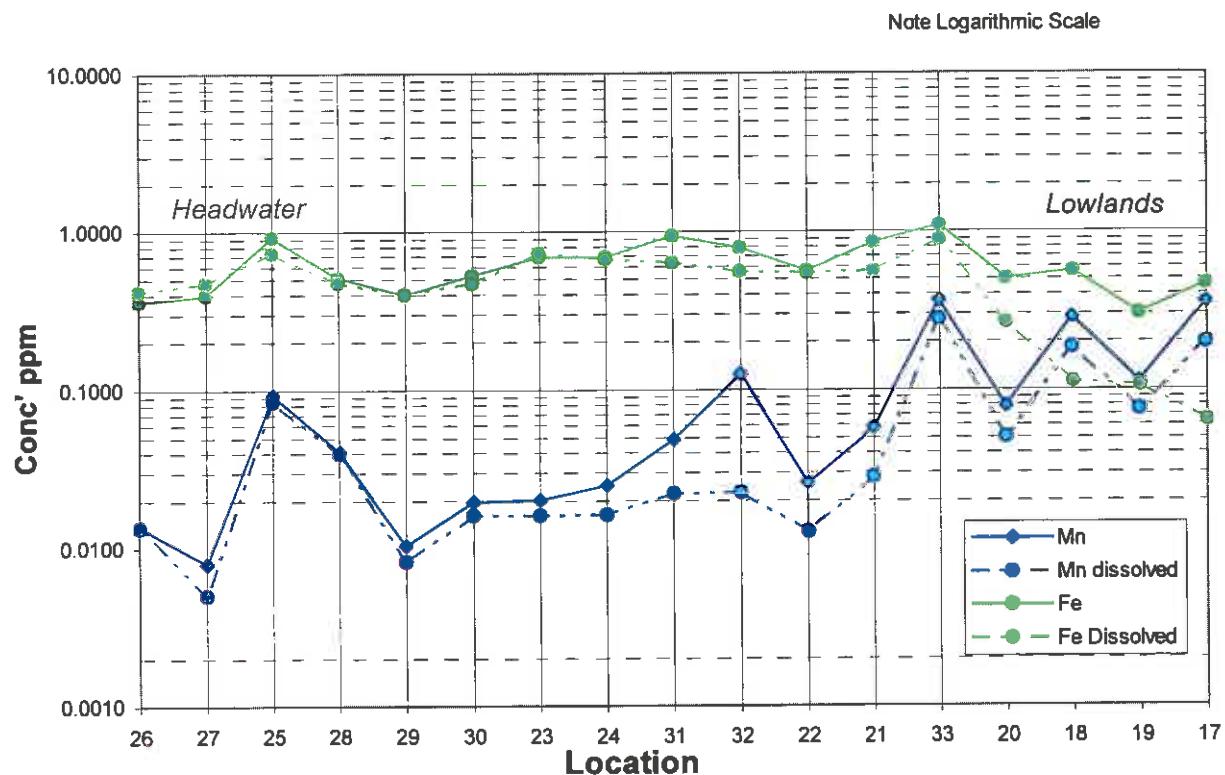


Figure 23. River Tyne (Fe, Mn Concentrations High – Flow)

Showing the concentrations of total and dissolved manganese and iron during high flow conditions

**Figure 24. River Tyne (Fe, Mn Concentrations Low – Flow)**

Showing the concentrations of total and dissolved manganese and iron during low flow conditions

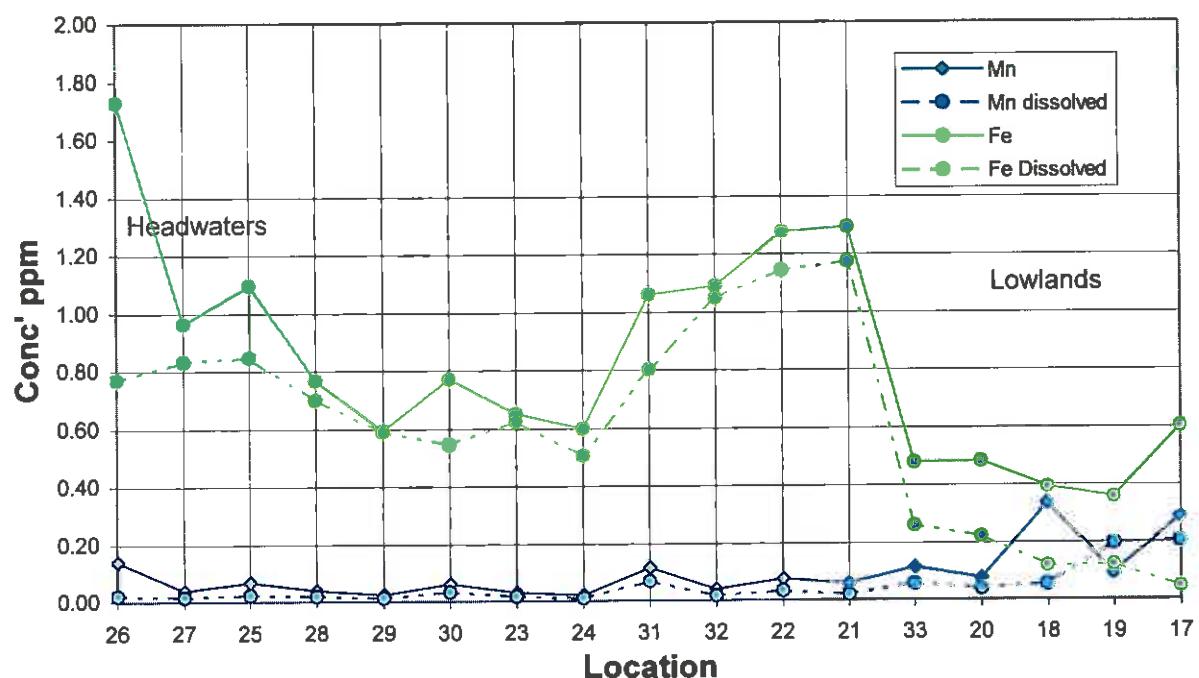
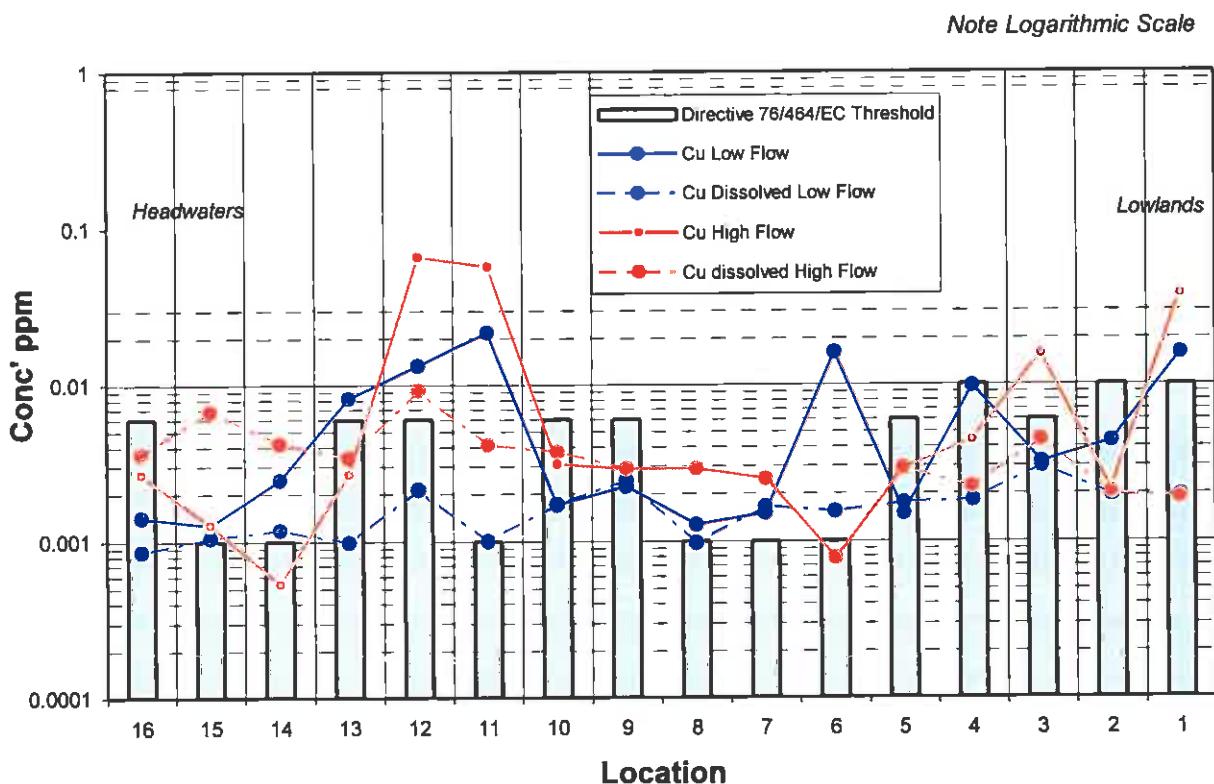


Figure 25. River Wear (Cu Concentrations)

Showing the concentrations of total and dissolved copper during low and high flow conditions

**Figure 26. River Tyne (Cu Concentrations)**

Showing the concentrations of total and dissolved copper during low and high flow conditions

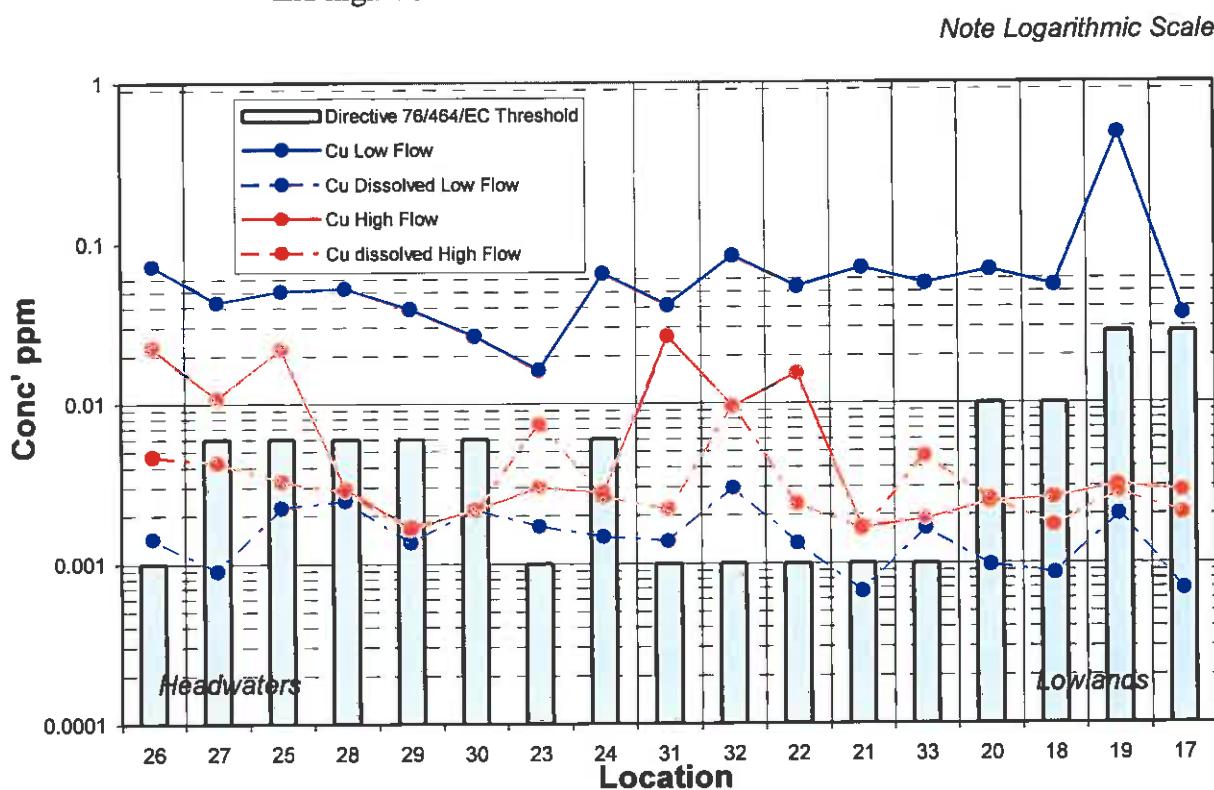
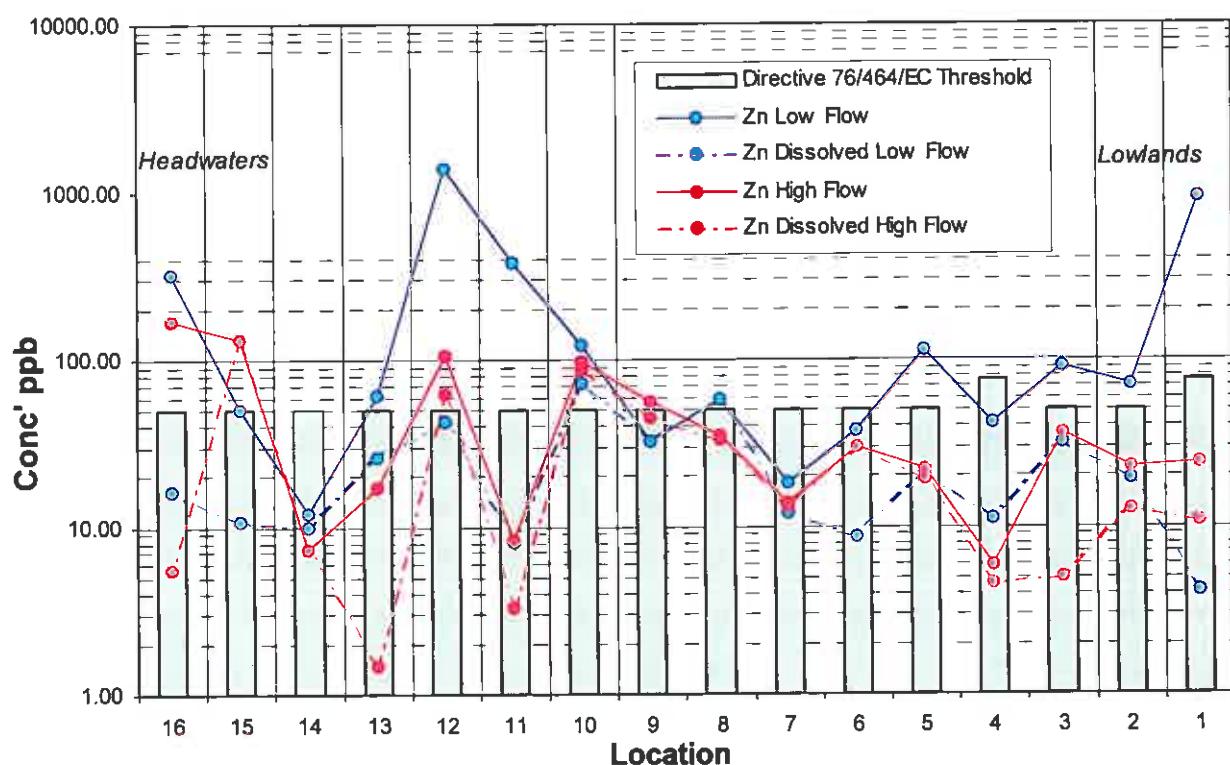


Figure 27. River Wear (Zn Concentrations)

Showing the concentrations of total and dissolved zinc during low and high flow conditions

**Figure 28. River Tyne (Zn Concentrations)**

Showing the concentrations of total and dissolved zinc during low and high flow conditions

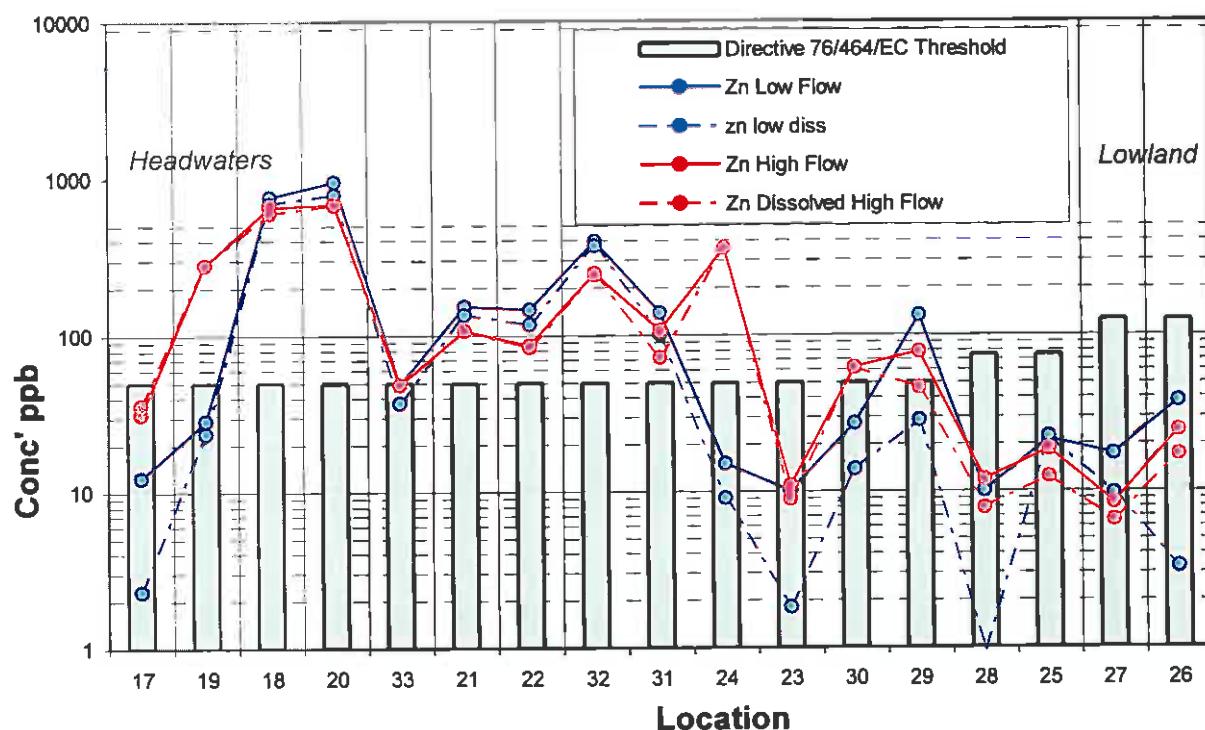
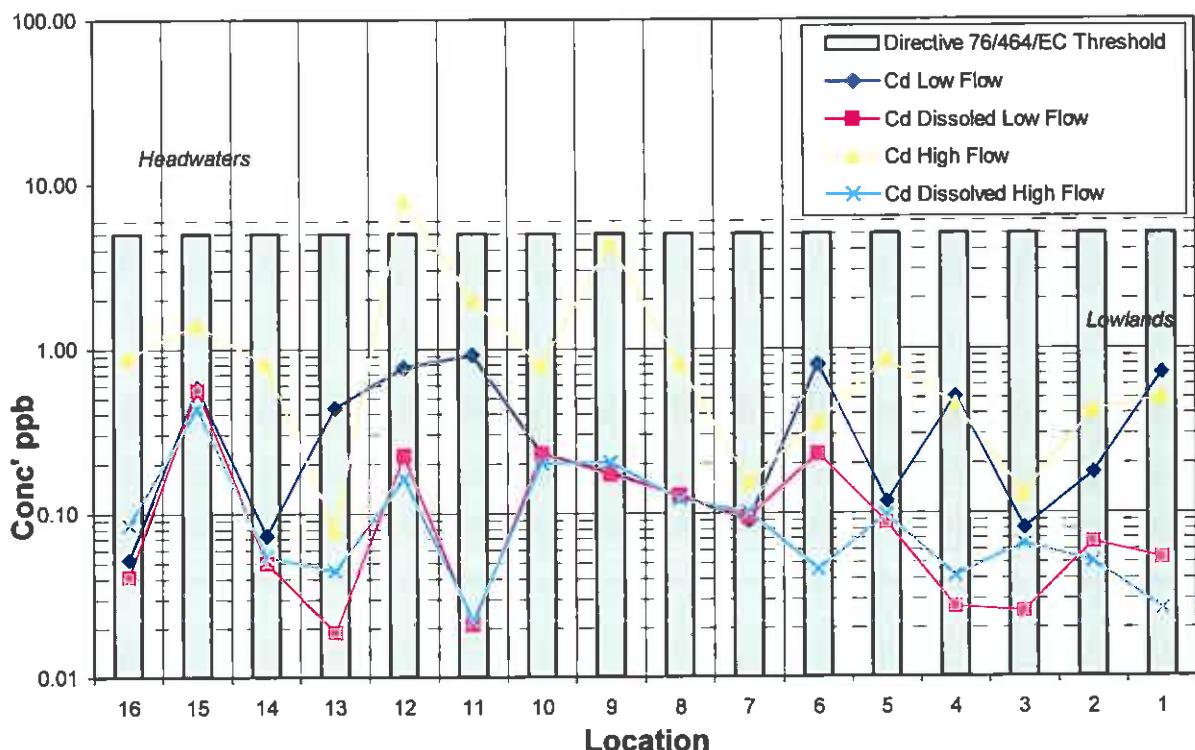


Figure 29. River Wear (Cd Concentrations)

Showing the concentrations of total and dissolved cadmium during low and high flow conditions

**Figure 30. River Tyne (Cd Concentrations)**

Showing the concentrations of total and dissolved cadmium during low and high flow conditions

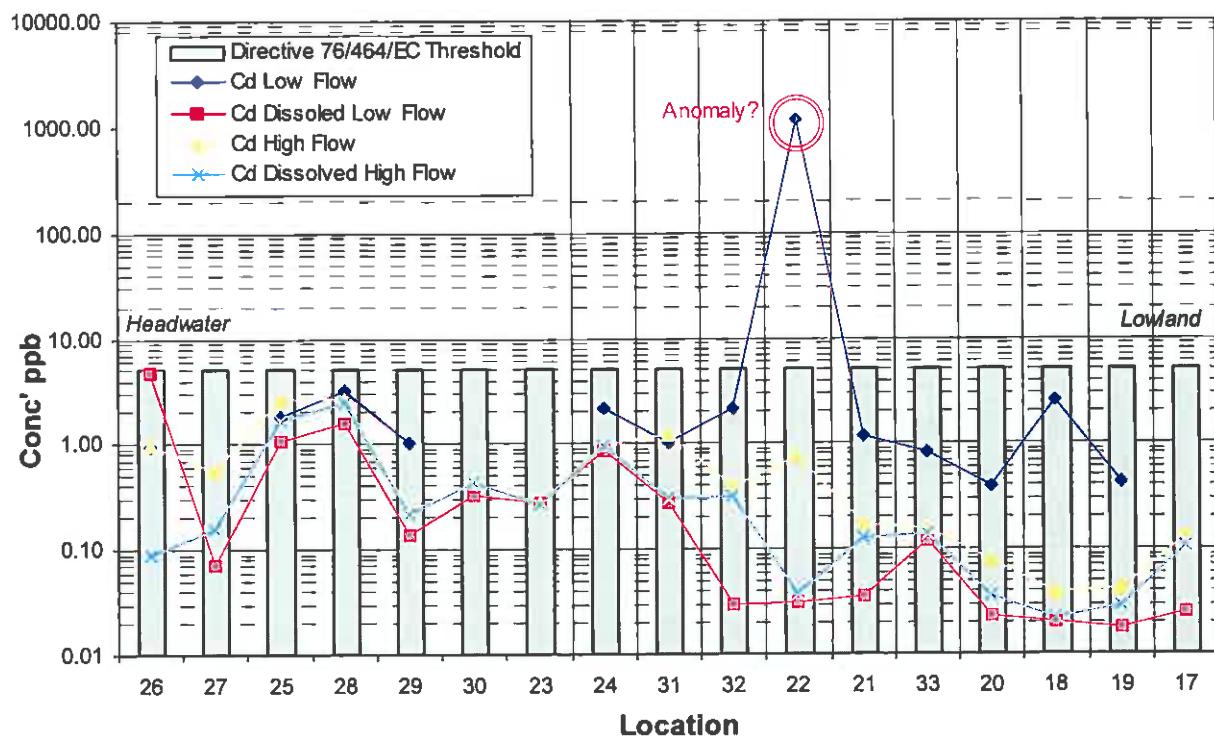
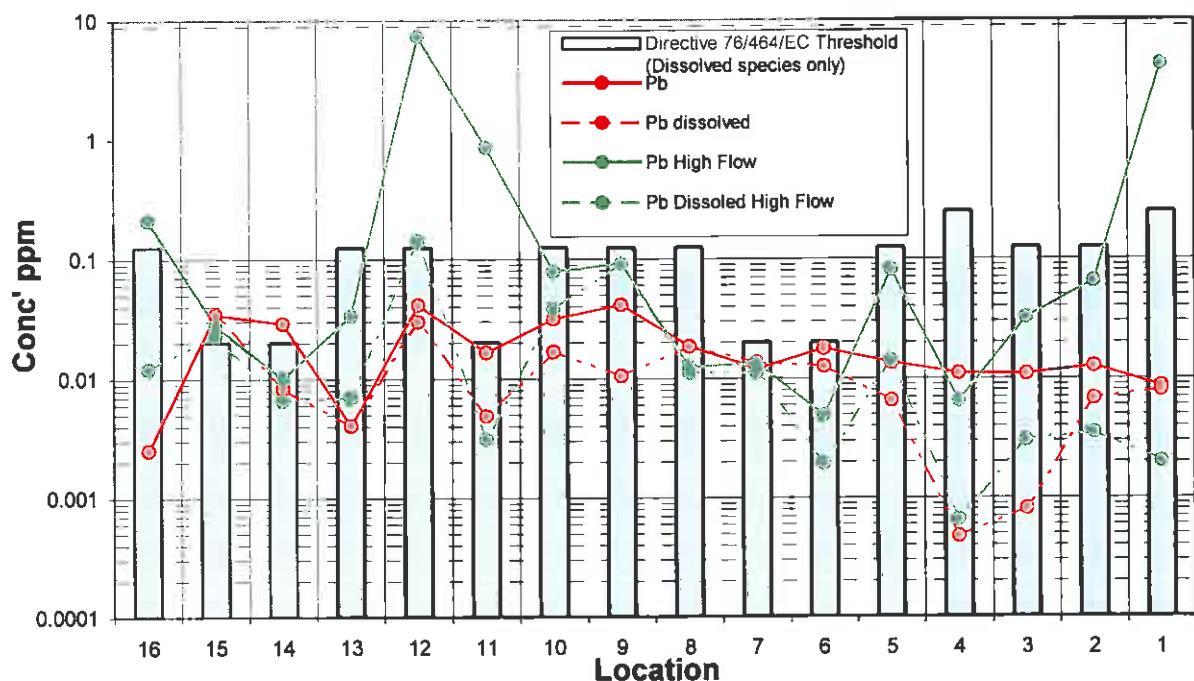
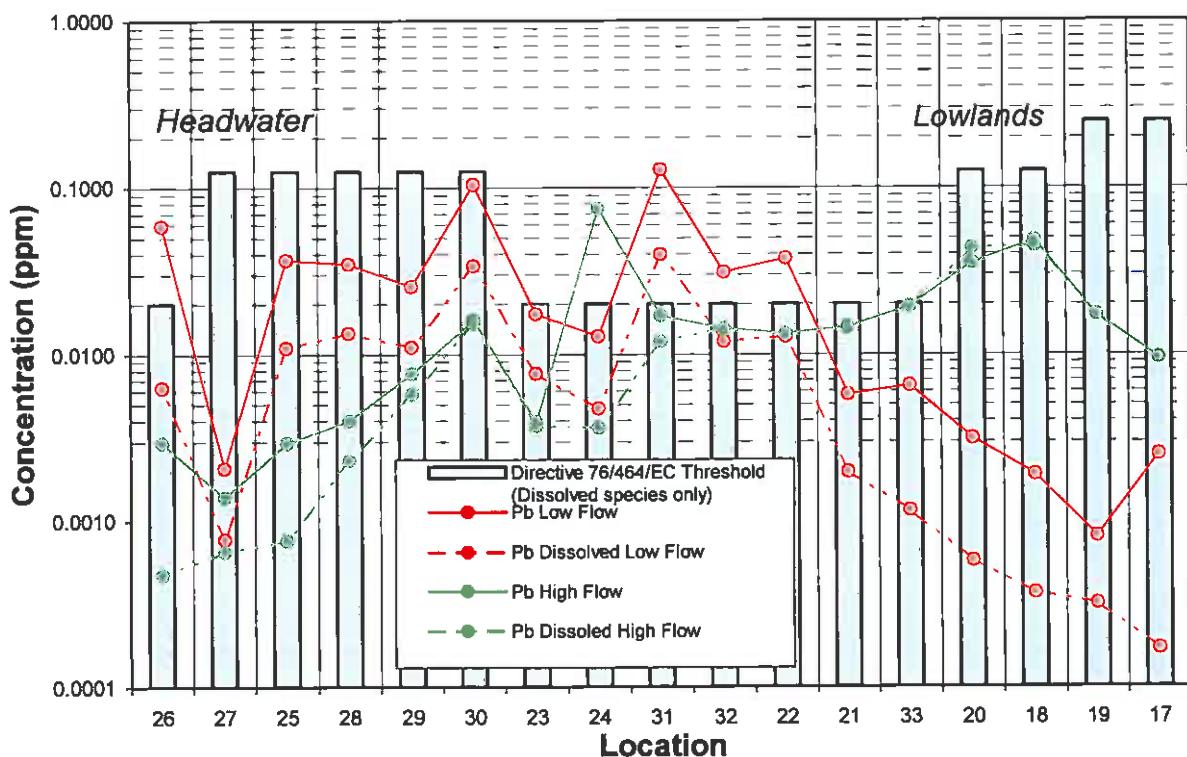


Figure 31. River Wear (Pb Concentrations)

Showing the concentrations of total and dissolved lead during low and high flow conditions

**Figure 32. River Tyne (Pb Concentrations)**

Showing the concentrations of total and dissolved lead during low and high flow conditions



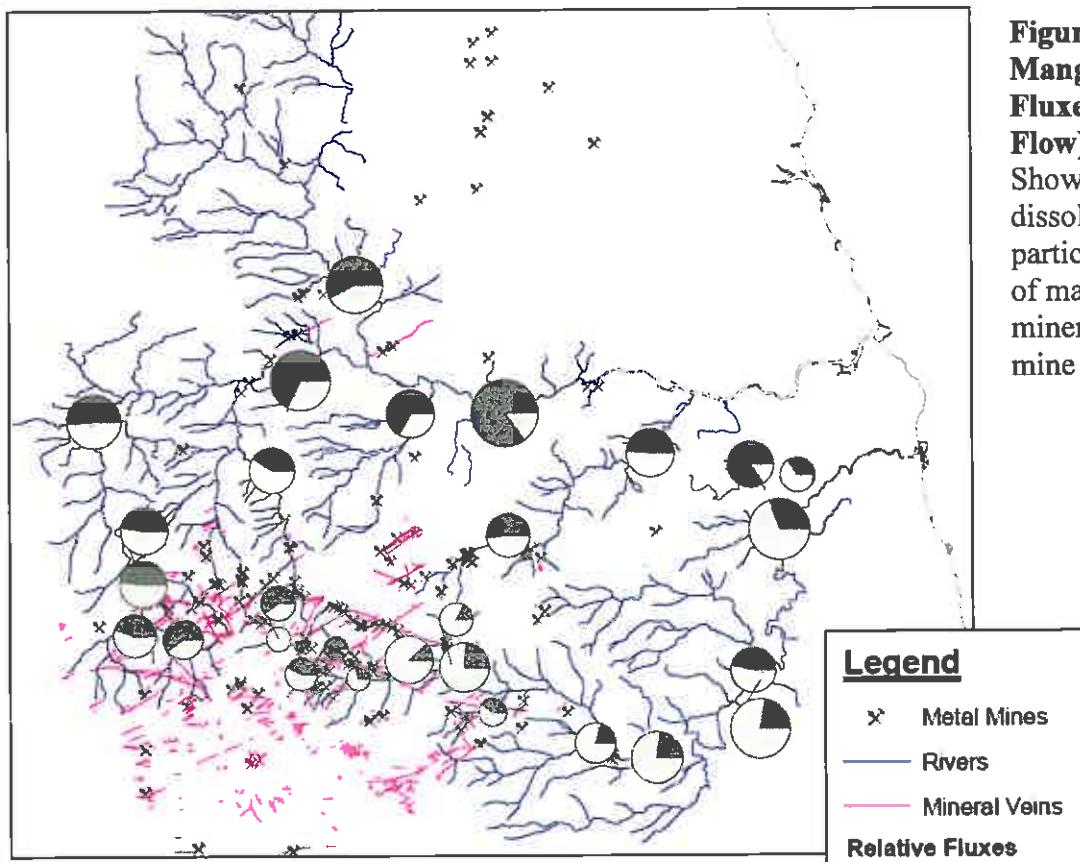


Figure 33.
Manganese Fluxes (Low-Flow)
Showing the dissolved and particulate fluxes of manganese, mineral vein and mine locations.

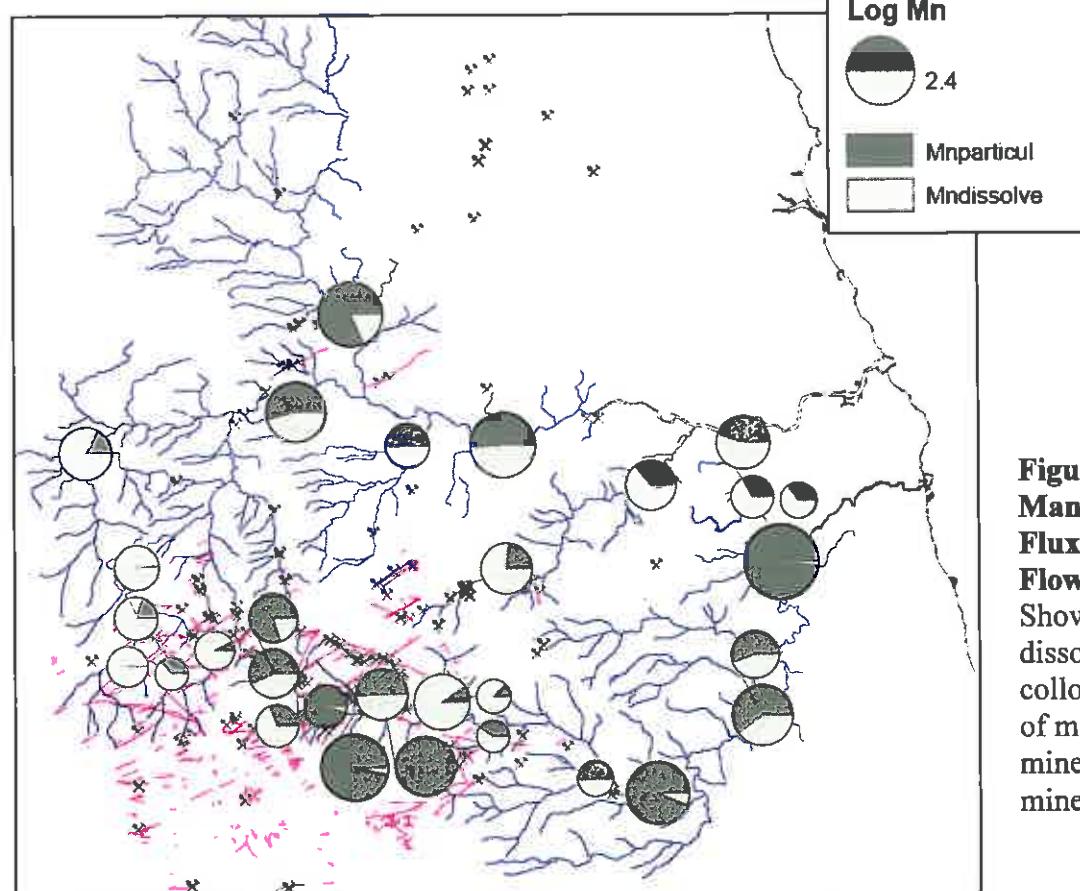


Figure 34.
Manganese Fluxes (High-Flow)
Showing the dissolved and colloidal fluxes of manganese, mineral vein and mine locations.

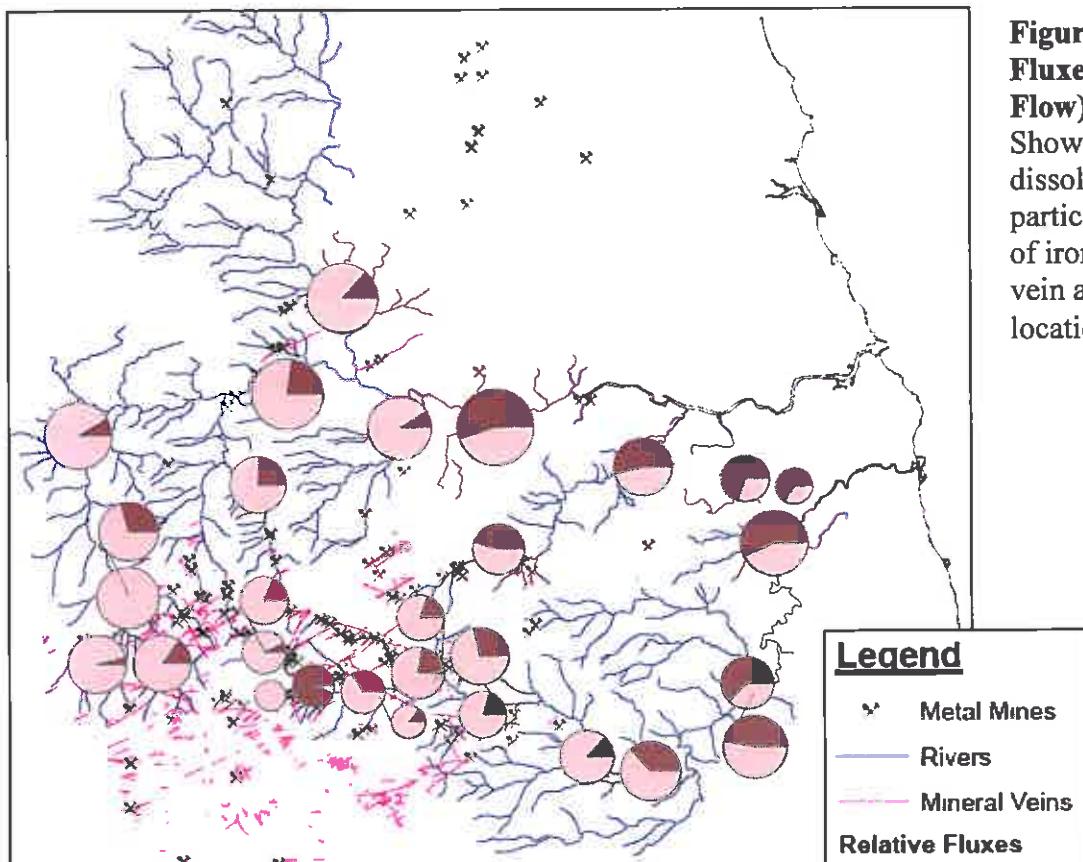


Figure 35. Iron Fluxes (Low-Flow)

Showing the dissolved and particulate fluxes of iron, mineral vein and mine locations.

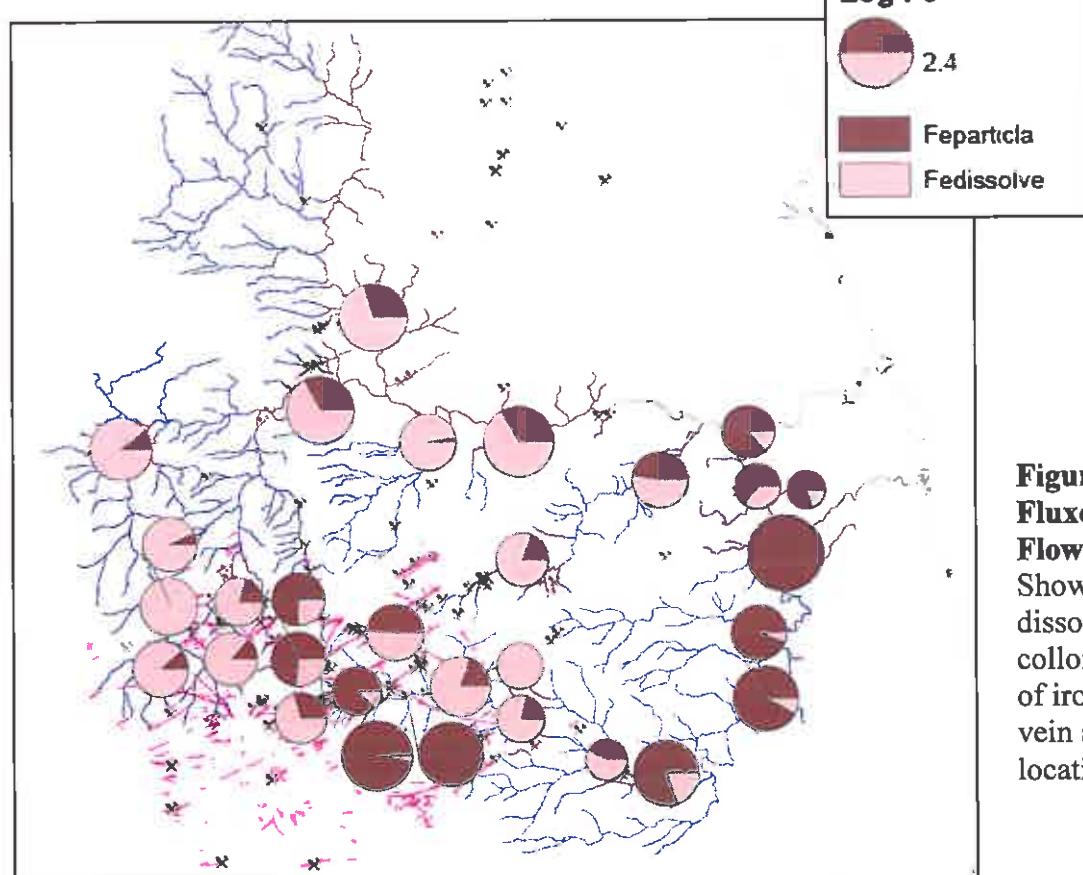


Figure 36. Iron Fluxes (High-Flow)

Showing the dissolved and colloidal fluxes of iron, mineral vein and mine locations.

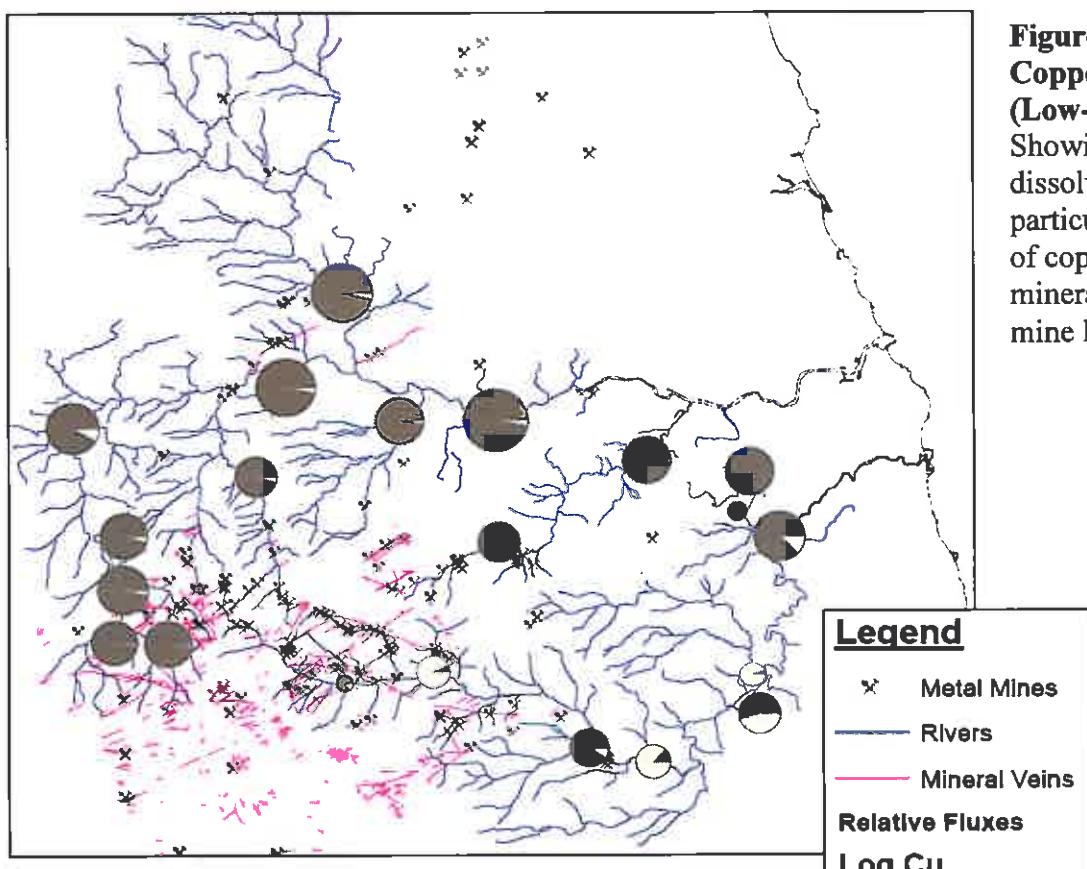


Figure 37.
Copper Fluxes (Low-Flow)
Showing the dissolved and particulate fluxes of copper, mineral vein and mine locations.

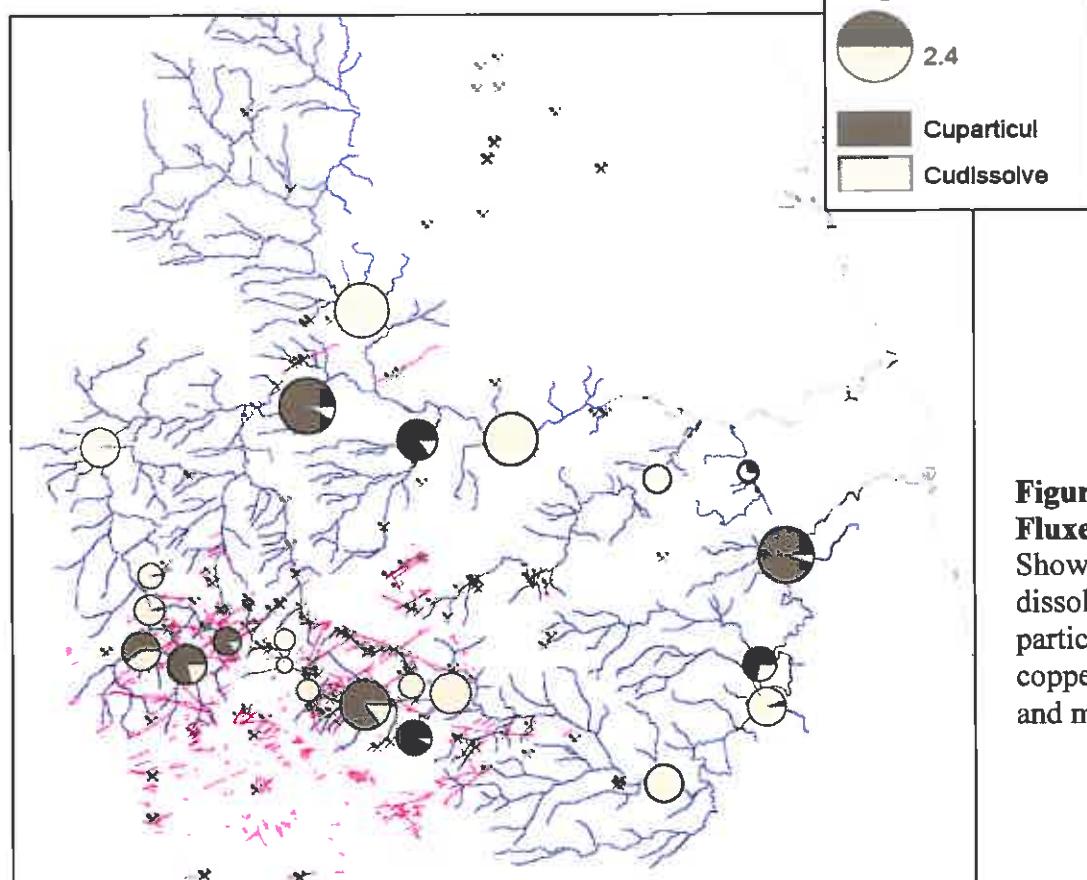


Figure 38. Copper Fluxes (High-Flow)
Showing the dissolved and particulate fluxes of copper, mineral vein and mine locations.

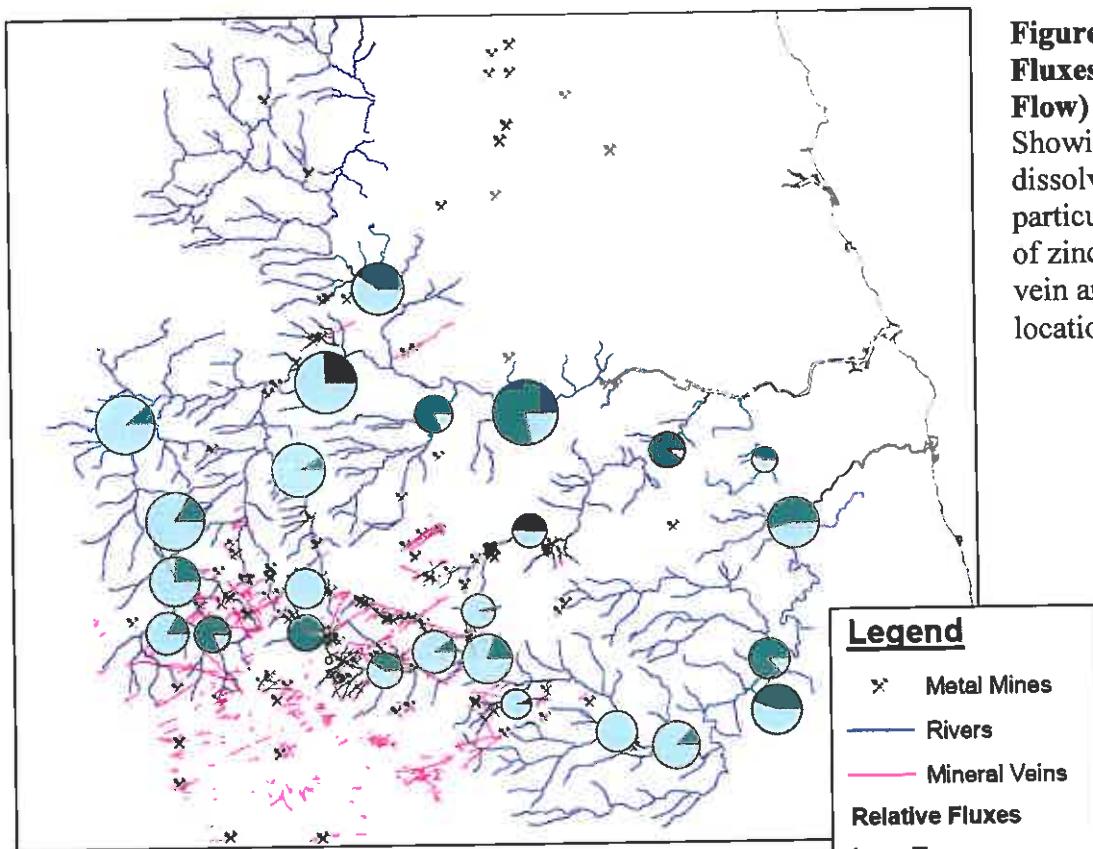


Figure 39. Zinc Fluxes (Low-Flow)
Showing the dissolved and particulate fluxes of zinc, mineral vein and mine locations.

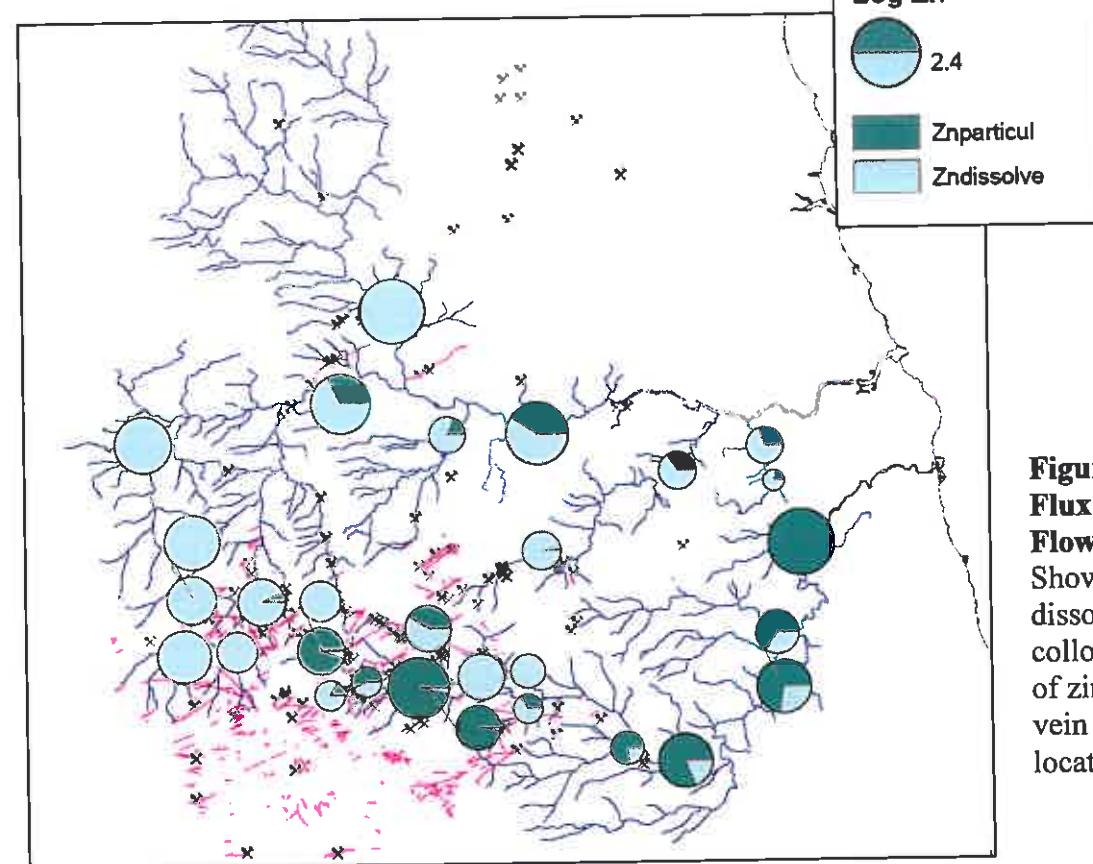


Figure 40. Zinc Fluxes (High-Flow)
Showing the dissolved and colloidal fluxes of zinc, mineral vein and mine locations.

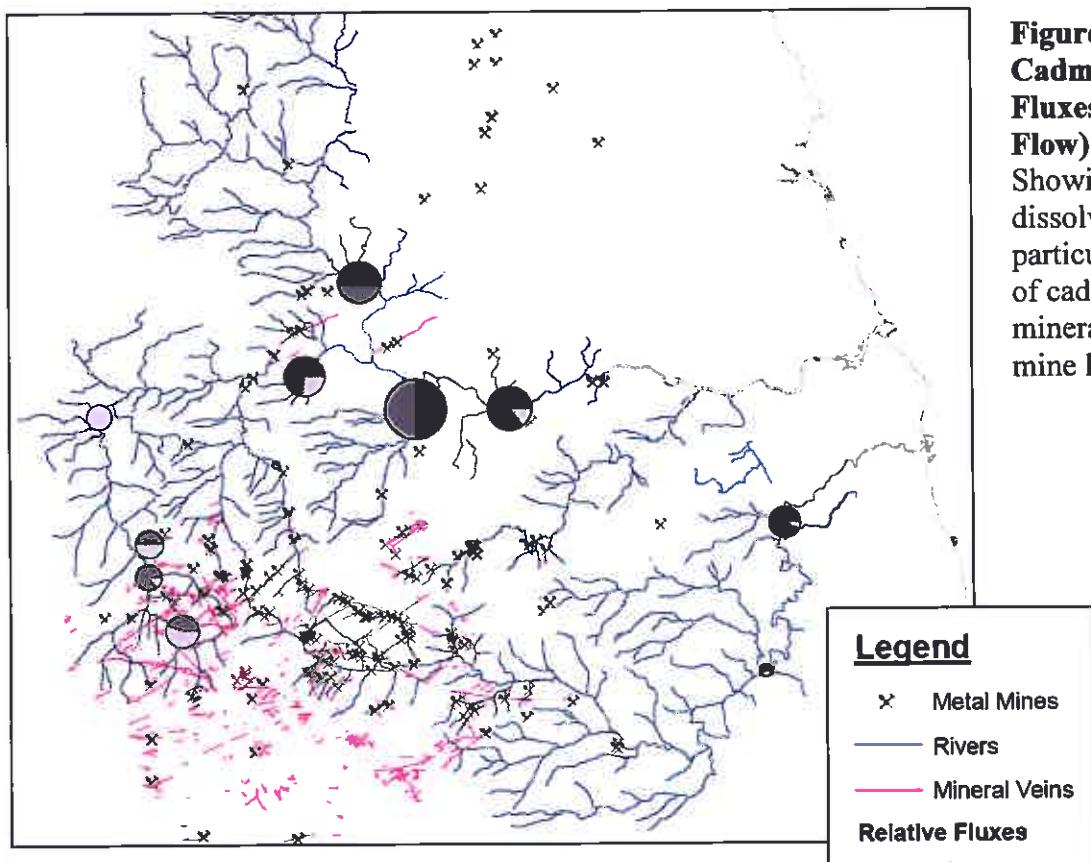


Figure 41.
Cadmium
Fluxes (Low-
Flow)
Showing the dissolved and particulate fluxes of cadmium, mineral vein and mine locations.

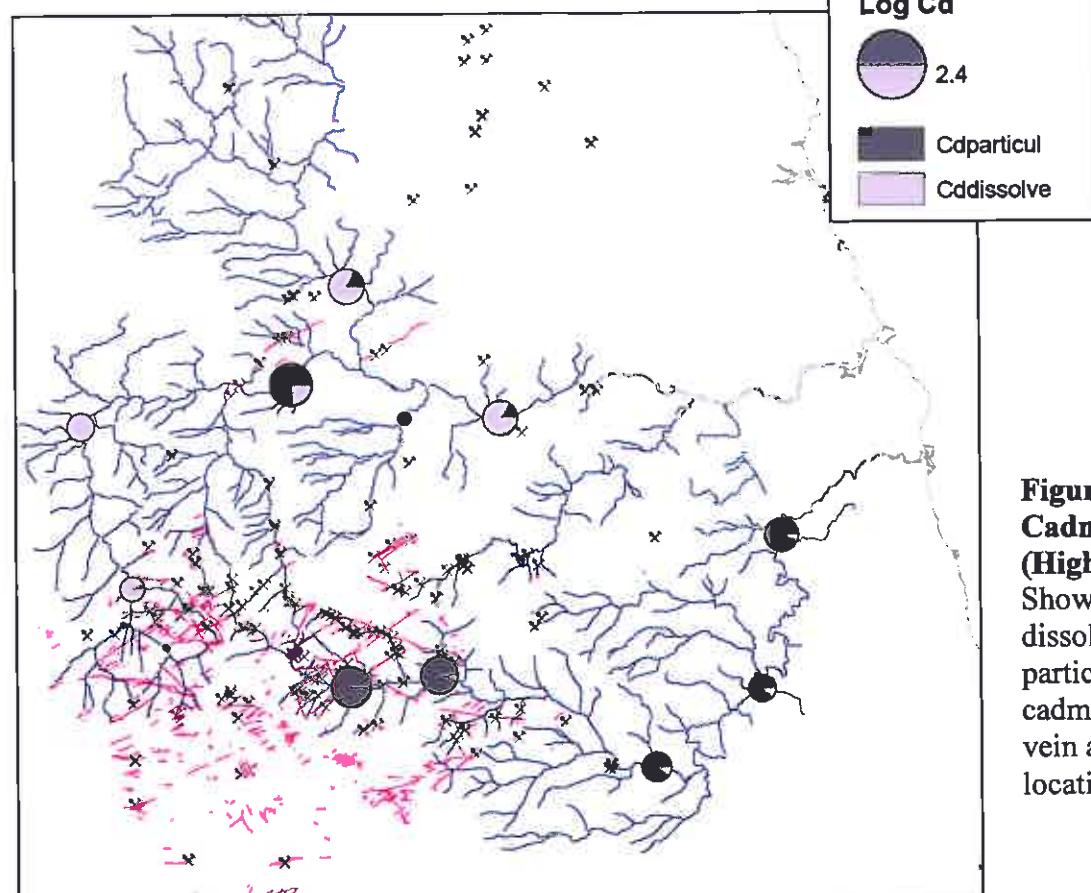


Figure 42.
Cadmium Fluxes
(High-Flow)
Showing the dissolved and particulate fluxes of cadmium, mineral vein and mine locations.

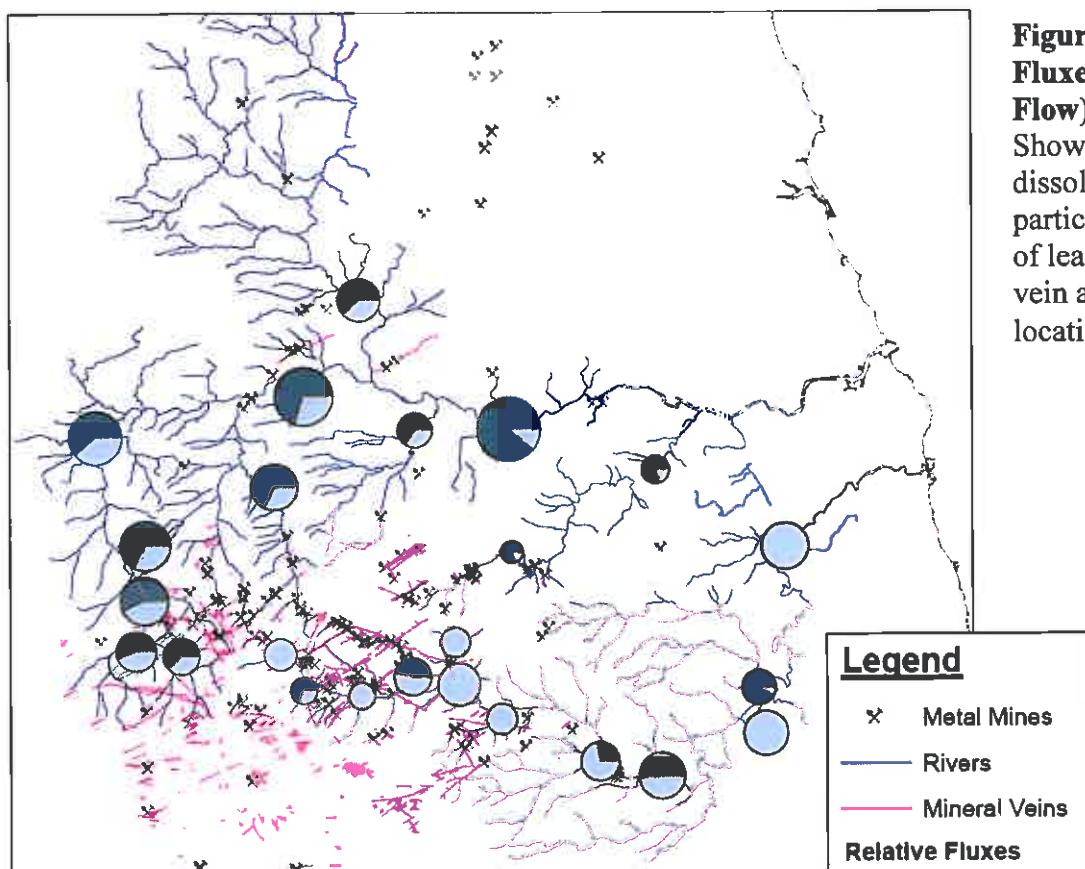


Figure 43. Lead Fluxes (Low-Flow)
Showing the dissolved and particulate fluxes of lead, mineral vein and mine locations.

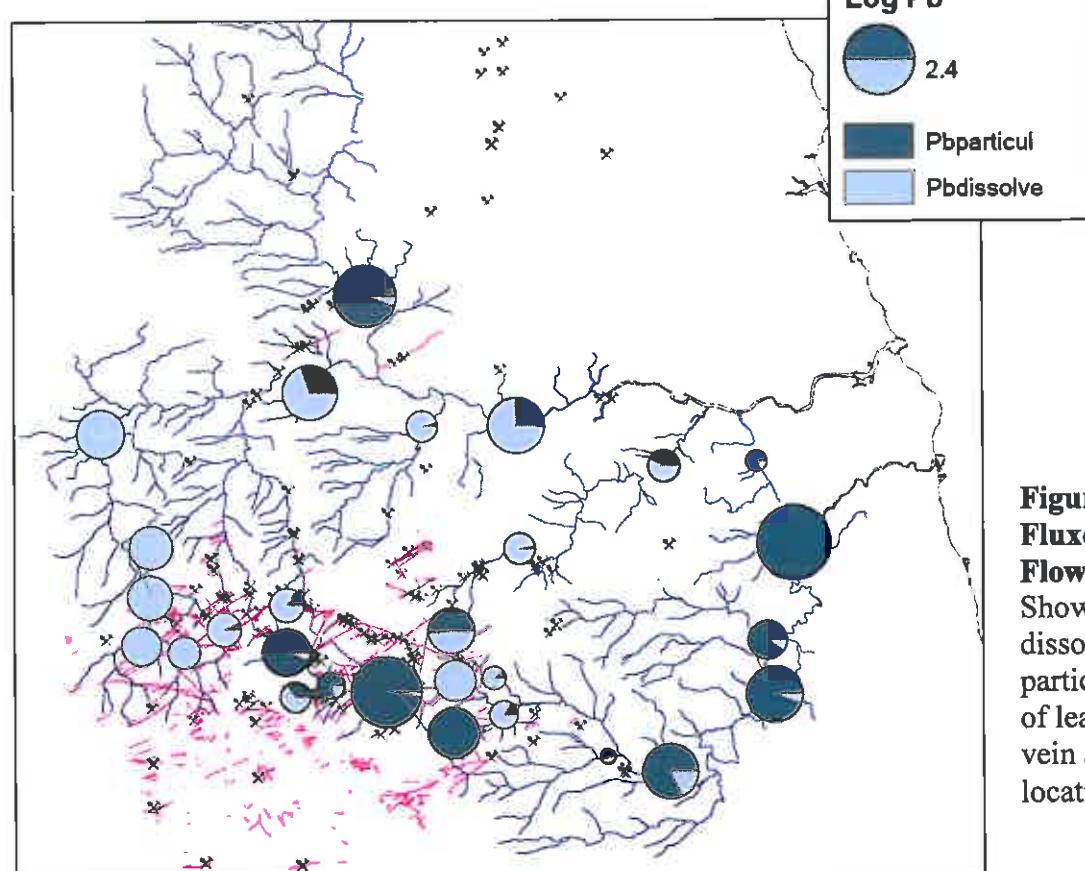


Figure 44. Lead Fluxes (High-Flow)
Showing the dissolved and particulate fluxes of lead, mineral vein and mine locations.

Table 1: Environmental Quality Standards (EQS) for List 1 dangerous substances, EC Dangerous Substances Directive (76/464/EEC)

Table 1: Environmental Quality Standards (EQS) for List 1 dangerous substances, EC Dangerous Substances Directive (76/464/EEC)

Substance	All freshwater EQS (annual average, µg/l)	Coastal and estuarine EQS (annual average, µg/l)	Sediment
Mercury (total)	1	n/a	Standstill (no deterioration)
Mercury (dissolved)	n/a	0.3	Standstill (no deterioration)
Cadmium (total)	5	n/a	Standstill (no deterioration)
Chlorophenols	n/a	2.5	Standstill (no deterioration)
Carbon tetrachloride	12	12	n/a
Total DDT	0.025	0.025	Standstill (no deterioration)
Pentachlorophenol	2	2	Standstill (no deterioration)
Aldrin	0.01	0.01	Standstill (no deterioration)
Endrin	0.005	> 0.005	Standstill (no deterioration)
Total 'Drins	0.03	0.03	Standstill (no deterioration)
Hexachlorobenzene	0.03	0.03	Standstill (no deterioration)
Hexachlorobutadiene	0.1	0.1	Standstill (no deterioration)
Chloroform	12	12	n/a
1,2-dichloroethane	10	10	n/a
Trichlorethylene	10	10	n/a
Perchlorethylene	10	10	n/a
Trichlorobenzene	0.4	0.4	Standstill (no deterioration)

Highlighted Fields indicate investigated substances

Source: Environment Agency 2007c.

Table 2a: Environmental Quality Standards (EQS) for List 2 dangerous substances, EC Dangerous Substances Directive (76/464/EEC)

Table 2a: Environmental Quality Standards (EQS) for List 2 dangerous substances, EC Dangerous Substances Directive (76/464/EEC)

Substance	EQS Type	All Freshwater EQS (ug/l)	Coastal and Estuarine EQS (ug/l)
1,1,1-Trichloroethane	Annual average	100	100
1,1,2-Trichloroethane	Annual average	400	300
2,4-D (ester)	Annual average	1	1
2,4-D (non-ester)	Annual average	40	40
2,4-Dichlorophenol	Annual average	20	20
2-Chlorophenol	Annual average	50	50
4-Chloro-3-methylphenol	Annual average	40	40
Arsenic (dissolved)	Annual average	50	25
Atrazine & Simazine	Annual average	2	2
Azinphos-methyl	Annual average	0.01	0.01
Bentazone	Annual average	500	500
Benzene	Annual average	30	30
Biphenyl	Annual average	25	25
Boron (dissolved)	Annual average	2000	7000
Chloronitrotoluenes	Annual average	10	10
Chromium (dissolved)	Annual average	Hardness related (see table 2b for details)	15
Copper (dissolved)	Annual average	Hardness related (see table 2b for details)	5
Cyfluthrin	95th percentile	0.001	0.001
Demeton	Annual average	0.5	0.5
Dichlorvos	Annual average	0.001	0.04
Dichlorvos	Maximum concentration	-	0.6
Dimethoate	Annual average	1	1
Endosulphan	Annual average	0.003	0.003
Fenitrothion	Annual average	0.01	0.01
Fluocuron	95 percentile	1	1
Ion (dissolved)	Annual average	100	1000
Lead (dissolved)	Annual average	Hardness related (see table 2b for details)	25
Linuron	Annual average	2	2
Malathion	Annual average	0.01	0.02

Revised to 7.2

Mecoprop	Annual average	20	20
Mevinphos	Maximum concentration	0.02	-
Naphthalene	Annual average	10	5
Nickel (dissolved)	Annual average	Hardness related (see table 2b for details)	30
Omethoate	Annual average	0.01	-
PCSDs	95th percentile	0.05	0.05
Permethrin	95th percentile	0.01	0.01
pH	95th percentile	6-9	6-8.5
Sulcofuron	95th percentile	25	25
Toluene	Annual average	50	40
Triazaphos	Annual average	0.005	0.005
Tributyltin	Maximum concentration	0.02	0.002
Trifluralin	Annual average	0.1	0.1
Triphenyltin	Maximum concentration	0.02	0.008
Vanadium (dissolved)	Annual average	Hardness related (see table 2b for details)	100
Xylene (m and p, o)	Annual average	30	30
Zinc (total)	Annual average	Hardness related (see table 2b for details)	40

 indicate investigate substances

Source: Environment Agency 2007c.

Table 2b: Environmental Quality Standards (EQS) for hardness related List 2 dangerous substances, EC Dangerous Substances Directive (76/464/EEC)

Table 2b: Environmental Quality Standards (EQS) for hardness related List 2 dangerous substances, EC Dangerous Substances Directive (76/464/EEC)

Substance	EQS type	EQS (ug/l) for Hardness bands (mg/l CaCO ₃)					
		0-50	>50-100	>100-150	>150-200	>200-250	>250
Freshwaters, suitable for all fishlife							
Copper (dissolved)	Annual average	1	6	10	10	10	25
Manganese (total)	95th percentile	1	40	40	40	40	40
Nickel (dissolved)	Annual average	50	100	150	150	200	200
Vanadium (dissolved)	Annual average	20	20	20	20	60	60
Freshwaters, suitable for Salmonid (game) fish							
Chromium (dissolved)	Annual average	5	10	20	20	50	50
Lead (dissolved)	Annual average	2	10	10	20	20	20
Zinc (total)	Annual average	5	50	75	75	75	75
Manganese (total)	95th percentile	200	300	300	300	300	300
Freshwaters, suitable for Cyprinid (coarse) fish							
Chromium (dissolved)	Annual average	150	175	200	200	250	250
Lead (dissolved)	Annual average	20	125	125	250	250	250
Zinc (total)	Annual average	75	175	250	250	250	500
Zinc (total)	95th percentile	300	700	1000	1000	1000	2000

Highlighted Fields indicate investigate substances