

CHAPTER 1

INTRODUCTION: METALS IN FLUVIAL SEDIMENTS

1.1. INTRODUCTION

Metals occur widely in the natural environment, and are observed in sedimentary rocks, soils, water, and organic matter (Davies, 1983b). Concentrations vary greatly according to the source and the environment in which the metals are found, and can range from trace levels to high concentrations. From a biological perspective, metals can be loosely divided into two groups; those that are beneficial to life, and those that can be detrimental to life (Hatch, 1977). The former group consists of elements such as chromium, copper, iron, and zinc, which play an essential role in the basic biological functions of plants and animals (Davies, 1980b). In sufficiently high concentrations, however, these elements can become extremely toxic to plant and animal life. The second group consists of elements such as cadmium, lead, mercury, and thallium, for which any beneficial biological functions have not been identified. These elements are toxic even at low concentrations, and are therefore likely to pose a threat to plant and animal life where they occur (Davies, 1980b).

These toxic metals have frequently been described as ‘heavy’ metals. However, the precise definition of this term is rather vague (Hodson, 2004). Davies (1980b) defines a heavy metal as a metal or metalloid with an atomic density of more than 6 g cm^{-3} . Other authors describe metallic elements with a density greater than 3.5 g cm^{-3} as ‘heavy’, while others place the boundary at greater than 4.5, 5 or even 7 g cm^{-3} (Passow *et al.*, 1961; Jarvis, 1983). Heavy metals have also been defined on the basis of their crustal abundance, atomic weight, atomic number, chemical reactivity and toxicity (Nieboer and Richardson, 1980; Alloway, 1995; Duffus, 2002). For the purposes of this study, the term ‘metals’ will be used alone to refer to elements such as cadmium, lead, and zinc, which can cause considerable environmental problems in sufficient concentrations.

Metals are released into the terrestrial, aquatic and atmospheric environments by a wide range of processes, such as the natural chemical and physical weathering of source rocks, volcanic eruptions, and anthropogenic processes such as mining and smelting (Nriagu, 1979). For most metals, the quantities released by anthropogenic activities far outweigh the contribution from natural sources (Nriagu, 1989). Terrestrial environments, particularly soils, have been identified as the main sink of metals released by both natural and anthropogenic processes (Nriagu, 1990), and the fluvial system is recognised as the most important agent in the transport and dispersal of metals through the terrestrial environment (Macklin, 1992).

Metal mining can dramatically increase the supply of metal-rich sediment to the fluvial environment, largely through the direct discharge of waste from water-based gravimetric separation techniques employed to remove metal ores from gangue materials, tailings dam failures and the erosion of spoil tips (Allan, 1988, 1995, 1997; Hudson-Edwards, 2003). Modern metalliferous mining is subject to a series of environmental quality controls in an attempt to limit the environmental impact of such activities. However, historic metal mining was not subject to any environmental legislation. During the eighteenth and nineteenth centuries, waste from metal mining operations was often discharged directly into the fluvial system. Inefficient processing techniques employed during this time meant that significant amounts of contaminated material were transported and stored within the fluvial system, causing widespread pollution (Macklin, 1992). The problem of environmental pollution due to mining activities was identified in the late nineteenth century. This led to the introduction of the Rivers Pollution Prevention Acts of 1876 and 1893 in an attempt to reduce pollution of the fluvial environment, although these were not wholly effective (Haworth, 1906).

The release of large quantities of potentially toxic sediment-associated metals from historic and contemporary mining activities has led to the severe contamination of a large number of river systems. This chapter presents a brief review of the behaviour of these metals in fluvial sediments. The transport and storage of metal-rich sediments will be discussed, and the potential threat that these deposits pose will be outlined. The geomorphological impacts of sediment-associated metal release as a result of mining will also be considered. Finally, the aims of this thesis will be discussed, and the structure of the thesis will be outlined.

1.2. METALS IN FLUVIAL SEDIMENTS: A REVIEW

1.2.1. Introduction

Sediments are extremely important in the transport and cycling of metals within the fluvial system (Salomons and Förstner, 1984; Horowitz, 1991). Metal concentrations in sediments are usually considerably higher than those observed in the dissolved phase, and, as such, riverine metal fluxes are dominated by fluvially transported sediments (Horowitz, 1991; Macklin, 1992). Indeed, it is estimated that between 30 and 98 % of the total metal load of a river can be transported in a sediment-associated form (Gibbs, 1973; Salomons and Förstner, 1984). These metals occur either in the form of fragments of ore material and gangue minerals, or sorbed onto the surface of other fluvially transported sediments (Förstner and Wittmann, 1979; Miller, 1997).

Sediment-associated metals are not static within the fluvial environment. Instead, they are influenced by a range of physical and chemical processes that control their behaviour, availability for transport and ultimately the concentrations in which they are found. The chemical and physical processes that influence the behaviour of sediment-associated metals will be discussed in the following section.

1.2.2. The behaviour of metals in fluvial sediments

The behaviour of metals in fluvial sediments is strongly influenced by a range of physical and chemical processes (Salomons, 1988). The two broad groups of processes do not operate independently; instead, they are strongly interrelated and the behaviour of metals within sediments is dependant on both groups of processes operating in combination with each other (Horowitz, 1991).

A number of physical characteristics, including particle size, surface area, specific gravity, surface charge, and bulk density, influence the behaviour of metals within sediment (Horowitz, 1991). Of these, the closely related parameters of grain size and surface area are considered to be the most important. It has long been recognised that many metals are more closely associated with fine-grained sediments than with coarser material (*e.g.* Gibbs, 1973; Ramamoorthy and Rust, 1978). Indeed, there is a strong positive correlation between decreasing grain size and increasing metal concentrations (Horowitz, 1991). Fine sediments have a much greater surface area than coarser particles of the same weight

(Jones and Bowser, 1978), and a positive correlation between increasing surface area and decreasing grain size has been recorded (Horowitz and Elrick, 1987). As a result, fine particles, especially clay minerals, organic matter and iron hydroxides, are able to adsorb large quantities of metals through cation exchange processes (Förstner and Wittmann, 1979; Salomons and Förstner, 1984). It has also been suggested that clays accumulate high concentrations of metals through mechanical processes alone, without the aid of chemical reactions (Jenne, 1976). This means that metal concentrations are usually greatest in the clay size fraction, while the lowest concentrations are usually observed in the quartz-dominated silt and fine sand fractions (Horowitz, 1991). However, coarser sediments may contain elevated metal concentrations due to the presence of heavy mineral particles (Förstner and Wittmann, 1979).

Grain size therefore plays an important role in determining metal concentrations in fluvial sediments. Consequently, it is of vital importance that this is taken into consideration in investigations of metal contamination in river systems. A variety of studies have focussed on material of less than 2 mm diameter (Hudson-Edwards *et al.*, 1996; Macklin *et al.*, 1997; Hudson-Edwards *et al.*, 1998; Hudson-Edwards *et al.*, 1999b; Zhao *et al.*, 1999). However, additional investigations have shown that metals are often most concentrated in material of less than 63 μm diameter (Macklin and Klimek, 1992; Liu *et al.*, 1995; Ciszewski, 2001). Analysis of material of this size is recommended in order to minimise grain size effects (Salomons and Förstner, 1984). Several studies, however, have indicated that all size fractions are important contributors of metals (Bradley, 1988; Leenaers, 1989; Macklin and Dowsett, 1989; Moore *et al.*, 1989).

A number of chemical factors also influence the accumulation and retention of metals in fluvial sediments. Five primary chemical processes have been identified: adsorption onto fine-grained sediment, precipitation, co-precipitation with iron and manganese oxides and carbonates, association with organic matter by adsorption or organometallic bonding, and incorporation in crystalline minerals (Gibbs, 1977; Ramamoorthy and Rust, 1978). Adsorption is defined as the sorption of metals from solution onto the surface of soil and sediment particles (Kabata-Pendias and Pendias, 2001). Elements such as Pb and Cu are strongly bound to sediment particles, while elements such as Ni, Cd and Zn are held less strongly (Basta and Tabatabai, 1992). Adsorption may be strongly influenced by the cation exchange capacity of the sediment; the higher the cation exchange capacity, the greater the amount of metal adsorption. Cation exchange capacity is governed chiefly by

surface area; the greater the surface area of a particle, the greater its capacity for transfer cations to and from solution through ion exchange processes (Horowitz, 1991). Cation exchange capacity is therefore dependent on factors such as grain size, and the amount of clay minerals, organic matter and iron and manganese oxides found within sediment (Förstner and Wittmann, 1979). Adsorption is strongly influenced by pH; the amount of adsorption of metals by particulates can increase by 100 % as pH increases by 1 – 2 critical units (Benjamin *et al.*, 1982). The oxidation-reduction potential of sediment also influences the amount of adsorption that can occur. In reducing conditions, when sediment has high water content, metals form insoluble sulphides. Conversely, in oxidising conditions, when water content is low, metals become more mobile. A change from reducing to oxidising conditions within a body of sediment can therefore lead to the release of metals into solution (Förstner, 1987). In addition, an increase of pH, or changes in oxidation-reduction potential or metal concentrations can lead to the direct precipitation of dissolved metals out of solution (Salomons and Förstner, 1984).

Iron and manganese oxides play an important role as ‘collectors’ of metals in aquatic sediments (*e.g.* Goldberg and Arrhenius, 1958; Duchart *et al.*, 1973; Horowitz and Elrick, 1987). These materials are excellent scavengers of metals from solution, and often form a coating on mineral grains and other fine particles (Förstner and Wittmann, 1979; Salomons and Förstner, 1984). Dissolved metals co-precipitate with the iron and manganese oxides, and therefore become concentrated on the surface of fluvial sediments (Horowitz, 1991). Organic molecules transported within the fluvial sediment load also act as a focus for the accumulation of metals (*e.g.* Swanson *et al.*, 1966; Gibbs, 1973). Metals are bound to organic molecules by a variety of processes, including adsorption, chemical bonding and physical trapping. The strength of the bond is dependent on the type of organic matter involved (Swanson *et al.*, 1966). Between 1 and 10 % of metals such as Cu, Pb, and Zn observed in fluvial sediments may be associated with organic material, highlighting its importance in riverine metal transport (Swanson *et al.*, 1966; Horowitz, 1991). The concentration of organic matter is closely related to grain size; total organic carbon and nitrogen display a strong positive relationship with decreasing grain size and decreasing surface area (Kuenen, 1965; Horowitz and Elrick, 1987). Finally, metals can become incorporated into crystalline minerals through the process of substitution, where an element within the crystal structure is replaced with another from solution outside it. However, this reaction is more common in solid solutions than in sediment-water

interactions, and may not play a major role within fluvial sediments under most conditions (Horowitz, 1991).

Metals may not be stable in the fluvial sediments, and may transfer to and from solution if chemical conditions are altered. The distribution of metals between solution and particulate-bound phases is influenced by chemical form, interactive processes such as precipitation, dissolution, sorption and desorption, and the concentration and composition of particulates (Förstner and Kersten, 1988). This section therefore demonstrates that metals in the fluvial system are controlled by the complex interaction of a range of physical and chemical processes, and that, despite the often short-term importance of solution, sediments are the ultimate sink of metals in the fluvial environment (Dossis and Warren, 1980). Factors that influence the transport and cycling of sediment-associated metals through the fluvial system will be discussed in the subsequent sections.

1.2.3. Metal transport in fluvial sediments

The previous section has demonstrated that sediments play an important role in the transport of metals through the fluvial system. Sediment-associated metals can be released into the fluvial system through the direct discharge of mine waste (Allan, 1988), or through the remobilisation of metal-rich material from spoil tips and the bed and banks of the river channel (*e.g.* Mann and Lintern, 1983; Leenaers, 1989; Macklin *et al.*, 1992; Merrington and Alloway, 1994). Once released, the behaviour of metals in the river system is governed by fluvial sediment transport processes, which themselves are controlled by factors such as discharge, stream power and the physical and chemical properties of the sediment (Salomons and Förstner, 1984).

Sediment-associated metals can be transported as part of the bed load of the river, or in suspension (Bradley, 1988). Bed load moves in near-continuous contact with the river bed, through processes such as saltation, rolling and basal sliding, while the suspended load is transported within the water column (Collinson, 1996). Sediments transported as bed load generally consist of sands and gravels, although finer sediment may also be transported in this way (Rust and Nanson, 1989). In contrast, the suspended load is generally dominated by clays, although silt and fine sand is frequently carried in suspension (Horowitz, 1995). These differences in grain size between each load mean that metals associated with bed load generally remain static during low flows, and are cycled

during periods of higher discharge (*e.g.* Bradley, 1988; Ciszewski, 2001). Metals in the suspended load are transported more continuously, although the total volume of metals transported in river sediments increases markedly during periods of high discharge (Bradley, 1984; Horowitz, 1995).

The downstream dispersal of metals in the fluvial system is likely to be controlled by several important factors, namely:

1. Hydraulic sorting according to differential particle density, size and shape (Lewin and Macklin, 1987; Langedal, 1997; Leigh, 1997).
2. Chemical dispersal through solution, precipitation or biological uptake (Lewin and Macklin, 1987; Leenaers, 1989; Evans and Davies, 1994).
3. Mixing with sediment from uncontaminated sources such as areas upstream of mining, unmineralised tributaries and pre-mining sediments exposed on channel banks (Lewin and Macklin, 1987; Marcus, 1987; Hudson-Edwards *et al.*, 1996; Langedal, 1997).
4. Loss to floodplain sediment storage (Lewin and Macklin, 1987; Rang and Schouten, 1989; Macklin *et al.*, 1992).
5. Abrasion of contaminated sediment grains (Macklin and Dowsett, 1989; Langedal, 1997).
6. Downstream changes in metalliferous mineralogy, and Fe and Mn content (Hudson-Edwards *et al.*, 1996; Hudson-Edwards, 2003).

As a result of the interaction of some or all of these parameters, metal concentrations in channel sediments (*e.g.* Lewin *et al.*, 1977; Wolfenden and Lewin, 1978; Axtmann and Luoma, 1991; Macklin, 1996; Marcus *et al.*, 2001) and overbank and floodplain deposits (*e.g.* Bradley and Cox, 1986; Leenaers, 1989; Macklin and Dowsett, 1989; Macklin and Klimek, 1992; Macklin *et al.*, 1997) have been observed to decline with distance downstream from the source of contamination. Of the factors described above, mixing with uncontaminated material, especially from tributaries, is thought to have the greatest influence in determining the observed decline in metal concentrations with downstream distance (Marcus, 1987; Miller, 1997; Hudson-Edwards *et al.*, 1998; Hudson-Edwards *et al.*, 2001; Marcus *et al.*, 2001), although this may not always be the case (Axtmann and Luoma, 1991). For example, hydraulic sorting may be more important when metals are associated with denser sediment (Macklin and Dowsett, 1989).

The relationship between metal concentrations in fluvial sediments and distance from the source of contamination has been approximated using regression analysis (Wolfenden and Lewin, 1978; Lewin and Macklin, 1987; Leenaers *et al.*, 1988; Leenaers, 1989) and simple mixing models (Marcus, 1987). However, the simple relationship is somewhat complicated by physical processes such as the reworking of floodplain material (Wolfenden and Lewin, 1978; Leenaers, 1989) and chemical processes such as differential mobility between elements (Leenaers *et al.*, 1988; Axtmann and Luoma, 1991). Metal concentrations have also been shown to vary in an inverse relationship with stream power, with lower concentrations observed in reaches with higher unit stream power (Graf, 1990). Increased shear stresses and greater erosion from the channel bed and banks in high power reaches may also enhance this pattern (Graf, 1990). Furthermore, a complex, wave-like decay pattern has also been described (Macklin, 1996). This pattern is thought to be a result of alternating steep, narrow transport reaches and wider, shallower sedimentation zones where metals are stored (Macklin and Lewin, 1989; Macklin, 1996). Metals are rapidly cycled through the transport reaches, and accumulate in large quantities in the low-gradient sedimentation zones (Macklin and Smith, 1990). Metal concentrations in the trunk channel are generally greatest in the sedimentation zones, reflecting the remobilisation of metals in these reaches (Macklin and Dowsett, 1989; Macklin, 1996). The relationship between metal concentrations and valley width may be sufficiently strong to force concentrations to increase with distance from the metal source, as a steep, narrow channel opens out into a shallow, wide reach where sediment storage is favoured (Hren *et al.*, 2001). It has also been suggested that the movement of sediment in the form of a large bed wave or 'slug' creates a wave-like dispersal pattern (*cf.* Nicholas *et al.*, 1995). It is likely that this process leads to the superimposition of peaks and troughs of metal concentrations on the overall downstream trends, as bodies of metal-rich bed sediments move down the river channel (Lewin and Macklin, 1987; Merefield, 1987).

Although a number of investigations have demonstrated that absolute metal concentrations tend to decrease with distance downstream from the source of contaminated sediment, several studies have demonstrated that the chemical reactivity of these metals actually increases with distance downstream (Leenaers, 1989; Macklin and Dowsett, 1989; Hudson-Edwards *et al.*, 1996). This is likely to be attributable to the action of chemical processes such as sorption and desorption with iron and manganese oxides and organic matter (Macklin and Dowsett, 1989), and mineralogical processes such as the release of metals from the residual phase to more mobile fractions (Leenaers, 1989). This suggests

that, while physical factors are most important in the initial downstream decay of metals, chemical processes become more important further downstream. Indeed, Hudson-Edwards *et al.* (1996) have highlighted the importance of the oxidation of unstable primary minerals into secondary iron and manganese hydroxides with a lower metal content as a major cause of the observed decrease in metal concentrations in the lower reaches of formerly mined rivers.

1.2.4. Metal storage in fluvial sediments

The previous section has demonstrated that sediment-associated metals are transported alongside the natural load of the river, and are subject to the same dispersal processes. It therefore follows that metal-rich sediment is subject to the same storage processes as the remainder of the fluvial sediment load. A significant proportion of metals associated with fluvially transported sediments become incorporated into the floodplain through overbank deposition and lateral accretion processes (*e.g.* Rang and Schouten, 1989; Macklin *et al.*, 1992; Walling and Owens, 2002, 2003; Walling *et al.*, 2003a). Metal dispersal patterns within floodplain sediments are therefore dictated by the predominant style of sedimentation that operates within an individual reach.

In historically stable river channels, vertical accretion is the dominant process of floodplain formation (Lewin, 1983), with metal concentrations reflecting the history of metal production in the vertical sediment record (*e.g.* Knox, 1987; Ottesen *et al.*, 1989; Macklin and Klimek, 1992; Macklin *et al.*, 1994; Swennen *et al.*, 1994; De Vos *et al.*, 1996; Swennen and Van der Sluys, 1998, 2002). This relationship is attributable to the addition of metals as a thin veneer across the floodplain surface, and therefore the age of the overbank deposit increases with increasing depth (Miller, 1997). This leads to considerable variation in metal concentrations with depth, and allows the direct comparison between known phases of fluvial activity and peaks in metal concentrations in floodplain sediments (*e.g.* Macklin, 1985; Macklin *et al.*, 1994; Swennen *et al.*, 1994). However, local variations in metal deposition across the floodplain surface complicate this simple relationship, so that it may only be possible to distinguish between mining-age and pre-mining sediments (Graf *et al.*, 1991). Such variations have been attributed to localised flooding as a function of irregular bank heights, leading to overbank deposition in discrete areas on the floodplain surface (Bradley and Cox, 1986; Swennen *et al.*, 1994). Variations in metal concentrations in vertically accreted floodplain sediments have also been

attributed to spatial differences in precipitation intensity. Variable precipitation patterns across a catchment can lead to variations in sediment source area (Graf *et al.*, 1991) and changes in the degree of mixing with uncontaminated sediments (Marcus, 1987). Differences in metal content in ores from different mines may accentuate these variations (Bradley and Cox, 1986).

Significant variation in the lateral distribution of metals in historically stable reaches has also been reported. In many mined river systems, metal concentrations are greatest in sediments adjacent to the channel (Alloway and Davies, 1971; Macklin, 1988; Marron, 1989; Graf *et al.*, 1991; Marron, 1992; Macklin, 1996; Miller *et al.*, 1999; Zhao *et al.*, 1999; Martin, 2004). This trend has been attributed to the increased incidence of flooding in near-channel zones and the receipt of more highly contaminated sediment during small floods (*cf.* Marron, 1989; Brewer and Taylor, 1997; Middelkoop, 2002). Metal concentrations in suspended sediment decrease with increasing discharge due to dilution effects from clean sediment (Bradley, 1988; Leenaers, 1989; Marron, 1989). Higher floodplain surfaces are only inundated during periods of high discharge, which suggests that they only receive diluted sediments (Alloway and Davies, 1971; Rowan *et al.*, 1995). Conversely, lower floodplain units are inundated more frequently with less diluted sediment, causing them to receive greater volumes of contaminant metals (Leenaers, 1989; Graf *et al.*, 1991; Lecce and Pavlowsky, 2001; Martin, 2004). In addition, in situations where metals are closely associated with coarse sediment, they are generally deposited closer to the channel as a result of gravitational effects (Macklin, 1996; Zhao *et al.*, 1999). Conversely, in situations where metals are most concentrated in silt and clay-sized sediment, contaminants are generally dispersed evenly across the floodplain surface as a thin veneer (Bradley and Cox, 1990). In such conditions, areas subject to the preferential deposition of fines, such as palaeochannels, may become foci of metal accumulation (Lewin *et al.*, 1977; Marron, 1992; Brewer and Taylor, 1997). This suggests that grain size variations play an extremely important role in determining the lateral dispersal patterns of metals in overbank sediments (*cf.* Macklin, 1996). However, grain size relationships have not been observed in all river systems (Marron, 1989; Swennen *et al.*, 1994); in such cases, it is likely that floodplain morphology combines with flood frequency and magnitude to determine metal dispersal patterns.

In historically unstable channels, floodplain development is generally dominated by lateral accretion processes (Lewin, 1983). Progressive reworking of the floodplain in such

reaches results in abrupt changes in metal concentrations across the valley floor (*e.g.* Wolfenden and Lewin, 1977; Lewin *et al.*, 1983; Macklin and Lewin, 1989). Furthermore, metal concentrations are defined by the intensity of mining operations at the time of deposition, resulting in further variability between units of different ages (*e.g.* Davies and Lewin, 1974; Lewin *et al.*, 1983; Macklin and Lewin, 1989). A direct relationship between floodplain age and metal concentrations does not always exist, however, since changes in flood frequency and magnitude in relation to mining activities can be more dominant in dictating patterns of metal dispersal across the floodplain (Taylor, 1996; Brewer and Taylor, 1997). Floodplain surfaces deposited during the peak of mining activities may not be the most highly contaminated if the incidence of flood events was low at the time of their formation.

As a result of the storage processes outlined above, soils that develop on a river floodplain can become highly enriched with metals. Many of these metals have long residence times within floodplain soils (Salomons and Förstner, 1984). The duration over which metals remain stored within the floodplain is dependent on a range of factors, such as the rates of physical, chemical and biological remobilisation, and the geomorphology of the reach in which they are stored (Förstner and Kersten, 1988; Marcus *et al.*, 2001; Hudson-Edwards, 2003). In stable reaches, metals can remain stored for hundreds to thousands of years (*e.g.* James, 1989; Macklin *et al.*, 1992; Miller *et al.*, 1996). In temperate soils in stable reaches, metals are gradually depleted by leaching and plant uptake. Cd can remain for up to 380 years, Hg for between 500 and 1000 years, and Ag, Cu, Ni, Pb and Zn for between 1000 and 3000 years (Salomons and Förstner, 1984; Kabata-Pendias and Pendias, 2001). In unstable reaches, however, residence times may be considerably shorter, with the cycling of metals accelerated by increased erosion rates (James, 1989; Macklin *et al.*, 1992).

1.2.5. Remobilisation of metals

The previous section has demonstrated that, once deposited by a range of fluvial processes, metals can remain stored in the floodplain for a long period of time. The depletion of metals in floodplain storage is linked to natural leaching and biological uptake, and, crucially, the chemical and physical remobilisation of such elements from the floodplain (Chester, 1988; Hudson-Edwards, 2003). The importance of the latter is considerably enhanced during periods of high discharge, when greater amounts of material

are eroded from the bed and banks of the river channel (Bradley and Lewin, 1982; Bradley, 1984, 1988; Leenaers, 1989; Marcus *et al.*, 2001; Middelkoop *et al.*, 2002). Furthermore, spoil tips are also likely to be ‘activated’ as sources of metals during high flow events, through erosion by surface runoff and direct fluvial erosion (Bradley and Lewin, 1982; Leenaers, 1989). Metal-rich floodplain sediments are therefore an important diffuse source of metals to the fluvial system (Marron, 1989; Macklin, 1992; Macklin and Klimek, 1992). Indeed, two thirds of the Pb entering the channel of the River Geul, the Netherlands, are thought to have been derived from the banks of the river (Leenaers, 1989).

The remobilisation of metal-rich sediments from floodplain stores has been identified as a potentially serious environmental problem (*e.g.* Axtmann and Luoma, 1991; Stigliani, 1991; Stigliani *et al.*, 1991; Konsten *et al.*, 1993). The release of large volumes of sediment-bound contaminants can severely damage the aquatic ecosystem and, if deposited overbank further downstream, cause problems for floodplain-surface activities such as agriculture. Such releases of metal-rich sediment can occur during extreme events such as large floods (*e.g.* Middelkoop, 2000; Dennis *et al.*, 2003) and tailings dam failures (*e.g.* Hudson-Edwards *et al.*, 2001; Macklin *et al.*, 2003), or, perhaps more commonly, as a result of longer-term geomorphological responses to changes in discharge or sediment load (Graf, 1985; Macklin, 1996). These changes may be attributable to variations in general climatic conditions that accelerate floodplain erosion (Stigliani *et al.*, 1991), or anthropogenic changes such as the construction of flood protection schemes (Macklin and Klimek, 1992).

1.2.6. The geomorphological impacts of metal mining

The previous sections have demonstrated that metal mining has a significant impact on the geochemistry of a river catchment, releasing large quantities of metal-rich material that is transported within the channel and stored within floodplain sediments. The release of mining-related sediment can also have a pronounced effect on the geomorphology of the river catchment, with dramatically enhanced sediment supply leading to major geomorphological adjustments (Lewin and Macklin, 1987). The previous sections have outlined metal dispersal patterns under conditions of ‘passive dispersal’, whereby metal-rich sediment from mining activities is transported and deposited alongside the ‘natural’ load of the river with minimal geomorphological impact (Lewin and Macklin, 1987). This

is not always the case, however; metal mining can increase sediment supply to such a degree that the transport capacity of the river is exceeded, causing considerable morphological changes. This response has been defined as ‘active transformation’ by Lewin and Macklin (1987).

A range of geomorphological adjustments have been observed in actively transformed river systems. In many river catchments, the primary response has been the marked accretion of channel and floodplain sediments (*e.g.* Gilbert, 1917; Macklin, 1985; Bradley and Cox, 1986, 1987; James, 1989; Knighton, 1989; Macklin and Lewin, 1989; James, 1991; Passmore and Macklin, 1994; Rowan *et al.*, 1995; Rowan and Franks, 2002). Aggradation in mined tributaries can also lead to the formation of tailings fans where they meet the main channel, diverting the river and causing a decrease in its sinuosity (James, 2004). In addition to floodplain aggradation, a mining-related increase in sediment supply can also lead to the development of a wide, shallow channel and the initiation of braiding, particularly in reaches with a wide valley floor and easily erodible alluvial deposits (*e.g.* Lewin *et al.*, 1983; Knighton, 1989, 1991; Rowan *et al.*, 1995). In other catchments, mining has led to a period of pronounced incision, as a result of vegetation removal and catchment destabilisation (Graf, 1979; Rang and Schouten, 1989).

Once mining waste is no longer actively introduced, an actively transformed river system begins to readjust to a lower sediment supply. Braided channels generally revert to a single thread pattern (Knighton, 1989, 1991; Rowan *et al.*, 1995; Rowan and Franks, 2002), and rivers gradually incise into their aggraded floodplain (Gilbert, 1917; Lewin *et al.*, 1983; Lewin and Macklin, 1987; James, 1989; Macklin and Lewin, 1989; James, 1991; Sear and Carver, 1996). This may lead to the formation of valley-spur cut-offs in catchments where considerable aggradation and channel diversion occurred (James, 2004). The response to, and recovery from, mining-related sediment input has been described as a symmetrical wave, with sediment transport and channel bed elevation peaking after the influx of mining-related sediment before returning to their pre-mining levels relatively rapidly (Gilbert, 1917; Graves and Eliab, 1977). This may not always be the case, however, since changes in bed elevation cannot be directly related to sediment load (James, 1989). Instead, it is likely that response occurs as an asymmetric wave, with floodplain and terrace units formed during the initial aggradation phase continuing to supply large amounts of sediment long after the cessation of mining (James, 1999). Furthermore, the recovery process is likely to be episodic, strongly reflecting the nature of

sediment transport observed in many river systems (James, 1989, 1999). The postulated symmetrical wave of sediment transport (Gilbert, 1917) is further complicated by variations in the intensity of mining activities and the introduction of mining-related sediment from multiple and/or diffuse sources (Knighton, 1991; Bartley and Rutherford, 2001).

The pronounced geomorphological alterations observed within actively transformed river systems strongly influence the dispersal of metals within the catchment. In reaches that have experienced episodes of aggradation, metal-rich sediments frequently become stored along the channel margins, primarily in the form of vertically accreted overbank deposits (*e.g.* Marron, 1989, 1992). Metal dispersal is therefore likely to be subject to similar controls as those observed in historically stable river channels, albeit on a larger scale. Where incision has occurred after the cessation of mining, these deposits become exposed in terrace fronts and the banks of the channel (Macklin *et al.*, 1992; Marron, 1992). In reaches where mining activities caused the initiation of braiding, floodplain formation is likely to have been dominated by lateral accretion processes (Collinson, 1996). Metal dispersal is therefore likely to be subject to similar controls as those observed in historically unstable river channels (Miller, 1997).

Although the fundamental controls of metal dispersal in actively transformed river catchments are the same as those that operate under conditions of passive dispersal, the scale of the geomorphological changes that occur in the former can lead to considerable variations in metal concentration patterns. This is often a result of the large volumes of mining-age sediment stored adjacent to the channel, which becomes a source of metals when the channel begins to readjust after the cessation of mining (*e.g.* Leenaers, 1989; Macklin, 1992). The erosion of channel bank material and mine spoil may lead to localised increases in metal concentrations downstream of the original sources of mine waste, and similar decreases where uncontaminated deposits are eroded (*e.g.* Miller *et al.*, 1996; Miller *et al.*, 1999). Further variations from expected patterns may also be attributable to the processes of floodplain development in actively transformed rivers, which may include metal-rich gravel splays and channel lag gravels in addition to vertically and laterally accreted deposits (Miller, 1997).

1.2.7. Summary: Metals in fluvial sediments

This section demonstrates that the behaviour of sediment-associated metals in fluvial system is complex and highly variable. Once released as a by-product of historical or contemporary mining activities, sediment-associated metals are subject to the same transport processes as the ‘normal’ load of the river. Metals are transported downstream as part of the suspended and bed loads, during which they are subjected to a range of chemical and physical processes such as hydraulic sorting, precipitation, loss to solution, physical dilution and loss to floodplain storage. The interaction of these processes generally leads to a pronounced decay in metal concentrations with distance from the source of contamination, although this may be somewhat complicated by the physical characteristics of the river channel and valley floor and the remobilisation of metal-rich sediment from diffuse sources. Metals can become incorporated into the floodplain through both vertical and lateral accretion processes, leading to complex patterns of metal dispersal in floodplain sediments. Once in the floodplain, metals can remain stored for many hundreds of years. Floodplain storage is not permanent, however. Metals are slowly depleted by leaching and biological uptake, and more rapidly by physical and chemical remobilisation. In addition to having a pronounced effect on metal concentrations in fluvial sediments, the release of large volumes of material from mining activities can also have a dramatic influence on the fluvial geomorphology of the catchment. Excess sediment supply can cause the marked accretion of channel and floodplain deposits, and can lead to the initiation of braiding. These changes may be reversed after the cessation of mining, although this process is extremely slow.

1.3. THESIS BACKGROUND AND AIMS

The previous section has demonstrated that fluvial sediments play an important role in the transport, storage, and cycling of metals released from mining operations. This thesis aims to examine the impact of the processes described above on metal dispersal in the River Swale catchment, North Yorkshire, U.K. The River Swale catchment has a long history of metal mining, with detailed records dating back to before the start of the eighteenth century (Dunham and Wilson, 1985). These activities have had a major and long-lasting impact on fluvial geomorphology and environmental quality within the catchment. A number of previous studies in the Swale have reconstructed patterns of

contamination in floodplain (Macklin *et al.*, 1994; Taylor and Macklin, 1997; Carter, 1998; Sedgwick, 1998; Sparks, 1998; Hudson-Edwards *et al.*, 1999b; Sedgwick, 2000) and channel sediments (Gamesby, 1997; Grove and Sedgwick, 1998; Sedgwick, 2000; Owens *et al.*, 2001; Walling *et al.*, 2003a), demonstrating that severe contamination can be observed in a wide range of locations and environments. Although these investigations have provided a large body of useful data, none of them has successfully produced a fully representative and high-resolution characterisation of contaminated sediment transport and storage in the Swale catchment.

This thesis aims to bring together data from the existing literature with new data collected for this investigation to identify current and long-term patterns of metal-rich sediment dispersal, transport and storage in the River Swale catchment. This investigation has four principal objectives:

1. To identify patterns of metal dispersal in formerly mined tributaries, floodplain sediments, and contemporary flood sediments, and to examine the role of geomorphology in controlling these patterns.
2. To evaluate the relative importance of tributary and floodplain sediments as sources of metals to contemporary flood sediments.
3. To consider the likely environmental impact of metal mining in the Swale catchment.
4. To assess the long-term significance of metal storage and cycling in the Swale catchment, and examine the likely future implications of the remobilisation of metal-rich sediment from tributaries and floodplains.

In order to achieve these research objectives, a detailed geochemical survey has been undertaken. In addition to identifying metal dispersal patterns in the Swale catchment, the results of this survey have also been used in the construction of a detailed contaminant budget for the Swale catchment.

This thesis is divided into nine chapters. Following this introduction, the study area is discussed in detail in Chapter 2, and the field sampling and geochemical techniques employed in this investigation are outlined in Chapter 3. The impacts of metal mining on metal dispersal in tributary sediments, floodplain sediments and contemporary flood sediments are discussed in Chapters 4, 5, and 6, respectively. A contaminant budget for

the Swale catchment is presented in Chapter 7, and the likely environmental impact of metal contamination in the catchment is discussed in Chapter 8. Finally, conclusions from the previous results chapters will be drawn together in Chapter 9, along with directions for future research.