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Assessment of Metal Mining-Contaminated River Sediments in England and Wales

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Executive summary

The long history of metal mining in England and Wales has polluted sediments in rivers, estuaries and lakes, as well as floodplain soils. This study reviewed literature on the sources, dispersal controls and storage of metal contaminants in mining-affected river systems. We found numerous significant breaches of draft Environment Agency sediment quality guidelines (predicted effect levels or PEL) for cadmium, lead, copper, zinc and arsenic. This indicates adverse biological effects are likely to be occurring, with damage to ecosystem health, and implications for delivering the Water Framework Directive. The most affected rivers are those draining abandoned metal mining areas including the Tyne, Wear (Northumbria River Basin District or RBD), Swale, Ouse (Humber RBD), Rheidol, Ystwyth, Conwy, Afon Goch Dulas (Western Wales RBD), Clywedog (Dee RBD), Wye, Yeo, Axe (Severn RBD), Fal, Fowey, Tamar (South West RBD), Newlands Beck (North West RBD) and Glenridding Beck (Solway-Tweed RBD).

Although metal discharges were greater during the peak period of active mining in the nineteenth century, significant inputs of dissolved and particulate metals still occur. Past discharges have left a substantial reservoir of highly contaminated sediments in lowland rivers many kilometres downstream of the mines, and these sediments are likely to be causing ecological damage. Re-suspension of these sediments during floods has the potential to cause additional harm to aquatic life, and to contaminate floodplain soils used for agriculture. In this study, metal concentrations in floodplain soils affected by mining activities were compared with government guidelines for grazing livestock on former metal mines. Observed concentrations significantly exceeded these guidelines in many catchments, particularly for cadmium, lead and zinc. Climate change is expected to increase the frequency and magnitude of floods, leading to increased re-suspension of sediments containing high metal concentrations and, therefore encouraging the transfer of contaminated sediments from river channels to floodplain soils which are often used for agriculture.

Clear guidelines on the sediment metal concentrations that represent an unacceptable risk to ecosystem health are not available in England and Wales. This report recommends how the Environment Agency could reduce uncertainty over the risk to good ecological status posed by sediments (and soils) contaminated by abandoned metal mines. Where these risks are found to be unacceptable, we propose a tiered method to carry out catchment-scale risk assessments so that management and remediation strategies can be set up where necessary. Our recommendations are to:

1. Finalise sediment quality guidelines (such as TEL/PEL) that can be used to assess harm to ecosystem health (and hence ecological status).

2. Develop guideline metal concentrations in floodplain soils that represent an unacceptable risk for livestock or other agricultural uses.

3. Investigate the impact of short-lived flood events on the release of metals from sediments into the water column, and consequent effects on aquatic life.

4. Review all Environment Agency sediment quality data (and ideally other sources) and compare with guidelines (such as PEL values). This should initially be restricted to catchments that have been identified by the SC030136/14 project (Environment Agency, 2008) as being impacted by abandoned metal mines.

5. Where this review identifies that ecosystem health is threatened by contaminated sediments from metal mines, apply the tiered risk assessment method in this report.

6. Carry out monitoring of contaminated sediments in affected catchments.
7. Develop risk management strategies including remediation measures, where necessary, and following cost-benefit assessments.

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1. Introduction

Many river basins in England and Wales have been significantly contaminated with metals released from past mining operations. The Water Framework Directive (WFD) River Basin Characterisation exercise in 2005 estimated that 453 surface water bodies in seven of the eleven River Basin Districts were at risk of pollution by abandoned mines (including coal mines). This estimate is being refined by an ongoing project to identify and prioritise abandoned non-coal mines (Jarvis *et al.,* 2008; Environment Agency, 2008: SC030136/14).

The peak period of metal mining was the mid to late nineteenth century, although pollution continues to be discharged from many sites. In such catchments, as much as 90 per cent of the metals are associated with sediment rather than in aqueous forms, and metal contaminants are primarily mobilised and transported downstream, and deposited, by river processes. This has created a legacy of highly contaminated sediments, often a considerable distance (tens of kilometres) downstream from the mines themselves. There is a concern that these sediments may be causing damage to aquatic ecosystems (such as benthic organisms, fish, plants) in rivers. In addition, they may pose a risk to agricultural and other uses of floodplains as a result of the mobilisation of contaminated sediments during floods, which cause the heavy metal-laden sediments to be deposited on the floodplain.

The purpose of this report is to use data from selected catchments to test the potential environmental impact of these contaminated sediments and establish if a wider, more comprehensive, investigation is needed for all rivers impacted by abandoned mines.

The target audience is policy makers, river basin district managers and scientists responsible for dealing with the threats posed to ecosystem health in rivers, particularly in the light of the WFD. The report recommends ways that the Environment Agency could further investigate the scale of this problem in England and Wales.

The report does not attempt to define acceptable contaminant concentrations to protect the health of ecosystems, humans or animals which live in or on sediments and soils contaminated by metals. Therefore, whilst the report highlights the hazard associated with metal-contaminated sediments and soils, it is not able to evaluate the consequent risk. In addition, before any large-scale remediation could be implemented, an assessment of the costs and benefits of such work would need to be carried out. The nature of such a cost-benefit analysis is beyond the scope of this report.

The first part of this report describes the sources, dispersal controls and storage of metal contaminants in mining-affected river systems in England and Wales. The second part describes a simple method to assess contaminated sediments and floodplain soils in English and Welsh river systems affected by contamination from abandoned metal mines. Potentially affected water bodies are being identified and prioritised through a separate project (SC030136/14) funded by the Environment Agency, Department for Environment, Food and Rural Affairs (Defra) and the Welsh Assembly Government (WAG).

2. Metal mining-related contamination of river systems in England and Wales

2.1 Introduction

England and Wales have a long history of metal mining dating back over 4,000 years to the Bronze Age (see Pattrick and Polya, 1993; Ixer and Budd, 1998). Hundreds of thousands of tonnes of lead, zinc, and copper ore have been extracted since this time from several major mining areas (Figure 2.1; Table 2.1); many other metals and metalloids including iron, tin, arsenic and silver have also been mined. The last major mine closed in the late twentieth century, and currently there are no operating metal mines in either England or Wales. Early mining methods were primitive, involving pick and shovel. Separation of metal sulphide ore minerals was carried out by crushing and gravity sorting in nearby streams, and in many areas tailings and other solid and liquid mining effluent were disposed of directly into the nearest river channel. In some areas (especially the Northern Pennines and Yorkshire Dales), a hydraulic form of mining known as 'hushing' was carried out by constructing dams upslope of mineral veins, then opening sluices to release water that eroded overburden and exposed metal ores for easy excavation. The resulting torrent exposed underlying bedrock and mineral veins, which were worked using simple quarrying techniques. Hushing was repeated periodically to remove debris from workings. All of these methods involved water, and led to the transfer of significant quantities of metal-rich, fine-grained sediment to river systems. English and Welsh river catchments most affected by mining-related metal contamination are listed in Table 2.2.

Table 2.1: Examples of total metal concentrate output (tonnes) from selected mining areas in England and Wales (from Manning, 1959, Schnellman and Scott, 1970, Lewin and Macklin, 1987 and Jenkins *et al.*, 2000).

Ore field	Lead (Pb)	Zinc (Zn)	Copper (Cu)
Northern Pennines-Yorkshire Dales	4,064,000	271,000	
Lake District	230,000[1]	34,000	
Derbyshire	689,000[2]	92,000[2]	60,000[3]
West Shropshire	240,000	21,000	
Mynydd Parys			130,000
Central Wales	487,000	153,000	
Llanrwst-Harlech	48,000	33,000	
Halkyn-Minera	1,900,000	295,000	
Mendip	203,000		
Devon-Cornwall	327,000	90,000	
Isle of Man	272,000	260,000	

[1] Ninety per cent from Greenside mine.
[2] Seventy per cent of Pb and almost all Zn from Mill Close mine.
[3] Ecton Hill mine.

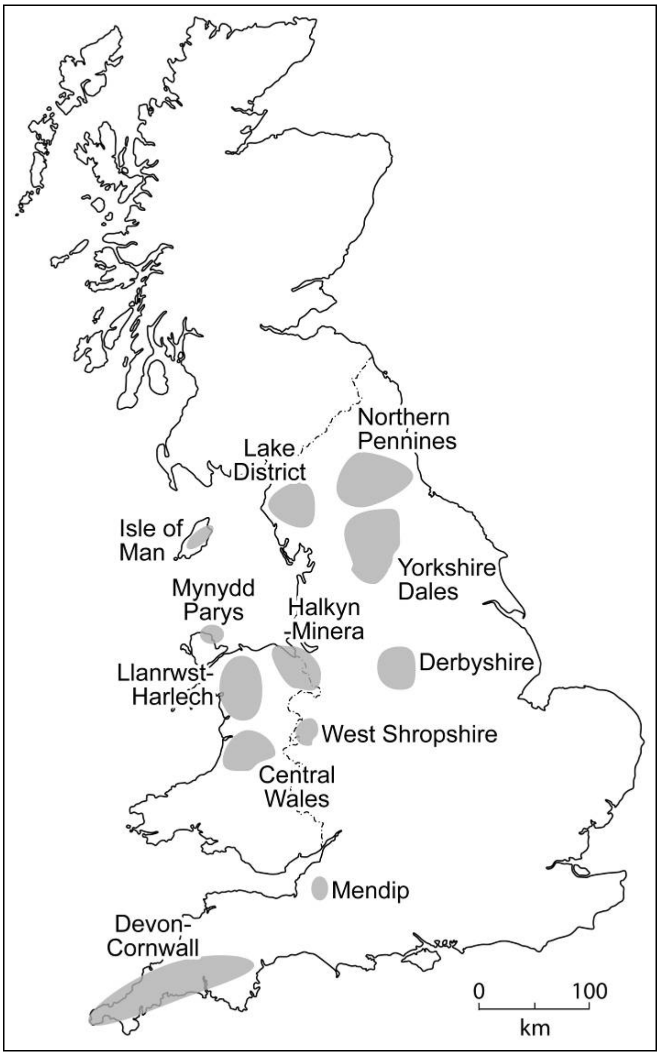

Figure 2.1: Metal mining areas of England and Wales (after Dunham *et al*., 1978, and Lewin and Macklin, 1987).

Table 2.2: River basins most affected by metal mining in England and Wales (main metals of concern are cadmium, lead, zinc and copper).

Water Framework Directive River Basin District	Catchment	Ore field
Dee	Clywedog	Halkyn-Minera
Humber	Swale, Wharfe, Nidd, Ure	Yorkshire Dales
	Ecclesbourne, Hamps, Manifold, Derwent	Southern Pennines (Derbyshire)
Northumbria	South Tyne, Wear, Tees	Northern Pennines
North West	Newland's Beck, Coledale Beck	Lake District
Severn	Rea Brook	West Shropshire
	upper Severn	Central Wales
	Yeo, Axe	Mendip
Solway Tweed	Glenridding Beck	Lake District
South West	Camel, Erme, Fal, Fowey, Gannel, Tamar	Devon-Cornwall
Western Wales	Afon Goch Twymyn, Rheidol, Ystwyth	Mynydd Parys Central Wales

2.2 Environmental impact of historical metal mining on English and Welsh river systems

2.2.1. Sediment quality

A significant, long-term impact of metal mining on river systems in England and Wales is the contamination of fine-grained (under two mm) suspended, channel and floodplain sediment with metals, principally cadmium, copper, lead and zinc. In Devon and Cornwall, tin and the metalloid element arsenic are also recognised contaminants. Water quality has also been significantly affected in rivers draining abandoned metal mines (see Section 2.2.3). Iron-rich discharges from abandoned coal mines have polluted many rivers and deposited iron oxides (ochre) which blanket the river bed and damage aquatic life; the impact of these ferruginous discharges will not be considered further in this report as they are primarily associated with coal mines.

Table 2.3 and Appendix 1 provide selected data on sediment metal concentrations in river systems in England and Wales affected by historical metal mining and show that sediment-borne metal concentrations exceed background concentrations and guideline limits by up to several orders of magnitude in many cases. The worst affected rivers in terms of sediment quality are the South Tyne (Macklin and Lewin, 1989) and its tributaries (see Nent: Macklin, 1986; Allen: Aspinall and Macklin, 1985; upper Derwent: Harding and Whitton, 1978), the upper Tees (Hudson-Edwards *et al*., 1997), the upper Swale (Dennis *et al*., 2003; Brewer *et al*., 2005; Dennis, 2005) and the Ystwyth (Lewin *et al*., 1983). Estuaries such as the Tamar and Humber also show significantly elevated metal concentrations relative to pre-industrial levels from mining in upstream rivers (see Table 2.3: Pirrie *et al*., 2002; Rawlins *et al*., 2003; Cave *et al*., 2005). These, and many of the other rivers in Table 2.3 (and Appendix 1), have metal concentrations that exceed those in river systems affected by mining activity elsewhere in the world, particularly for lead and zinc. An interesting comparison is with the Guadiamar catchment in South West Spain which was affected by the 1998 Aznalcóllar tailings dam spill and partially remediated afterwards (Macklin *et al*., 1999; Hudson-Edwards *et al*., 2003; Turner *et al*., 2008). Sediment concentrations in the Guadiamar prior to remediation were similar to many mining-impacted British rivers, yet unlike the Guadiamar, no British rivers have been remediated to improve poor sediment quality caused by metal mines.

Although mining has affected river and overbank (including floodplain soils) sediment quality in England and Wales since at least late Roman times (see Hudson-Edwards *et al*., 1999a, b; Pirrie *et al*., 2002), the peak period of metal mining occurred in the mid and late nineteenth century (Figure 2.2). Highest metal concentrations in overbank sediment and floodplain soils typically occur at a depth corresponding to deposition in the mid-nineteenth century during the peak period of mining. A number of studies (see Macklin and Dowsett, 1989; Dennis *et al*., 2003) have shown that this highly contaminated material can be remobilised and dispersed downstream in major floods. The largely uncontrolled discharge of particulate mining waste during active mine operations caused accelerated channel and floodplain sedimentation, which has resulted in complete transformation of some rivers, with river bed aggradation and development of braided channel patterns (Figure 2.3); this has been termed 'active transformation' by Lewin and Macklin (1987). The phytotoxic effects of contaminant metals on riparian vegetation were among the most important factors in creating bank instability and the slow recovery (still ongoing) of many mining-affected river systems (Macklin and Lewin, 1989; Macklin and Smith, 1990; O'Grady, 1981).

Table 2.3: Selected metal concentrations in sediment and floodplain soils affected by metal mines. Range and (mean).

Figures in **bold** exceed the predicted effect level (PEL) in channel sediments or the livestock grazing trigger concentration in overbank sediments or floodplain soils; 'nr' = 'not recorded'..

River system	As mg/kg	Cd mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg
Channel sediments					
River Swale at Reeth (Yorkshire Ouse catchment), fine-grained channel sediment (Macklin *et al*., 1994; Grove and Sedgwick, 1998).		0 - **22**	nr	22 - **4,818**	26 - **12,203**
River Swale (Yorkshire Ouse catchment), 2000 flood, < 63 µm channel edge sediments (Dennis *et al*., 2003).		**0.6 - 29.5**		49 – **20,310**	55 – **6,500**
Upper River Wear, < 150 µm channel sediment (Lord and Morgan, 2003).	<10 - **65**	nr	<10 - **340**	20 - **15,000**	40 - **1,500**
River Conwy, active channel sediment, < 63 µm (Elderfield *et al*., 1979).				85 - **10,000**	**1,000 - 10,000**
Humber Estuary sediments (Cave *et al*., 2005).	**44**	nr	55	**129**	**316**
River Tamar, channel sediments (Rawlins *et al*., 2003)	4.4 - **11,000 (73.1)**	0.25 - **22.1** (1.1)	11.4 - **8,000** (85.4)	13.2 - **450** (42.5)	48 - **1,901** (194)
Floodplain soils and overbank sediments					
River West Allen (Tyne catchment), < 2 mm overbank sediment (Aspinall and Macklin, 1985).	nr	5 - 33 (17)	22 - 40 (32)	98 - **3,166** (**1,300**)	74 - 1,131 (763)
River Nent (Tyne catchment), < 2 mm overbank sediment (Macklin, 1985).	nr	nr	nr	224 - **15,800** (**5,262**)	**4,360 - 38,000** (**16,320**)
River South Tyne, floodplain sediment (Macklin and Lewin, 1989).	nr	nr	nr	15 - **10,490**	130 - **15,270**
Rivers South Tyne and Tyne, < 2 mm overbank sediment (Macklin and Smith, 1990).	nr	2.3 - **116.9** (14.0)	8 - 384 (57)	410 - **9,798** (**2,834**)	590 - **16,520** (**5,504**)
River Tyne at Prudhoe, < 2 mm overbank sediment (Macklin *et al*., 1992; Hudson-Edwards *et al*., 1998).	nr	2.6 - 8.0 (3.8)	11.1 - 42.5 (18.3)	615 - **2,340** (**1,310**)	722 - 2,340 (1,360)
Hudeshope Beck (Tees catchment), < 2 mm overbank sediment (Lee, 1989).	nr	<0.05 - 17 (6.1)	0.5 - 388 (17)	63 - **26,800** (**9,690**)	190 - **5,180** (**1,630**)
River Swale at Catterick (Yorkshire Ouse catchment), < 2 mm overbank sediment (Macklin *et al*., 1994; Taylor and Macklin, 1997).		1 - 18	nr	56 - **5,507**	15 - **3,066**
Hamps and Manifold rivers (Trent catchment), < 2 mm floodplain and channel sediment (Bradley and Cox, 1986).		0.25 - 21.8 (2.33)	11.4 - **5,318** (**560.3**)	15.5 - **1,107.7** (162.8)	92 - **6,391** (667)
River Axe at Wookey Hole Cave, < 2 mm overbank sediment (Macklin, 1985).	nr	nr	3 - 27 (14)	226 – **25,124** (**2,642**)	89 - 660 (245)

River Ystwyth, < 2 mm overbank sediment (Lewin *et al.*, 1983).	nr	nr	nr	73 - **4,646** (**1,791**)	123 - 1,543 (533)
River Rheidol, floodplain sediments, < 2 mm (Swain *et al.*, 2005).	nr	0.4 - 4.4	28 - 76	440 – **2,520**	120 - 680
Catchments elsewhere in the world					
Mining- and industrially-contaminated sediments in Belgium, Germany and the Netherlands (De Vos *et al*., 1996).	<5 - **69** (16)	nr	<10 - **736** (25)	<10 - **1,600** (89)	**378 - 2,477** (**716**)
Rio Guadiamar sediments, Spain (Aznalcóllar), (Hudson-Edwards *et al*., 2003).	**20 - 1,200** (**320**)	0.5 - **12** (4.7)	17 - **490** (**260**)	50 – **2,700** (**990**)	140 - **4,600** (**1,200**)
Pre-industrial metal concentrations – Humber Estuary sediments (Cave *et al*., 2005)	**22**	nr	17	22	84
Guideline concentrations - sediments					
Environment Agency draft sediment quality guidelines: threshold effect level (TEL)	5.9	0.596	36.7	35	123
Predicted effect level (PEL)	17	3.53	197	91.3	315
Guideline concentrations - soils					
Livestock grazing (ICRCL 70/90) threshold trigger concentrations for mining sites	nr	50	500	1,000	3,000
Crop growth for animal consumption (ICRCL 70/90) threshold trigger concentrations for mining sites		30	250		1,000

High concentrations of metals at mine sites have also led to the development of rare ecosystems which in some cases have been designated as Sites of Special Scientific Interest (SSSI). For example, past mining of lead and zinc in the Pennine Orefield has raised levels of heavy metals in the alluvial plain at Ninebanks on the River West Allen in Northumberland; the river shingles have been designated as a SSSI since the site supports an unusual community of metal-tolerant plants. There are many similar examples in the former mining areas of England and Wales (see Swain *et al.*, 2005), and so any remediation measures taken to address water and sediment quality concerns must take account of these and other local interests.

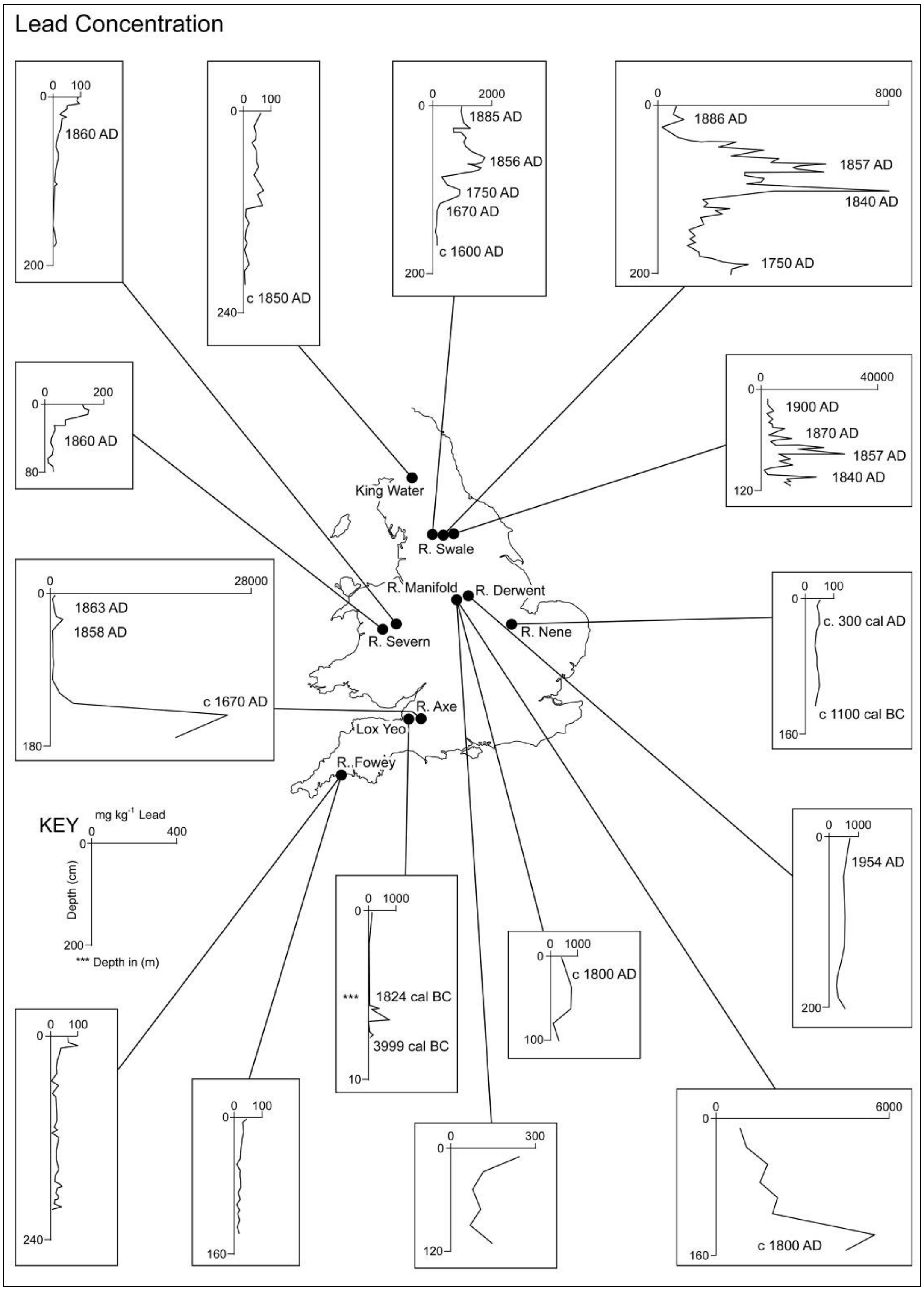

Figure 2.2: Lead concentrations in overbank sediment and floodplain soils in selected English and Welsh rivers (after Macklin *et al.*, 1994).

Declining mining activity in the twentieth century resulted in lower inputs of mine waste, although erosion of spoil heaps and tailings deposited adjacent to the river channel continues to be an important source of particulate and dissolved metals in many rivers. This is reflected in lower metal concentrations in most English and Welsh overbank sediments deposited at this time and the incision of mining-age channels and floodplains (Figures 2.2 and 2.3). In some cases, however, concentrations have increased since the mid-twentieth century (like the Derbyshire Derwent, downstream from the Mill Close mine; Lewin and Macklin, 1987; Macklin *et al.*, 1994).

The erosion, transport and deposition of historically-contaminated alluvium is a very important source of sediment-borne metals in all mining-affected river systems in England and Wales (Macklin, 1992). This has been shown by a number of studies, where overbank sediment sampled directly after flood events has been found to contain high metal concentrations (relative to rivers without mining) that can be linked to upstream alluvial sources (Macklin and Dowsett, 1989; Dennis *et al.*, 2003; Walling *et al.*, 2003, Macklin *et al.*, 2006). The autumn 2000 floods in the River Swale (a tributary of the Yorkshire Ouse), for example, resulted in the deposition of overbank sediments with extreme metal concentrations (above 10,000 mg kg^{-1} lead) in trunk streams, particularly downstream of mined tributaries. More than 80 km downstream of the mining district, concentrations remained above 1,000 mg kg^{-1}. Even compared to sediment metal concentrations in rivers affected by the recent tailings dam failures in Bolivia, Romania and Spain (Hudson-Edwards *et al.*, 2001, 2003; Macklin *et al.*, 1999, 2003) these values are high, particularly when one considers that mining in the Swale catchment ended more than 100 years ago. Furthermore, an increase in the frequency of flooding, as witnessed in the Yorkshire Ouse over the last 20 years (Longfield and Macklin, 1999), has resulted in much higher rates of metal cycling and increased contaminant delivery to riparian farmland. The deposition of contaminated sediment on floodplains may be an unexpected by-product of more frequent flooding due to climate change. Controlling diffuse sediment-associated contaminant sources is therefore important in managing affected river systems to achieve good ecological status (Macklin *et al.*, 2002).

Dennis *et al.* (2003), and in a later study Brewer *et al.* (2005), reported that sites in the River Swale that are inundated every year display strong relationships between sediment-borne metal concentrations and flooding. In other sites and river systems, the patterns of metal deposition across floodplains are more complex and difficult to predict. This is due to a number of factors, including flood magnitude, morphology of the floodplain surface and grain-size controls. Hudson-Edwards *et al.* (1999a) showed that flood embankments restricted deposition of metal-contaminated sediment within the inter-embankment area close to the channel of the River Aire, while in reaches on the Rivers Swale, Nidd and Wharfe, contaminated sediment was spread more thinly across most of the floodplain surface because large-scale contamination occurred before embankments were constructed in the first decade of the nineteenth century (Figure 2.4). In terms of grain-size, the highest metal concentrations are often found in the finest-grained (such as silt- and clay-rich) sedimentary deposits because of the positive relationship between grain surface area and metal concentration (Gibbs, 1977). This is not always the case: in situations where metals are closely associated with the sand fraction, they are generally deposited close to the channel as a result of gravitational sediment sorting (Macklin, 1996).

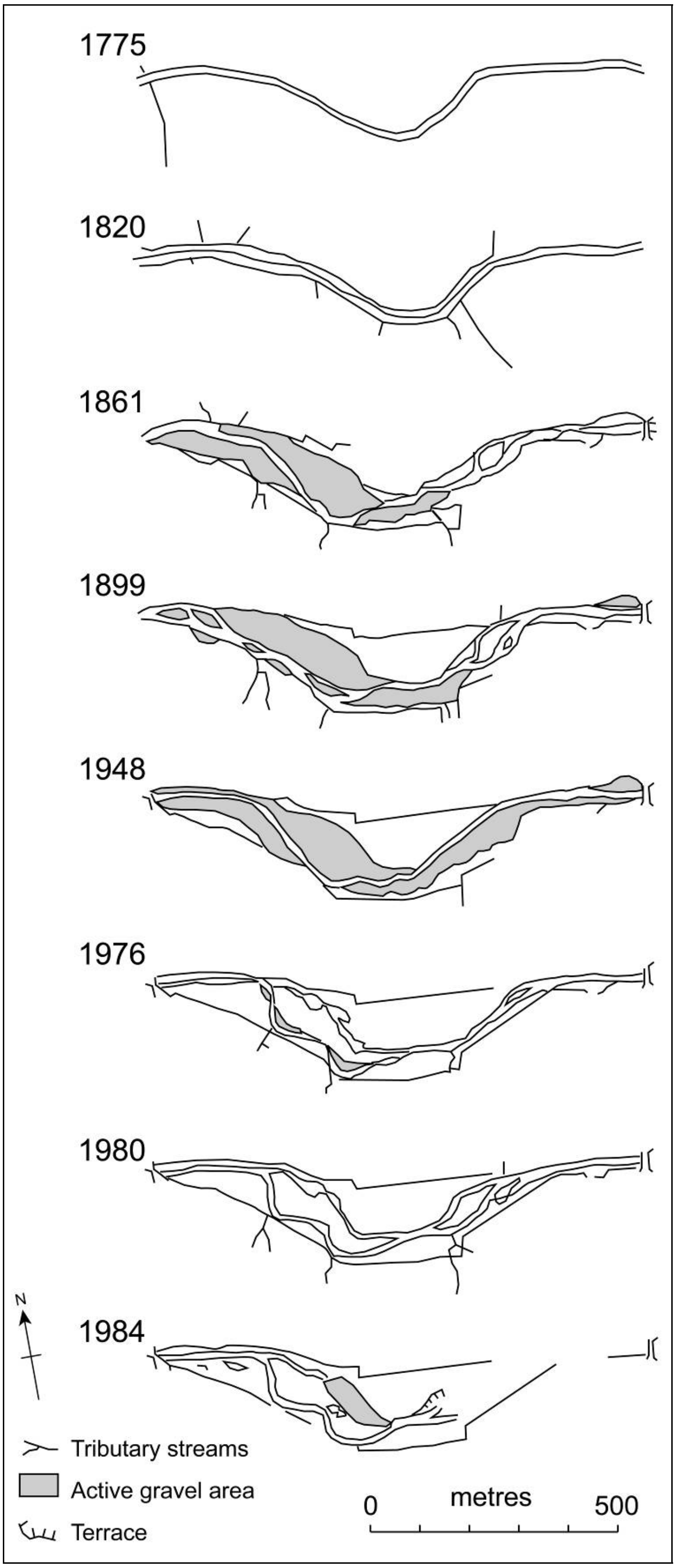

Figure 2.3: Channel changes between 1775 and 1984 on the River Nent, North East England. Active transformation has resulted in a change from a single thread to a braided channel, and deposition of fine-grained mining waste. The river channel and floodplain subsequently incised in response to declining inputs of mining waste since sometime between 1948 and 1976, and less frequent large floods (after Lewin and Macklin, 1987).

In-channel downstream patterns of metal concentrations are generally more predictable, with concentrations tending to decrease downstream from mines or mining areas in a systematic way that can be approximated using negative linear, exponential or power functions (Figure 2.5; Wolfenden and Lewin, 1977; Lewin and Macklin, 1987). Floodplain storage or inputs of contaminants from diffuse or point sources can modify these patterns (Axtmann and Luoma, 1991; Macklin, 1996). The downstream decreases have been attributed to the following:

(i) Dilution of contaminated sediment by uncontaminated sediment derived from channels and tributaries upstream of contaminant point sources and erosion of channel banks (Macklin, 1996; Hudson-Edwards *et al*., 2001).

(ii) Hydraulic sorting of channel bed sediment on the basis of density, size or shape, which selectively enriches sediment near the mining source in contaminant metals (Macklin and Dowsett, 1989).

(iii) Abrasion of contaminated sediment grains (Langedal, 1997).

(iv) Storage of contaminated sediment in channel and floodplain deposits and burial within the river channel in depositional environments (Macklin *et al*., 1992; Walling *et al*., 2003).

(v) Chemical sorption or dissolution of contaminants and/or contaminant uptake by biota (Lewin and Macklin, 1987; Hudson-Edwards *et al*., 1996).
In English and Welsh mining-affected rivers, the practice of discharging fine-grained mining and mineral-processing wastes into watercourses has resulted in sediment-associated metal contaminants being dispersed many tens of km, and in some cases more than 100 km, from their point of origin (Lewin *et al*., 1977; Macklin *et al*., 1997; Dennis *et al*., 2003).

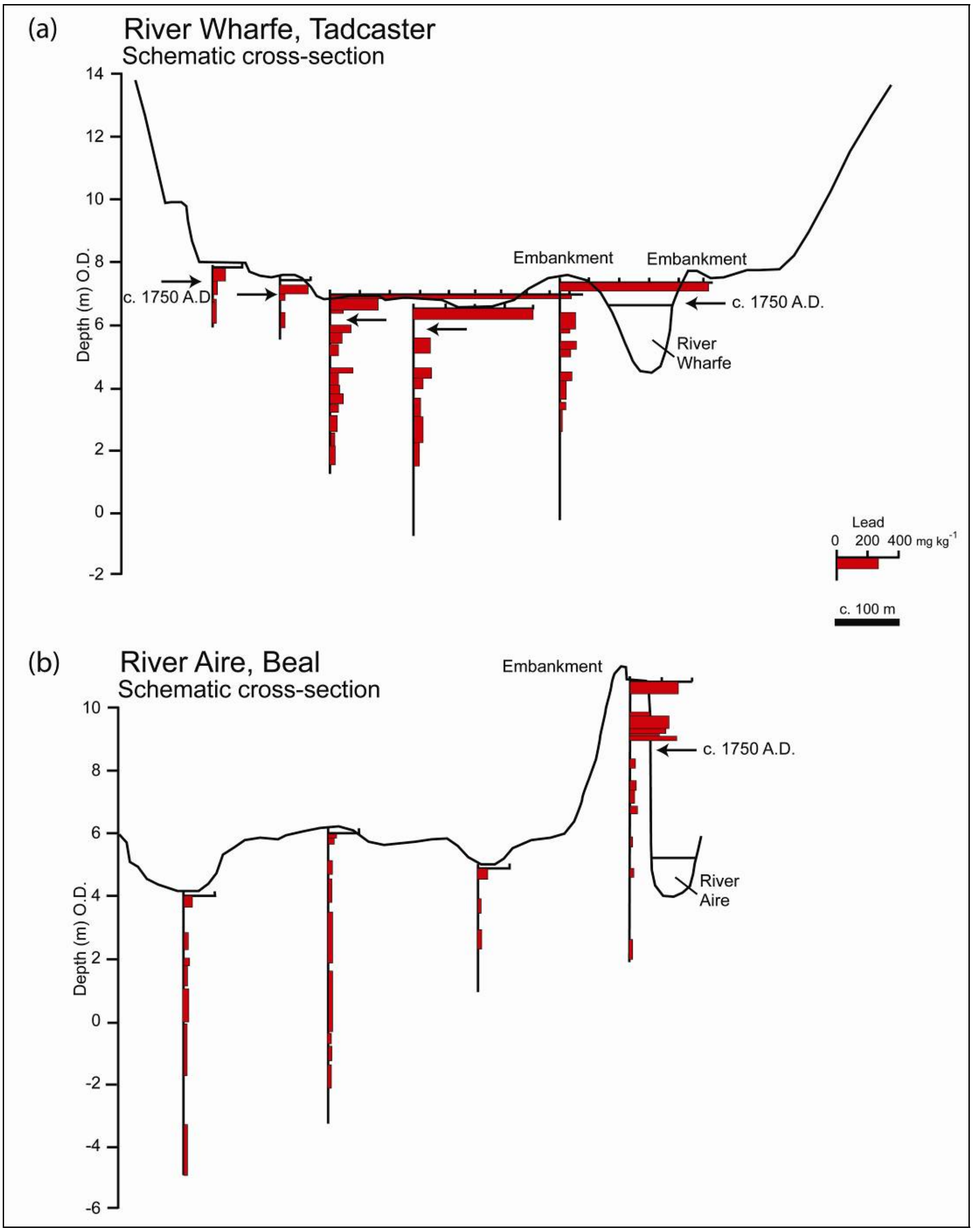

Figure 2.4: Lead concentrations in overbank sediments from (a) Tadcaster, River Wharfe and (b) Beal, River Aire. In (b), flood embankments restricted deposition of lead-contaminated sediment within the inter-embanked zone close to the channel of the River Aire, while in (a), lead-contaminated sediment was deposited across most of the floodplain surface. The higher lead concentrations in (a) result from intensive metal mining in the catchment of the Wharfe, compared to only minor mining (but heavy industrial activity) in the Aire (b) (after Hudson-Edwards *et al.*, 1999a).

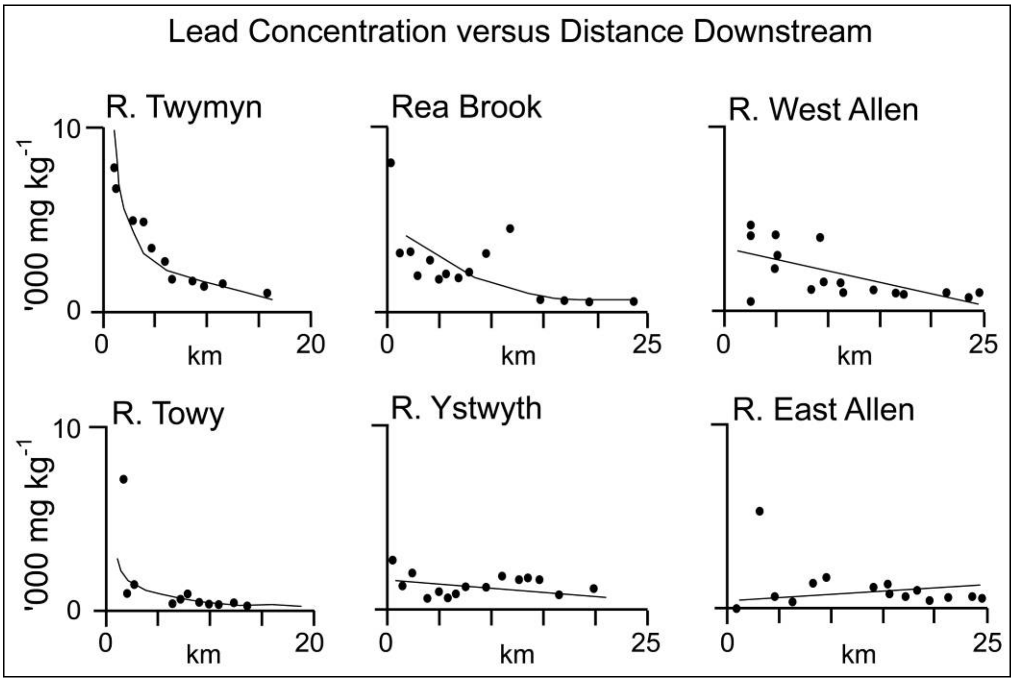

Figure 2.5: Relationship between sediment-borne lead concentration and distance downstream from mines for six English and Welsh rivers. Linear, exponential and power function least-square regression lines are fitted to the data (after Lewin and Macklin, 1987).

River channels can be regarded as temporary stores of metal-rich sediments, but floodplains, riparian wetlands, reservoirs, lakes and particularly estuaries (Cave *et al.*, 2005) are the long-term sinks for metal storage in river basins in England and Wales (Figure 2.6). Large quantities of metal contaminants can be stored in these environments (see, Macklin, 1985; Macklin *et al.*, 1992; Hudson-Edwards *et al.*, 1999a; Brewer *et al.*, 2005; Cave *et al.*, 2005). Hudson-Edwards *et al.* (1999a) showed that approximately 620 million tonnes of lead and 640 million tonnes of zinc were stored in floodplains of the Yorkshire Ouse basin, and suggested that these values were comparable to reserves for economically-viable metalliferous ore deposits. The residence times of contaminants in floodplains can be very long, from tens to hundreds or thousands of years (Macklin, 1992; Coulthard and Macklin, 2003), and depend on the rates of post-depositional physical, biological and chemical remobilisation, and on the geomorphology of the catchment or reach. In stable reaches or reaches where aggradation rates are relatively high, contaminants can be stored for extremely long periods (Bradley and Cox, 1990), whereas in reaches with more laterally mobile channels, the storage period may be relatively short (Lewin *et al.*, 1977; Macklin and Lewin, 1989), but still can exceed a century or more. Storage periods may also be short in systems with limited floodplains, such as the rivers in South West England, where much of the mine waste has been deposited as estuarine rather than fluvial sediments (Pirrie *et al.*, 2002).

A model for the dispersal and storage of particulate and dissolved mine waste is illustrated in Figure 2.6. Sediment and solid mine waste are physically and chemically weathered from their source areas, producing through rainsplash, wash, creep and subsurface flow, solutes, suspended sediments and bedload that are enriched in metals. These are transported downstream, and deposited on the bed of the river in a number of bedforms. Deposited sediment in river bars or on floodplains can, in turn, be physically and chemically weathered as well as eroded, starting the cycle again.

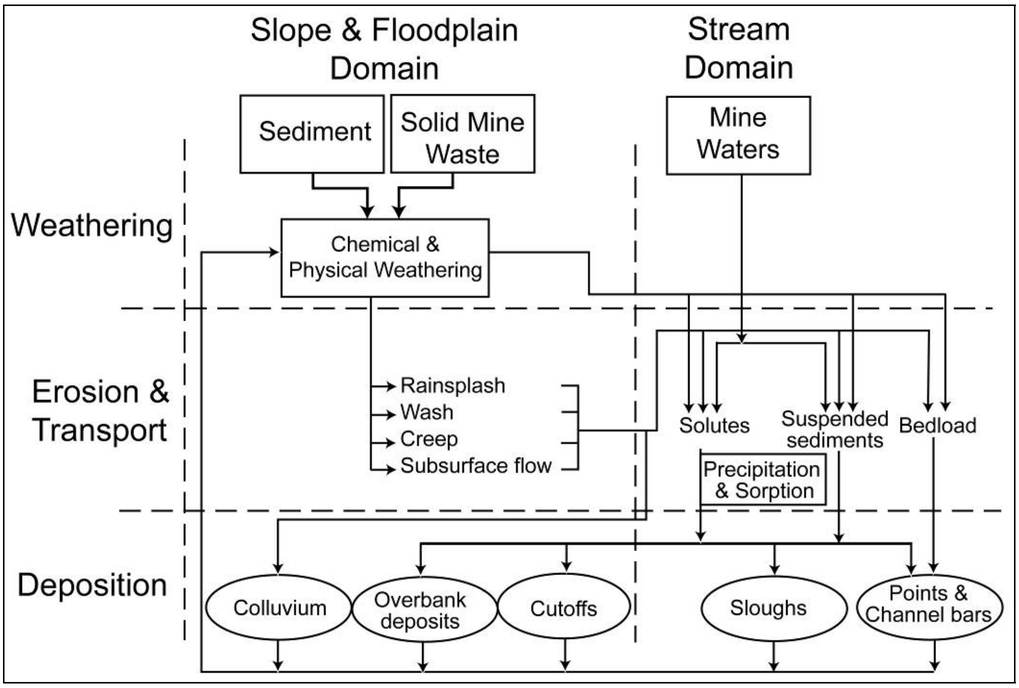

Figure 2.6 A model for the dispersal and storage of particulate and dissolved, metal-rich mining wastes (after Lewin *et al.*, 1977). Note that 'solid mine waste' includes waste spoil heaps, tailings and other solid residues from mineral processing.

2.2.2. Ecological impacts of sediment and soil contamination

Sediment contamination

An important part of river management is to determine the ecological impact of high metal concentrations in sediments. Many floodplains in the former metal mining areas of Great Britain are still significantly contaminated with metals. For example, a recent survey of contamination from historical metal mining in the Swale catchment, northern England (Brewer *et al.*, 2005) showed that more than 55 per cent of the floodplain, covering an area of nearly 30 km^2 and used for agriculture, is likely to be contaminated by metals significantly above background concentrations. The River Swale, both in terms of the environment legacy of mining and the scale of floodplain contamination, is by no means atypical. An estimated area of 12,000 km^2 of river catchments in northern England is directly affected by historical mining (Macklin *et al.*, 2002). These estimates were carried out using a similar method to that proposed later in this report (Section 3).

A potential obstacle to achieving integrated river basin management in catchments contaminated by mining activities is uncertainty about the maximum permissible concentrations of potentially toxic metals in river sediments (suspended material, channel bed), overbank sediments and floodplain soils. For example, there are no agreed European guidelines on metal concentrations in river or floodplain sediment (unlike metal concentrations in surface water, where standards have been set at EU or national level). Under the Water Framework Directive, environmental quality standards must be set to protect aquatic life from exposure via the water column, through the food chain or from contaminated sediments. The UK has not yet set mandatory standards in sediments (UKTAG, 2008), due to the difficulties in using measurements on sediments as the basis for environmental control regimes, given the high spatial variability of monitoring data. Furthermore, the limited availability of toxicological data for contaminants in sediments means there is considerable uncertainty over the appropriate level for environmental quality standards. Work is in progress to develop sediment guideline values that can be used to trigger further investigation, as opposed to statutory environmental quality standards (UKTAG, 2008).

A number of countries have soil/sediment protection and prevention and laws regarding environmental clean-up (Table 2.4). The Netherlands has one of the longest histories of soil/sediment protection policy dating back to 1962 (Visser, 1993), and guidelines were reformulated in the early 2000s using eco-toxicological methods and considering potential human exposure routes; these are based on different assumptions than those made in the UK (Defra, 2002). The Dutch intervention values for soil/sediment remediation (Table 2.4) are considered to be numeric manifestations of the concentrations above which there can be said to be serious contamination. These values indicate the concentration levels of metals above which the functionality of soil for human, plant, and/or animal life may be seriously compromised or impaired (Visser, 1993; 1995). Target values (Table 2.4) indicate the level at which there is a sustainable soil quality and give an indication of the benchmark for environmental quality in the long term assuming negligible hazard to the ecosystem (Macklin *et al.*, 2003). However, as is evident from Table 2.4 there are significant differences between European countries in maximum acceptable metal concentrations (see *Soil Contamination* section below for a discussion of the UK approach).

Given the potential impact of contaminated sediments on ecological health, particularly at Natura 2000 sites which are protected under the Habitats Directive (European Commission, 1992), the Environment Agency has begun to develop interim sediment quality guidelines. These guidelines are based on the Environment Canada “threshold effect level” (TEL) and “predicted effect level” (PEL) approach (Canadian Council of Ministers of the Environment, 2001). The TEL is the concentration below which sediment-associated contaminants are not considered to represent significant hazards to aquatic organisms. The PEL represents the lower limit of the range of concentrations associated with adverse biological effects. Under this approach, the TEL and PEL are used as triggers for further investigation rather than strict environmental quality standards. This is because there are many issues which affect the bioavailability and toxicity of contaminants in sediments including environmental parameters such as pH, the content of sulphides and natural organic matter, and particle size (Canadian Council of Ministers of the Environment, 2001). In addition, there is uncertainty about the exposure routes of benthic organisms to contaminants. There is a high probability of adverse biological effects in sediments with contaminant concentrations above the PEL. The interim sediment quality guidelines based on the TEL and PEL approach are shown in Table 2.4. Results from UK rivers (such as Table 2.1) show that sediment contamination from mining activities is likely to be damaging ecosystem health in certain catchments, particularly from cadmium, lead and zinc.

Table 2.4: Draft sediment quality criteria (TEL, PEL) for England and Wales, and soil quality criteria developed in the Netherlands (concentration in mg kg^{-1} dry weight) (after Bird *et al*., 2003, and Macklin *et al*., 2006).

	England & Wales						**The Netherlands**	
	Sediment (channel)		Soil (including overbank sediments)				Soil	
	TEL[a]	PEL[b]	Threshold[c]	Grazing livestock[d]	Crop growth[e]	SGV[f]	Target[g]	Intervention[h]
As	5.9	17	50	500	1,000	20[1,2,3] 500[4]	29	55
Cd	0.596	3.53	3	30	50	1 (pH6)[1,3] 2 (pH7)[1,3] 8 (pH8)[1,3] 30[2] 1,400[4]	0.8	12
Cr	37.3	90	-	-	-	130[1,3] 200[2] 5,000[4]	100	380
Cu	36.7	197	250	500	250	-	36	190
Pb	35	91.3	300	1,000	-	450[1,2,3] 750[4]	85	530
Ni	18	35.9	-	-	-	50[1,3] 75[2] 5,000[4]	35	210
Zn	123	315	1,000	3,000	1,000	-	140	720

[a] TEL: Threshold effect level; draft freshwater sediment quality guidelines.
[b] PEL: Predicted effect level; draft freshwater sediment quality guidelines.
[c] Threshold trigger concentration (ICRCL, 1990). Below this, phytotoxic or zootoxic effects are not expected.
[d] Maximum (action trigger) concentration for grazing livestock (ICRCL, 1990). Above this level, there is a very high probability of phytotoxic or zootoxic effects which may result in death of stock if continually exceeded.
[e] Maximum (action trigger) concentration for crop growth (risk of phytotoxicity) (ICRCL, 1990).
[f] SGV: Soil guideline values for human health. Calculated for specific conceptual exposure model using the Contaminated Land Exposure Assessment (CLEA) model (Defra, 2002).
[g] Target value: if concentrations are beneath this value, the site is considered clean with no eco-toxicological risk.
[h] Intervention value: if concentrations exceed this value, the site is considered to pose an environmental risk and clean-up is necessary.
[1] Residential with plant uptake.
[2] Residential without plant uptake.
[3] Allotments.
[4] Commercial/industrial land use.

Soil contamination

In the UK, Defra has published soil guideline values (SGVs) as a screening tool in the assessment of land affected by contamination. SGVs can be used to assess the risks posed to human health from exposure to contaminated soil. They represent “intervention values” which indicate that further investigation and/or remediation might be necessary, as soil concentrations above this level might present an unacceptable risk to the health of site users. SGVs have been calculated for specific exposure pathways based on residential, allotment and commercial/industrial land uses. Values have not been calculated for agricultural use or public open space, and are only applicable to human health and not ecosystems. No guidelines exist in the UK for the assessment of floodplains affected by historical mining and used for agricultural purposes, except on actual mine sites (ICRCL, 1990).

Flora, fauna and humans that live in, and rely on, the river for food and livelihood could potentially be affected by sediment-borne metal contamination. Unfortunately, the concentrations of metals in soils and sediments above which ecosystem damage occurs have not been clearly established. This uncertainty prevents the publication of values that demonstrate that an unacceptable risk is present. In addition, some ecosystems have developed because of elevated metal concentrations, a number of which are protected as SSSIs. Plants growing on valley floors are particularly vulnerable to metal contamination due to extreme changes in redox and episodic deposition of fresh, potentially metal-rich sediment. Uptake of metals by plants in contaminated floodplains is of significant concern, as these areas are often used for grazing animals and crops.

Studies of uptake of cadmium, lead and zinc concentrations by plants and crops growing on metal mining-contaminated floodplains in England and Wales have shown that the plants and crops contain high concentrations of these metals, which exceeded concentrations in plants from uncontaminated areas (Abrahams and Steigmajer, 2003; Smith, 2004; Druery, 2006). Metal concentrations in plants are controlled by the quantity present in substrate soils, availability within the root zone and the plant's capacity to absorb, transport and accumulate the metal species. Metal absorption is also controlled by physical soil properties such as pH, cation exchange capacity and organic matter (Haghiri, 1973; Wolfenden and Lewin, 1978; Page *et al.*, 1981; Cunningham *et al.*, 1995; Vousta *et al.*, 1996; Nagaraju and Marimulla, 2001). While metals such as zinc are essential to plant nutrition and enzymic function (Collins, 1981), others such as lead and cadmium are neither essential nor beneficial (Baker, 1989). Excess metals in plants are accumulated by compartmentalisation in plant parts or excluded from the rest of the plant by the roots (Cataldo and Wildung, 1978). Cattle and other grazing stock often ingest plant material and sediment (Smith, 2004), so grazing may need to be restricted if there is a risk of exposure to floodplain soils with high concentrations of metals. This is particularly important after flooding, when fresh, reactive, metal-contaminated sediment has been deposited. The type of pasture, soil, management, season, element bioavailability, supplementary foodstuffs, length of exposure and particularly the amount of soil ingested all influence metal uptake (Thornton and Abrahams, 1983; ICRCL, 1990; Smith, 2004).

The Inter-Departmental Committee on the Redevelopment of Contaminated Land (ICRCL) has published guidance on human health hazards from the re-use of various types of land contamination. Their most widely used guidance (ICRCL 59/83, 1987) was withdrawn by Defra in 2002 following the introduction of the soil guideline values. However, other guidance remains in place, including ICRCL 70/90 (ICRCL, 1990) which sets out trigger and maximum allowable metal concentrations for grazing livestock and crop growth on metalliferous mining sites (Table 2.4), and these could be used as screening guidelines for these activities. However, since the publication of these values by ICRCL, the UK approach to assessing the risks from land contamination has changed (such as soil guideline values: Defra, 2002) and so there is uncertainty over applying these values.

Risks to human health

Humans may also be at risk from sediment-borne mining contamination in England and Wales. In spite of the large number of mining-related contaminated river systems in the world, the degree to which this affects human populations living beside, and relying on, these rivers for food and livelihood is relatively unknown (see Albering *et al.*, 1999; Harada *et al.*, 2001; Miller *et al.*, 2004; Archer *et al.*, 2005, for exceptions). This is somewhat surprising, given the body of literature that suggests that excessive intake of many metallic and metalloid elements can lead to human health problems (Nordberg, 1978; Fergusson, 1990; Friberg *et al.*, 1986; Hughes, 1996; Wright and Welbourn, 2002). Many of these elements are required as micro-nutrients for biochemical processes, and thus are essential to human health, but in mining-contaminated areas, humans have the potential to take in excessive amounts of these elements.

The potential pathways of metallic and metalloid elements to humans in mining-impacted rivers include the ingestion of contaminated drinking water from private supplies (the quality of public water supplies is strictly controlled), soil, vegetables, fruit, fish and livestock (if grown on contaminated soils), or the inhalation of contaminated dust (see Miller *et al.*, 2004). Exposure of humans to contaminated tailings and spoil heaps at abandoned metal mines (primarily due to elevated Pb concentrations) has led to the designation of a limited number of sites as "contaminated land" under Part 2A of the Environmental Protection Act 1990. The relatively few studies that have investigated human health risks from exposure through some of these pathways in such river systems suggest that the effects of the contamination are minimal (Miller *et al.*, 2004; Archer *et al.*, 2005) due to good risk management (avoidance of contaminated drinking water supplies, growing metal-tolerant crops, not eating fish) although further research is needed to confirm the risks to humans.

Summary

Developing environmental protection guidelines that can help to protect ecosystem and human health is of paramount importance. The WFD represents a significant step towards attaining this goal, but the legacy of historical metal mining poses a major obstacle to achieving integrated river basin management. As highlighted earlier, this is primarily because sediment (the principal agent of metal transport and storage in the fluvial environment) and its chemical composition are rarely analysed by existing environmental monitoring networks. The long residence times of metallic elements in the fluvial environment, and the complex manner by which sediment-associated metals are dispersed, sequestered and remobilised in river systems, requires a shift from short-term, static and point-based monitoring towards catchment-scale environmental quality programmes, underpinned by a sound understanding of river basin sediment system dynamics. This is especially true for catchments affected by historical metal mining and metal-processing activities.

2.2.3. Water quality

Several studies have measured the concentrations of metals in river systems affected by metal mining in England and Wales. Some of the most intensely studied have been the catchments flowing to the North Sea, which drain the Northern Pennines and Yorkshire Dales ore fields in mid-Wales and in Cornwall (see Table 2.5 for selected data). In Wales, the Environment Agency and Welsh Assembly Government have published a *Metal Mine Strategy for Wales* to highlight the most polluting abandoned metal mines and prioritise their management and remediation (Environment Agency Wales, 2002). River waters in these catchments exhibit high dissolved cadmium, lead and zinc concentrations, primarily due to inputs from the former metal mining areas, although industrial activity, sewage treatment works and atmospheric fallout also contribute (Robson and Neal, 1997; Rees *et al.*, 1998; Neal *et al.*, 2000).

Whilst the concentrations of metals in mining-impacted rivers often exceed environmental quality standards (EQS), this is not always the case since metals such as Pb and Cd tend to be removed from the water column by precipitation and sorption (and so accumulate in sediments), particularly in rivers draining carbonate-rich geology. Furthermore, metal concentrations in rivers draining mineralised areas which have not been mined are often elevated relative to non-mineralised areas, but generally significantly less than where mining has occurred. The long time periods over which natural water quality has been affected by mining is illustrated in Cornwall, where the background geochemistry has been obscured by more than 2,000 years of mining and related activities (Runnells *et al.*, 1992).

Metals can become enriched in the aqueous phase through a number of processes (Figure 2.6). The first is direct discharge of mine waters. High metal concentrations in mine drainage results from the oxidation of metal-bearing sulphide minerals, most commonly pyrite [FeS_2], which host metallic and metalloid elements such as arsenic, cadmium, copper, lead and zinc (Younger *et al.*, 2002). The concentration of metals in, and pH of, mine drainage waters depends on factors including:

- the supply of oxygen and carbon (as fixed or bicarbonate);
- the grain size and composition of the pyrite or metal sulphides;
- the presence of iron- and sulphur-oxidising bacteria;
- temperature;
- any neutralisation of the acid solutions by reaction with carbonate minerals such as calcite and dolomite, and to a lesser extent, silicate minerals (Rose and Cravotta, 1998).

In England and Wales, discharge of metal-enriched mine drainage waters is common, not only from former metal mines, but also from former coal mines (Banks *et al.*, 1997). Although at many abandoned coal mines passive or active water treatment techniques are used at the discharge points to lower metal concentrations, there is only one full scale facility treating a metal mine discharge (Wheal Jane, Cornwall; Johnston *et al.*, 2007). The Mynydd Parys mine in North West Wales has some of the highest metal concentrations of mine drainage waters in the UK (Table 2.6) due to the uncontrolled oxidation of sulphide minerals within the underground workings and in the pyritic waste tips which have contaminated the Afon Goch with metals and acidity (Boult *et al.*, 1994; Jenkins *et al.*, 2000). In this and other mine drainage-affected rivers, aqueous metal concentrations are lowered downstream by the precipitation of hydrous iron oxide and sulphate phases, and co-precipitation or sorption of metals onto these phases (Nordstrom, 1982; Boult *et al.*, 1994; Figure 2.6). Once associated with particulate material, the further transport and deposition of the metal contaminants is sediment- rather than solute-controlled (Figure 2.6). This was shown most dramatically by the Cornish Wheal Jane incident in November 1991. Water levels in the abandoned mine rose quickly over a period of eight months, and a plume of water with an initial pH of 2.8 and total metal content of more than 5,000,000 $\mu g\ l^{-1}$ overflowed into the River Carnon via the main adit, 14.5 metres above sea level (Banks *et al.*, 1997). An orange cloud of metal-bearing iron hydroxides formed relatively rapidly in the river and this was transported out to the Fal Estuary where it blanketed the coastline.

The second process by which solute metals enter river systems is by the in situ chemical weathering of contaminated soils, alluvium and mining wastes (Figure 2.6). These weathering processes may be accelerated by changes in pH and redox potential (oxidation or reduction). Decreasing pH (below pH5), caused by acid mine drainage, acid rain, or by the breakdown (oxidation) of organic matter and formation of organic acids, can cause dissolution of metal-bearing silicate, carbonate, sulphide and oxide minerals and release of their metals to the solute phase. Oxidising conditions cause the breakdown of metal-bearing sulphide minerals, whereas reducing conditions cause the breakdown of metal-bearing iron and manganese hydrous oxide phases, which are volumetrically the most important metal contaminant hosts in most alluvium in England and Wales (Hudson-Edwards, 2003). Reducing conditions can be generated by flooding and fluctuation of water-table levels (Hudson-Edwards *et al.*, 1998), both of which are common processes in floodplains. Conversely, reducing conditions in river channel sediments encourage the formation of insoluble metal sulphides (Cd, Cu, Pb, Zn) and decrease the bioavailability and thus toxicity of these metals to aquatic life.

Table 2.5: Dissolved metal concentrations in water samples from some mining-impacted English and Welsh rivers. Values in **bold** exceed the environmental quality standard (EQS)

Catchment	**Lead Dissolved (μg l^{-1})**	**Zinc Dissolved (μg l^{-1})**	**Cadmium Dissolved (μg l^{-1})**	**Reference**
Wear	**9.31**	**1770**[5]	**0.32**[9]	Environment Agency
West Allen	**52**	**1562**[5]		Gozzard *et al.,* 2006
West Allen	**8.1**	**736**[5]	**2.17**[9]	Environment Agency
Swale (upper)	**175**	-	**0.8**[10]	Environment Agency
Ure	0.89	14.3		Neal *et al*., 1997
Nidd	**16.7**	19.4[5]	**0.25**[8]	Environment Agency
Ouse	2.25	17.9		Neal *et al*., 1997
Ouse	**11.7**	9.14		Environment Agency
Wharfe	1.51	16.7		Neal *et al*., 1997
Aire	1.29	31.0		Neal *et al*., 1997
Derwent	0.28	14.2		Neal *et al*., 1997
Calder	1.25	35.9		Neal *et al*., 1997
Don	0.84	26.9		Neal *et al*., 1997
Trent	1.21	29.3		Neal *et al*., 1997
Tamar	0.03 - 3.28	3.4 - 12.7	0.03 - 0.07	Rawlins *et al.*, 2003
Tamar	4.9	11.6	**0.181**[8]	Environment Agency
Ystwyth		**170 - 880**[3]		Grimshaw *et al*., 1976
Ystwyth	**92**	**363**[3]		Fuge *et al*., 1991
Ystwyth	**121**	**3040**[3]	**5.5**[7]	Environment Agency
Rheidol	**9.5**	**285**[3]		Fuge *et al*., 1991
Rheidol	**12.4**	**145**[3]	**0.34**[7]	Environment Agency
Conwy	2.7 - **16.3**	**94 - 3260**[5]		Elderfield *et al*., 1979
Conwy	**17 - 50**	**300 - 342**[5]		Brydie & Polya, 2003
Conwy	**27.7**	**2485**[3]	**9.8**[10]	Environment Agency
Environmental quality standards	7.2[1]	8 - 125[2]	0.08 - 0.25[5]	

All samples were passed through a 0.45 μm filter. Neal *et al.* (1997) values are averages of weekly samples from 1993-1995.
[1]Pb annual average (dissolved) EQS set for the Water Framework Directive.
[2]Zn annual average (total) suitable for salmonid (game) fish. EC Dangerous Substances Directive (76/464/EEC). Hardness (as $CaCO_3$) related standard.
[3]Zn EQS = 8 μg l^{-1} (total Zn, hardness related)
[4]Zn EQS = 50 μg l^{-1} (total Zn, hardness related)
[5]Zn EQS = 75 μg l^{-1} (total Zn, hardness related)
[6]Cd annual average (dissolved) EQS set for WFD. Hardness (as $CaCO_3$) related.
[7]Cd EQS = 0.08 μg l^{-1} (dissolved Cd, hardness related)
[8]Cd EQS = 0.09 μg l^{-1} (dissolved Cd, hardness related)
[9]Cd EQS = 0.15 μg l^{-1} (dissolved Cd, hardness related)
[10]Cd EQS = 0.25 μg l^{-1} (dissolved Cd, hardness related)

The third way of enriching river waters in metals is through the dispersal of metal-rich sediment during high flow events. At abandoned mines, wastes from ore processing (such as tailings) were commonly deposited next to or in rivers. These highly contaminated materials can be mobilised during rainfall and erosion by high river flows; this leads to the discharge of particulate material containing high concentrations of metals into the water column. In addition, when floodplain alluvium is eroded, a large total surface area of metal-contaminated sediment is brought into contact with water, causing desorption of metals from sediment surfaces to the aqueous phase. Nagorski *et al.* (2003) showed that aqueous concentrations of arsenic, copper, iron, manganese and zinc in a small and large mining-impacted stream in Montana, USA, were highest following spring runoff and short-term storm events. In the River Wear and River West Allen, aqueous concentrations of lead and zinc are greatest during high-flow events

(Neal and Davies, 2003; Gozzard *et al.*, 2006). There remains considerable uncertainty over the impact on water quality of re-suspension of metal-contaminated sediments. Oxidation of sediments containing metal sulphides will encourage the release of these metals into solution, at least temporarily, which may affect aquatic life. Further work is needed to understand whether these short-lived events, which are easily missed in monitoring programmes based on quarterly or monthly sampling, cause acute toxicity.

Table 2.6: Water quality in selected English and Welsh mines, mine spoil tips, and rivers affected by mine drainage. From Banks *et al.* (1997), Jenkins *et al.* (2000), Whitehead *et al.* (2005), Neal *et al.* (2005), Gozzard *et al.* (2006) and the Environment Agency.

	pH	**Cu ($\mu g\ l^{-1}$)**	**Pb ($\mu g\ l^{-1}$)**	**Zn ($\mu g\ l^{-1}$)**	**Cd ($\mu g\ l^{-1}$)**
Metal mines and adits					
Cae Coch (Wales, pyrite)	2.5	160		940	
Cwm Rheidol (Wales – Pb, Zn, Cu)	2.8 - 3.0	30 - 68	720	38,000 - 14,400	39
Coalcleugh adit, River West Allen (Northumberland)	6.3		196	6,139	
Wheal Jane adit (prior to treatment)	4.4	144		41,963	46
Mine discharge-affected rivers					
Afon Goch Amlwch (Mynydd Parys mine, Wales – Cu) 0 km downstream	2.4	6,150	245	21,300	7.6
Afon Goch Dulas (Mynydd Parys mine, Wales – Cu, Pb, Zn) 11 km downstream	4.5	755	8.3	2,020	5.7
River Carnon (downstream of Wheal Jane mine discharge before treatment)	4.6	667	6	7,365	8
River Carnon (after treatment of Wheal Jane discharge)	-	242	13.4	1,330	2.35

2.2.4. Implications of the Water Framework Directive

Sediment-borne metal contaminants stored in river systems are a potential hazard to the flora and fauna that live in, and rely on, the river for food and habitat. Metal-contaminated sediments also have the potential to contaminate water supplies through physico-chemical remobilisation. Agenda 21 of the UN Conference on Environment and Development held at Rio de Janeiro in 1992 specified the need to protect the quality and supply of freshwater resources by an integrated approach to the development, management and use of water in a sustainable way (Jones, 1997). Significant progress in integrated river basin management, at both a national and international level, has recently been made in the European Union by the Water Framework Directive (WFD) (European Commission, 2000) that came into force on 22 December 2000. The WFD establishes a new planning system for the assessment, protection, improvement and sustainable management of Europe’s water environment. Its central feature, around which all its other elements are arranged, is the use of water bodies (catchments) as the basic unit for all water planning and management, with these water bodies being assigned to river basins for reporting purposes.

The WFD introduces two key changes to the way the water environment must be managed across the European Union (Environment Agency, 2002). The first relates to the environmental objectives that it is designed to deliver. Previous European water legislation was designed to protect particular uses of the water environment from the effect of contamination and to protect the water environment itself from dangerous chemical substances, including metallic elements. The WFD is unique in setting ecological targets for surface waters, designed to protect and, where necessary, restore the structure and function of aquatic ecosystems themselves, thereby safeguarding the sustainable use of water resources (Environment Agency, 2002). The WFD's overall goals are to achieve "good status" for all of Europe's surface waters and groundwater by 2015 (although a longer period may be allowed under certain circumstances), and to prevent deterioration in status. The five different ecological status categories used in the WFD (high, good, moderate, poor and bad) represent a different level of disturbance from a reference state in which there are no, or only very minor, human alterations to the natural ecological condition of the water body. Developing an ecological status classification system is widely recognised as a major challenge and requires a well-developed understanding of the links between habitat variables and biota, particularly when comparing the biological quality elements of aquatic plants and animals (such as fish, invertebrates) with their predicted reference conditions (Logan and Furse, 2002).

This raises a problem in assessing correctly the hazard posed by contamination from past metal mining activities, as this hazard may threaten the ecological and chemical status of water bodies. Sediment contamination has been investigated when it is suspected of being the cause of damage to ecological or public health, for example in response to a specific contamination incident. However, there has been limited routine monitoring of river sediment (suspended, channel bed or overbank) for contaminants by European regulators which is unfortunate, since more than 90 per cent of the total metal load in rivers is often transported in the solid phase (Gibbs, 1977) with the potential to cause ecological damage . Identifying reference conditions in sediments, particularly background metal concentrations in mineralised catchments with a long history of mining, will be a difficult but essential task to effectively implement the WFD.

The second key change that the WFD brings is the introduction of a river basin management planning system (Figure 2.7). The WFD envisages a cyclical process, whereby River Basin Management Plans (RBMPs) are prepared, implemented and then reviewed every six years. There are four distinct elements to the river basin planning cycle: (1) characterisation and assessment of impacts on water bodies in each river basin district; (2) environmental monitoring and classification (status); (3) the setting of environmental objectives; and (4) the design and implementation of the programmes of measures needed to achieve them (Environment Agency, 2002). RBMPs would seem to be well suited to the remediation and rehabilitation of mining-affected river systems, such as the staged scheme outlined by Allan (1997) where historic mining activities threaten good ecological status. Indeed, the EU Mining Waste Directive (MWD: European Commission, 2006) recognises the central importance of the WFD to the remediation of mining-contaminated river systems by explicitly referring to the WFD's catchment-based approach to water management and the requirement in the MWD to draw up an inventory of closed waste facilities.

River sediment quality is only rarely measured on a regular basis by water management authorities in Europe and elsewhere. The reasons for this are partly historical in that during the 1950s and 1960s, when the first monitoring networks were established, reducing the effects of chronic water contamination from industrial, mining and urban sources was the priority in most countries. Since the 1980s, particularly in Western Europe, Japan and North America, there has been a considerable decrease in metal concentrations in river water (Meybeck, 2003) as a result of stricter controls on metal effluent discharges but also because larger-scale metal mining and processing has significantly declined or ceased altogether. Abandoned mines continue to be a source of metals to rivers through direct mine water discharges and by the erosion of tailings and waste spoil heaps which commonly form the river banks in former mining areas. However, past discharges mean that historically contaminated river channel and floodplain sediments considerably downstream of abandoned mines are now functioning as linear, diffuse sources of metals. Unfortunately, river monitoring networks and protocols have not been modified to deal with these changes in the form, source and dispersal patterns of metals associated with historical mining activities. This arises in part from uncertainty over sediment-associated metal dispersal, storage and remobilisation processes coupled with the absence of a direct regulatory requirement for monitoring of sediment quality. The WFD has begun to address this by requiring the setting of environmental quality standards to protect aquatic life from exposure via the water column, from exposure through the food chain, and from the risks from contaminated sediments.

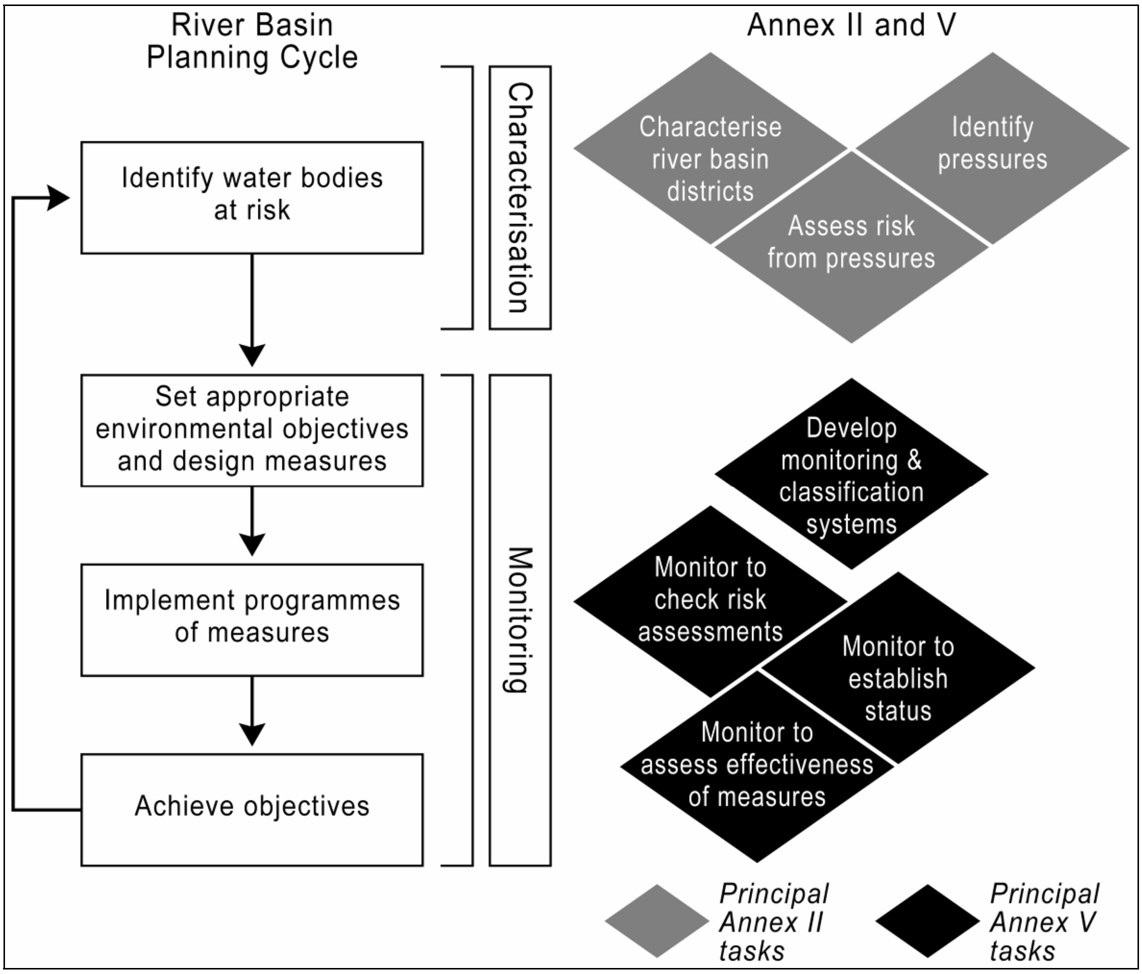

Figure 2.7: Relationship of Annex II and V tasks in the EU Water Framework Directive to the river basin planning cycle (after Environment Agency, 2002).

3. Assessing metal-contaminated river sediments and floodplain soils

3.1. Introduction

Metal-contaminated river systems, particularly those impacted by abandoned metal mines, are unlike more conventional parcels of land affected by contamination in that they are dynamic: fresh contaminated sediment is frequently added to channels and floodplain surfaces after flooding, and physico-chemical remobilisation of contaminated sediment is a long-term, ongoing process. Most conventional chemical and biological remediation methods (Table 3.1) for cleaning up contaminated sites are therefore not appropriate. This is evident in the recent unsuccessful attempts to remediate mining-contaminated river systems elsewhere in the world. For example, following the 1998 Aznalcóllar tailings dam failure in South West Spain, spilled tailings were physically removed to an open pit, and calcium carbonate applied to the scraped surface to control the generation of acid drainage from oxidising pyritic tailings (Galán *et al*., 2002; Hudson-Edwards *et al*., 2003). While the removal of the tailings undoubtedly reduced the potential for physical remobilisation of sediment-borne metal contaminants, the effectiveness of the chemical treatment was short-lived, as shown by high concentrations of arsenic in ephemeral pools that formed on the post-cleanup floodplain surface (Hudson-Edwards *et al*., 2005). In the mining-contaminated Coeur d'Alene river system in North West USA, contaminated alluvium has been treated with phosphate fertilizer in order to precipitate insoluble lead phosphate minerals that render the lead less bioavailable to aquatic birdlife (D. Strawn, personal communication 2005). Although the treatment did decrease the solubility of lead, it made arsenic 10 times more soluble, had little effect on zinc or cadmium and increased total phosphorus concentrations.

Clearly, an alternative approach to remediation is required to reduce the effects of mining-related metal contamination of sediments and soils in river systems in England and Wales. Most of the current remedial work in the UK is focussed on treating mine water discharges rather than the legacy of past inputs which have contaminated sediments, for example the Cwm Rheidol site in Wales (Edwards and Potter, 2007) and the Red River Pilot Treatment Plant in Cornwall (Potter and Jarvis, 2006).

Table 3.1: Examples of chemical and biological *in situ* remediation techniques for metal-contaminated sediments and soils.

Technique	Effect	Reference
Liming	Adding CaO, $CaCO_3$ or other alkaline material to raise soil pH and/or form relatively insoluble metal hydroxides or carbonates	Galán *et al*., 2002
Application of bonemeal, apatite or other form of soluble phosphate	Induce formation of very insoluble metal phosphates	Hodson *et al*., 2000
Application of iron hydroxides	Induce sorption of metal contaminants on iron hydroxide surfaces	Galán *et al*., 2002
Electrokinetic generation of iron-rich barriers	Generate sub-surface barriers rich in hydrous iron oxides that can sorb metal contaminants	Faulkner *et al*., 2005
Phytoextraction	Use of plants to take up contaminants into their biomass	Nathanail and Bardos, 2004

3.2. Scheme to assess contaminated sediments and soils in metal mining-affected rivers

A tiered scheme to assess contaminated sediments and soils in metal mining-affected rivers in England and Wales is outlined in Figure 3.1. This scheme involves four steps:

(i) identify catchments potentially impacted by sediment-borne metal contamination;

(ii) assess the extent and magnitude of contamination at a catchment scale;

(iii) carry out risk assessments in areas identified in (ii) to more fully investigate source-pathway-receptor relationships;

(iv) develop and implement contaminant monitoring and remediation programmes if the risks are unacceptable.

Each of these steps is described in more detail below.

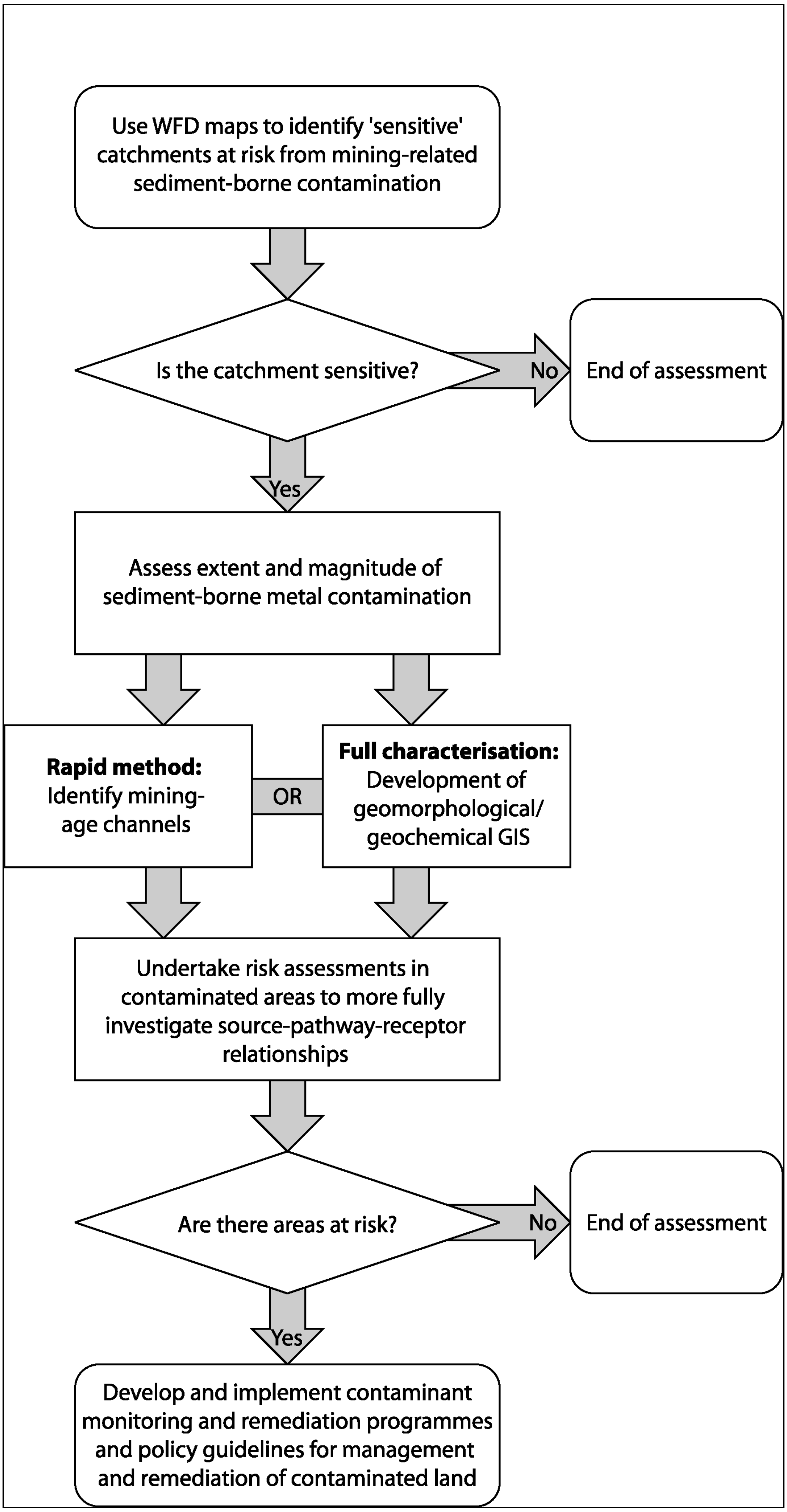

Figure 3.1: Tiered scheme for assessing metal-contaminated sediments and soils in river systems.

3.2.1. Identifying catchments at risk from sediment-borne metal contamination

As shown in Section 2.1, Figure 3.2 and Appendix 1, a large number of catchments are potentially at risk from sediment-borne contamination from metal mining in England and Wales. The WFD River Basin Characterisation maps, and the ongoing investigation of abandoned non-coal mines (SC030136/14: Environment Agency, 2008; Jarvis *et al;.,* 2008), should be used to identify catchments which are potentially impacted by such contamination.

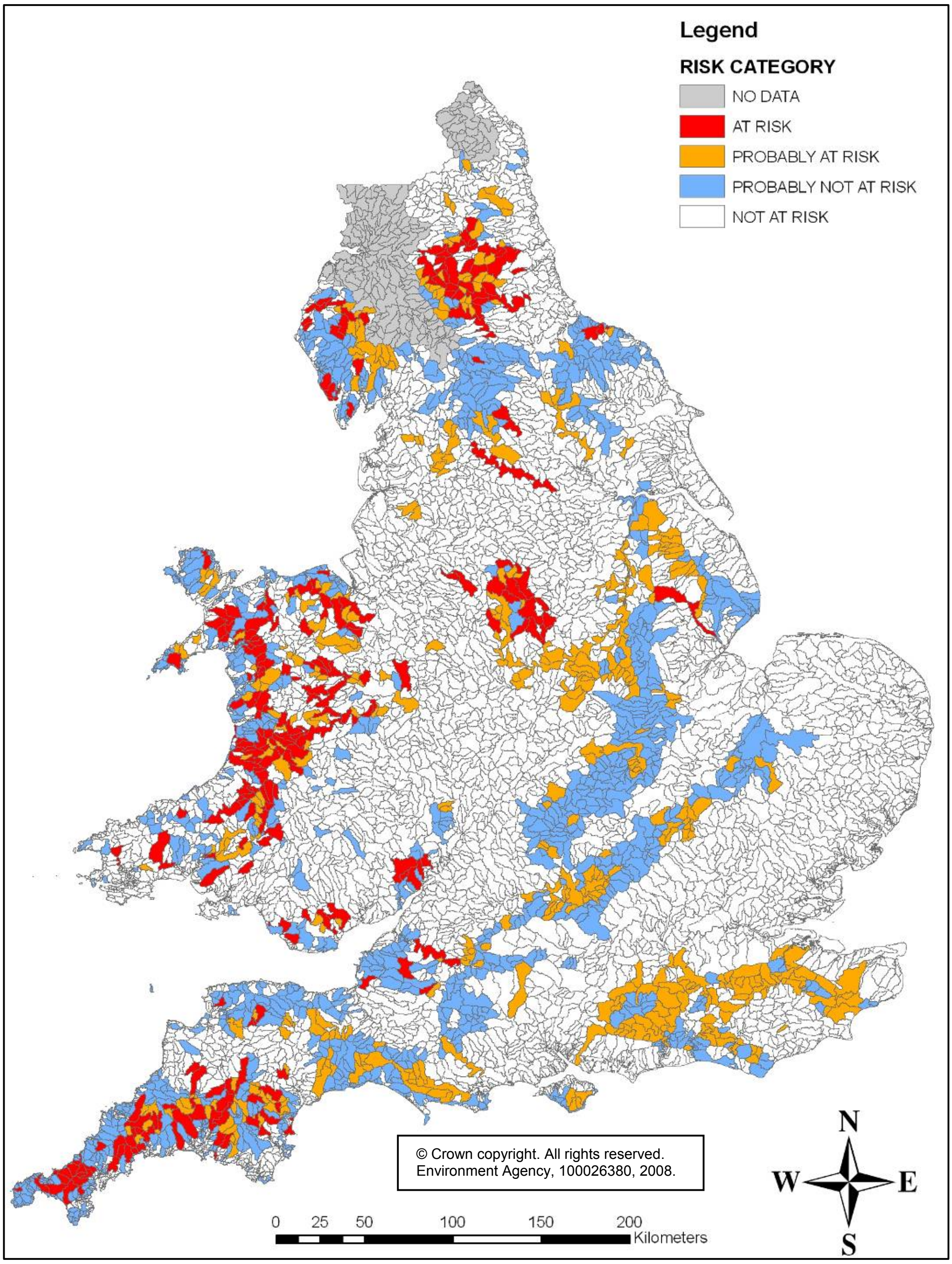

Figure 3.2: Map showing catchments of England and Wales sensitive ("at risk" and "probably at risk") to sediment-borne, mining-related metal contamination (after Environment Agency, 2008).

3.2.2. Identifying areas where contaminant metals may be elevated

Once potentially impacted catchments are identified, the next step is to assess the extent and magnitude of contamination at a catchment scale (Figure 3.3). This is critical, because it underpins the ability to make process-based decisions on managing the metal contaminants, design of monitoring schemes and protection of ecosystems and human health. The full procedure, outlined below, is taken from Brewer *et al*. (2005) and Macklin *et al*. (2006); further details on the method are given in Appendix 2.

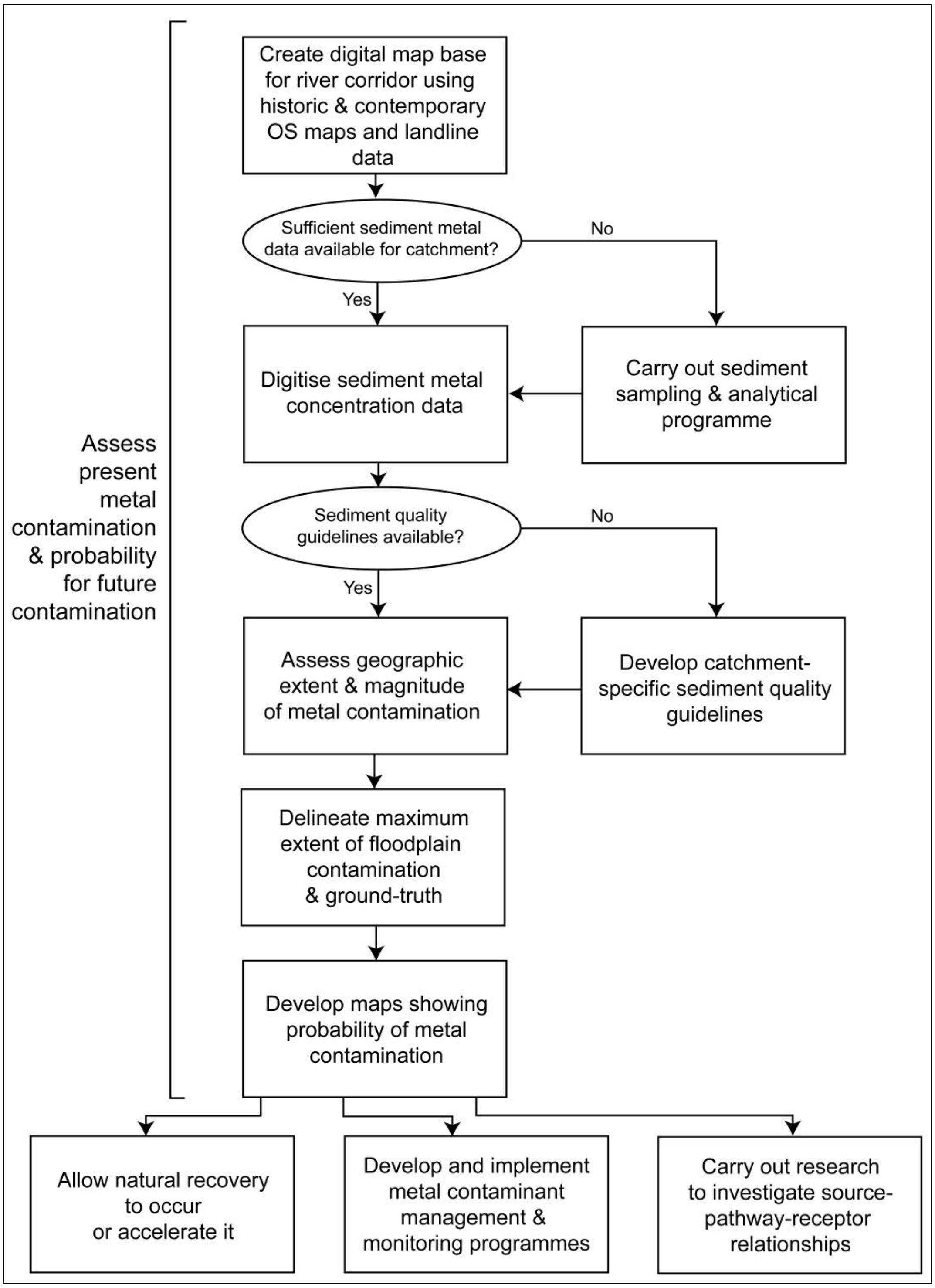

Figure 3.3: Scheme to assess metal-contaminated river systems in England and Wales (based on Macklin, 1996, Brewer *et al*., 2005 and Macklin *et al*., 2006).

The first step is an investigation of the geology, mining history, geomorphology and geochemistry of the catchment. This should incorporate collation of the mining production records, location of any mining and processing sites within the catchment, and available geomorphological, topographical and geochemical data.

Following this, it is necessary to identify the river corridor through which contaminated sediment is transported and deposited. In engineering terms, a river corridor is defined by the limit of the so-called “hundred-year flood” (Gardiner and Cole, 1992), that is, the extent of a flood with a one in 100 (one per cent) chance of happening in any year, shown by the Environment Agency’s Flood Maps (formerly known as Indicative Floodplain Maps). Although the hundred-year flood is an imaginary event, in that the discharge is an extrapolation not a measurement of a real flood, the concept of a river corridor is useful in emphasising longer-term linkages (and interactions) between river channels and their floodplains. During the period of mining in a catchment, under low flow conditions (sub-bankfull) contaminated material was deposited in-channel (on the bed of the channel and on river bars). Furthermore, because under low flow conditions mine waste would have comprised virtually the entire particulate load, and so sediment-associated metal concentrations in these deposits would have been very high. By contrast, under high flow conditions (bankfull and particularly overbank) mining waste would have been significantly diluted by cleaner non-mining sediment sources. But even though sediment metal concentrations would have been lower, overbank flooding would have dispersed, and deposited, mining waste over much larger areas of the floodplain.

In past work (such as Brewer *et al.*, 2005), the Environment Agency’s Indicative Floodplain Maps have been used to delineate the river corridor and to estimate the maximum extent of floodplain contamination. These new flood maps, which show the 100 year and 1,000 year flood limits, allow more sophisticated mapping of the river corridor and help to more accurately predict the presence or absence of flooding-associated contamination.

Details on creating digital maps of the river corridor are given in Appendix 2. The compiled maps will yield an accurate and visual record of channel change and floodplain deposition from the mid-late nineteenth century (peak mining period), and permit identification of those parts of the river corridor (such as river channels active during mining operations, river channel bars deposited during the mining period) most likely to be ‘hot spots’ of contamination (Figure 3.4).

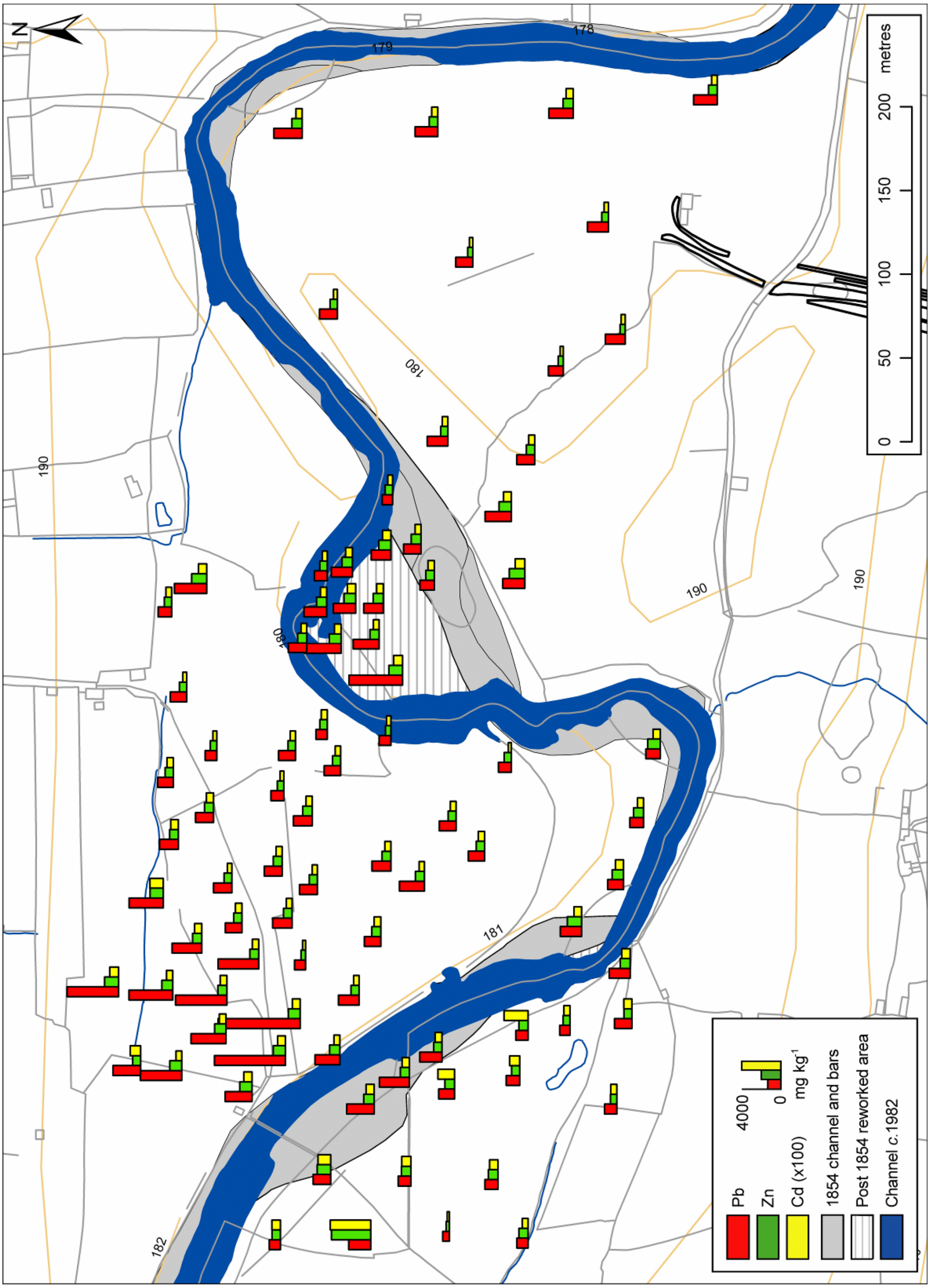

Figure 3.4: Geomorphology and sediment-borne metal concentrations at Reeth, River Swale, North East England (from Brewer *et al*., 2005).

Available data on metal concentrations in channel and floodplain sediments and river water should be added to the digital maps (preferably in a geographical information system (GIS) environment). Data sources include the Environment Agency, the Geochemical Baseline Survey of the Environment (G-BASE) dataset from the British Geological Survey, and published academic results. In many cases, adequate data on sediment and soil contamination will not exist and a programme of sampling may be necessary. A methodology for carrying out the sampling and geochemical analytical programme is proposed in Appendix 2.

Once the digital map and sediment metal data layers are integrated in the GIS database, these can be used to:

(i) evaluate the degree to which metal concentrations in floodplain soils vary spatially and how this relates to past and present river channel sediment dynamics;

(ii) establish the magnitude of floodplain soil contamination by metals, measured against background metal concentrations.

3.2.3. Estimating background metal concentrations in sediments and soils

Assessment of floodplains affected by historical metal mining and used for agricultural purposes is problematic, since no guidelines presently exist. To address this problem, Brewer *et al.* (2005) developed a system for estimating pre-mining background metal concentrations in the River Swale, a catchment affected by lead-zinc mining in the Yorkshire Dales. The estimation of background metal concentrations specific to the area takes into account local factors such as the enrichment of stream sediments with metals through natural weathering and erosion processes, which will be strongly influenced by the underlying and upstream geology (see Helgen and Moore, 1996). Sediment-borne metal concentrations in sampled fields can then be compared to these background concentrations to determine the magnitude of contamination.

Background concentrations give no indication of risk; rather, they help to identify locations that are contaminated (relative to background) and where further work is necessary to determine if there is a risk associated with this potential hazard. Brewer *et al.*'s (2005) system for estimating background metal concentrations is described in Appendix 2. Information on background metal concentrations in surface waters is being gathered by the British Geological Survey and the Environment Agency using the G-BASE dataset (SC050063: Environment Agency, 2007). The outputs from the SC050063 project may be useful in estimating background metal concentrations in floodplain soils and sediments.

3.2.4. Identifying maximum extent of floodplain contamination

Once the background concentrations have been estimated, and it has been established that sites within the river catchment show elevated concentrations, a thorough assessment of the relationships between the contamination and geomorphological variables should be carried out. This can be done using X-Y plots comparing two variables (such as concentration versus height above river channel, distance from present river channel, inundation frequency, age of sediment unit, distance downstream and sedimentary environment) either in the GIS or in a spreadsheet package such as Excel. The most significant relationships from the analysis can be used to identify the key criteria for mapping floodplain and river terrace metal contamination.

The final stage of mapping the geographical distribution of metals in the river system is to delineate the maximum likely extent of floodplain contamination along the entire river corridor. Brewer *et al*. (2005) recommended that this be done using the break of slope between the lower lying valley bottom (inundated both during and after the major mining period) and adjoining upstanding river terraces or hill slopes, visible on 1:5,000 colour aerial photographs. Once complete, if data are not already available it may be necessary to confirm the predictions by sampling floodplain sediment inside and outside of the mapped extent of floodplain contamination, particularly beyond structures such as flood embankments that may not be completely effective at containing contaminated sediment deposition during flood events.

These maps can be used as predictive tools to show the probability of contamination of floodplains by sediment-borne metals (Figure 3.5). Following Brewer *et al*. (2005), three zones can be identified:

(a) Land with a high probability of significant contamination.

(b) Areas with a likelihood of land contamination. Agricultural fields included in this category are likely to have some soils (probably those located closest to the present river or to the river channel active during the mining period) with metal concentrations that significantly exceed background metal concentrations (for example, by five times; see Brewer *et al*., 2005).

(c) Areas that have a very low probability of land contamination and are unlikely to have soils with metal concentrations significantly above background concentrations.

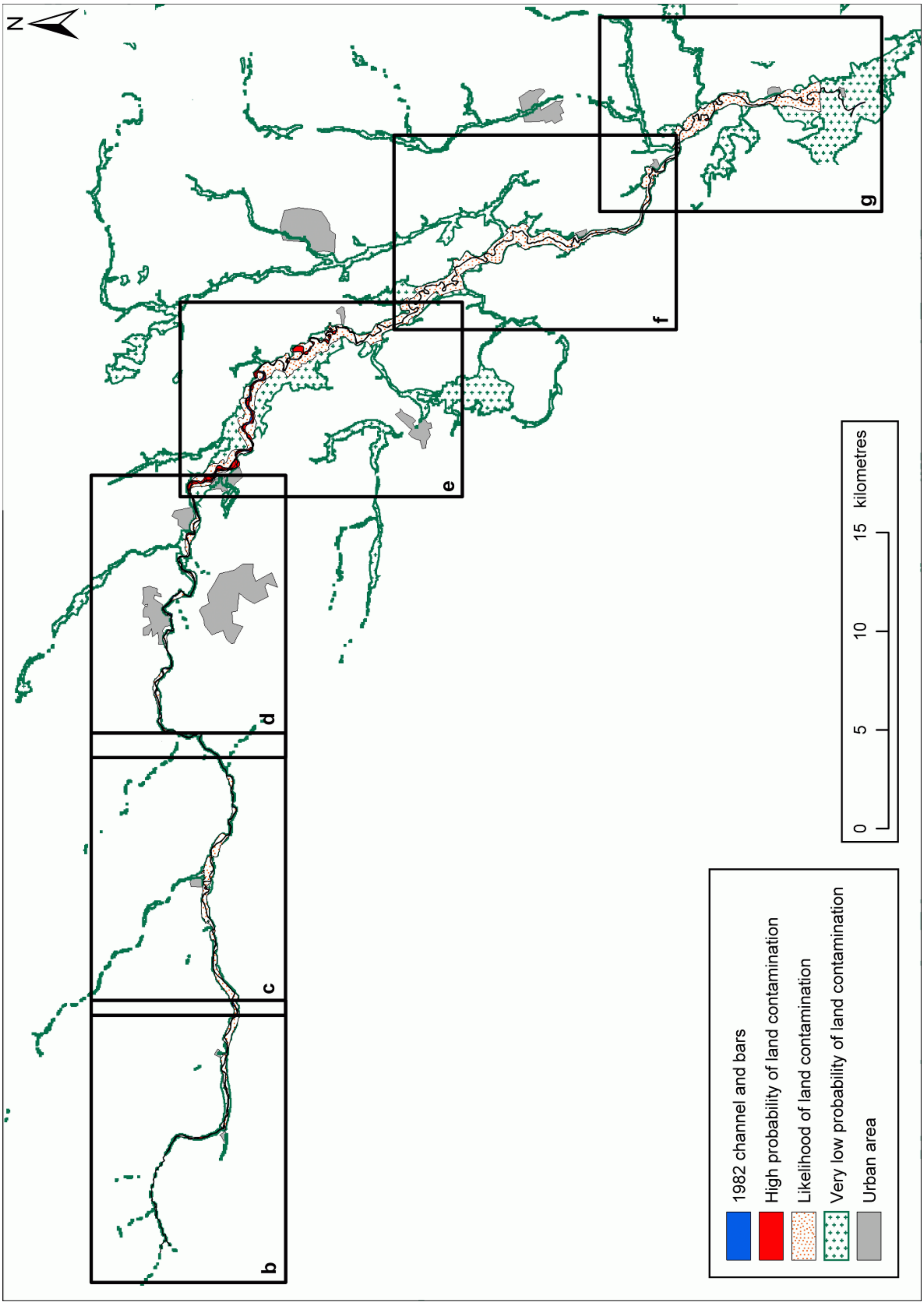

Figure 3.5: Example of floodplain maps showing probability of contamination. The likely extent of metal contaminated land along the River Swale. Isles Bridge – Downholme Bridge (from Brewer *et al*., 2005).

3.2.5. Further risk assessments for areas contaminated above background levels

One of the main aims of the WFD is to achieve good ecological status in river catchments. This report has clearly shown that channel and floodplain sediments in many catchments in England and Wales have been contaminated by historical metal mining, and thus may pose a hazard to ecosystem health. Whilst concentrations exceed the draft sediment quality standards (for example, concentrations above the predicted effect level) and the guideline values on using former metalliferous mining sites for agriculture (ICRCL, 1990), further work is needed to clarify if these are appropriate for assessing harm to ecosystem and human health. This requires the collection of evidence demonstrating damage to ecosystems and a policy decision on acceptable levels of risk, so that contaminant guideline values can be published for river sediments and floodplain soils.

Once these guideline values are available, the assessment scheme for characterising land with a high probability of contamination (outlined in Sections 3.2.3 and 3.2.4, Appendix 2 and Figure 3.3) can be used to identify sites within mining-affected catchments that require further consideration in the form of a detailed risk assessment. This detailed risk assessment involves an investigation of the source-pathway-receptor relationships in the catchment. As proposed in Environment Agency (2004) and Weeks and Comber (2005), the risk assessment should take into account a number of different data, including current and trend data on sediment metal concentrations, metal speciation, bioassays and bioaccumulation.

3.2.6. Developing contaminant monitoring and remediation programmes

Once detailed risk assessments have been carried out, contaminant monitoring and, if appropriate, remediation programmes should be implemented in those areas where unacceptable risks to ecosystem and human health have been identified (Figure 3.3) so that uncertainty over impacts can be minimised. Monitoring programmes that incorporate high-flow events and sample both water *and* sediment should be developed to take account of acute and chronic impacts on ecosystem health. Although remediation of entire catchments is unlikely to be appropriate, it may be necessary to control active, or potentially active, point sources of metals such as former mine sites, to reduce the potential for erosion, dispersal and deposition of contaminated sediment.

Cost-benefit assessments can be used to evaluate different management and remediation approaches so that risks to ecosystem and human health are reduced to acceptable levels. The catchment-scale mapping approach would allow identification of geochemical hotspots that should not be used for crop production or animal grazing (farmers should be discouraged from trying to improve soil quality unless the metal contamination is addressed), and targeted erosion control management to prevent bank erosion from remobilising highly contaminated soils. Vegetation and stabilisation of spoil heaps are common remedial methods, although these actions may not always significantly reduce leaching of metals, and may even increase the flux of metals to rivers. In some historically mined catchments in England and Wales, erosion of contaminated floodplain sediment several tens of kilometres downstream of mining areas is the principal source of metals (Coulthard and Macklin, 2003) and is not easily controlled using this approach. Further information on remediation of abandoned mines may be found in the ERMITE (Younger and Wolkersdorfer, 2004) and PIRAMID (PIRAMID, 2003) guidance.

4. Conclusions and recommendations

This report has highlighted the significantly elevated concentrations of metals such as cadmium, lead and zinc in river sediments and floodplain soils as a result of now abandoned metal mining activities. Although metal inputs were greater during the period of active mining in the nineteenth century, we continue to see significant inputs of dissolved and particulate metals in abandoned mining areas. This has left a substantial reservoir of highly contaminated sediments, which are likely to be causing ecological damage, in lowland rivers many kilometres downstream of the mines. Re-suspension of these sediments during flood events has the potential to cause additional harm to aquatic life, and to contaminate floodplain soils used for agriculture. Clear guidelines on sediment metal concentrations that represent an unacceptable risk to ecosystem and human health are not available in England and Wales. However, comparison of observed sediment concentrations with draft Environment Agency sediment quality guidelines reveal numerous significant breaches of predicted effect levels (PEL) for cadmium, lead and zinc. This indicates that adverse biological effects are likely to be occurring, with damage to ecosystem health and potentially poor ecological status.

Metal concentrations in floodplain soils impacted by mining activities were compared with government guidelines for grazing livestock on former metal mines. Observed concentrations significantly exceeded these guidelines in many catchments, particularly for cadmium, lead and zinc. Climate change is expected to increase the frequency and magnitude of floods. This will lead to increased re-suspension of sediments containing high metal concentrations and, therefore encourage the transfer of contaminated sediments from river channels to floodplain soils which are often used for agriculture.

Based on the findings of this report, we recommend that the Environment Agency act to reduce uncertainty over the risks to ecological status posed by contaminated sediments and soils as a result of abandoned metal mines. Specific recommendations are to:

1. Finalise sediment quality guidelines (such as TEL/PEL) that can be used to assess harm to ecosystem health (and hence ecological status).
2. Develop guideline metal concentrations in floodplain soils that represent an unacceptable risk for livestock or other agricultural uses (such as extension of ICRCL 70/90).
3. Investigate the impact of short-lived flood events on the release of metals from sediments into the water column, and consequent effects on aquatic life.
4. Review all Environment Agency sediment quality data (and ideally other sources such as BGS G-BASE database) and compare these with sediment quality guidelines (such as PEL values). This should initially be restricted to catchments that have been identified by the SC030136/14 project (Environment Agency, 2008) as being impacted by abandoned metal mines.
5. Where this review identifies that ecosystem health is threatened by contaminated sediments from metal mines, apply the tiered risk assessment method in this report.
6. Carry out monitoring of contaminated sediments in affected catchments.
7. Develop risk management strategies including remediation measures, where necessary, and following cost-benefit assessments.

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Glossary of terms

The definitions for the terms below marked with an * are taken from Bates, R.L. and Jackson, J.A. (1980) *Glossary of Geology*. Second Edition. American Geological Institute, Falls Church, VA.

Acid mine drainage: The formation of acid, high-sulphate and normally metal-rich waters as a result of the microbially-mediated oxidation of sulphide minerals.

Alluvium: Clay, silt or sand deposited by a stream or other body of running water in the channel or floodplain of a river system.

Background sediment-borne concentrations: The concentration of an element or compound in sediment present as the result of natural geological weathering and not as the result of anthropogenic activities.

**Bankfull conditions*: The elevation of the water surface of a stream flowing at channel capacity.

Bedload: The part of the total stream load that is moved on or immediately above the stream bed.

**Biologically available metals*: The fraction of metals in a sediment sample that is deemed to be available to organisms.

**Channel sediment*: Clay, silt, sand or gravel deposited by, or transported in, a stream in the channel of a river system.

**Chemically available metals*: The fraction of metals in a sediment sample that is extracted through use of single or a sequence of chemical reagents and deemed to be available to organisms or waters.

Creep: The slow mass movement of soil and rock fragments down slopes due to gravity, water saturation and alternating freezing and thawing.

Environment Agency Flood Map: Detailed flood maps released by the Environment Agency in 2004 as a replacement for the Indicative Floodplain Map. These maps are intended to help planning authorities reduce the risks associated with riverine and coastal flooding, in accordance with the Government's Planning Policy Guidance 25 on Development and Flood Risk (PPG25). Three flood risk zones have been defined: (1) areas with little or no risk of flooding; (2) areas with a low to medium risk of flooding, with an annual probability equivalent to a flood with a 1,000-year return period; and (3) areas with a high risk of flooding, with an annual probability equivalent to a flood with a 100-year return period. The Flood Map has been produced for England and Wales on a five-metre grid.

Environment Agency Indicative Floodplain Map: Flood risk maps released by the Environment Agency in 1999, as part of the survey duties listed under Section 105(2) of the Water Resources Act 1991. These maps were intended to identify areas at risk from riverine and coastal flooding, defined as areas inundated by a flood with a 100-year return period for river floodplains, and a 200-year return period for coastal floodplains. These maps were produced for England and Wales on a 50-metre grid.

Floodplain sediment: Clay, silt or sand deposited on the floodplain of a river system.

Mining waste: Unwanted rock or sediment remaining after the extraction of ores.

Overbank flow conditions: The elevation of the water surface of a stream flowing over channel capacity, so that the water overlaps the channel and flows over the floodplain.

Overbank sediment: Generally fine-grained sediment (< 2 mm) deposited from suspension on a floodplain by floodwaters that cannot be contained within the stream channel.

Rainsplash: The weathering of soil and rock fragments due to the impact of raindrops.

Subsurface flow: Water that flows underground and down gradient through soil, unconsolidated sediment or bedrock.

Tailings: Portions of washed or milled ore that are regarded as too poor to be treated further, and that historically have been discarded at a mine or processing site, or discharged into rivers.

Wash: The slow erosion, by rolling along the ground, of soil and rock fragments by the action of a thin film of water.

List of abbreviations

Defra	Department for Environment, Food and Rural Affairs
EA	Environment Agency
EC	European Commission
EQS	Environmental Quality Standard
EU	European Union
ICRCL	Inter-departmental Committee on the Redevelopment of Contaminated Land
MAFF	Ministry of Agriculture, Fisheries and Food
NRC	National Research Council
RBMPs	River Basin Management Plans
WFD	Water Framework Directive
WHO	World Health Organisation

Appendix 1 – Sediment and floodplain soil metal concentrations in river systems in England and Wales

Table A1. Ranges (mean) of metal concentrations found in English and Welsh alluvial soil and sediment and other mining-contaminated catchments in Spain and Bolivia. Figures in **bold** exceed the predicted effect level (PEL) in channel sediments or the livestock grazing trigger concentration in overbank sediments or floodplain soils (nr is not reported).

River system	As mg/kg	Cd mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg	Reference
Yorkshire Ouse catchment						
River Swale at Catterick < 2 mm overbank sediment		1-**18**	nr	56-**5507**	15-**3066**	Macklin *et al*., 1994; Taylor and Macklin, 1997
River Swale at Reeth fine-grained channel sediment		0-**22**	nr	22-**4818**	26-**12203**	Macklin *et al*., 1994; Grove and Sedgwick, 1998
River Swale at Catterick, < 2 mm post-1750 AD overbank sediment, n = 36	<2-8 (4)	nr	10-37 (18)	240-**4500** (1660)	142-**3000** (637)	Macklin *et al*., 1994 ; Hudson-Edwards *et al*., 1999a
Rivers Swale and Ure at Myton-on-Swale, n=4	6-10 (8)	nr	18-30 (24)	192-**932** (**500**)	198-**472** (307)	Hudson-Edwards *et al*., 1999a
River Nidd at Kirk Hammerton, n = 5	5-7 (6)	nr	12-25 (19)	283-**1100** (**602**)	102-284 (201)	Hudson-Edwards *et al*., 1999a
River Ouse at York, n = 6	4-17 (9)	nr	15-37 (23)	108-**1050** (**522**)	105-**701** (198)	Hudson-Edwards *et al*., 1999a
River Wharfe at Tadcaster, n = 5	9-19 (15)	nr	33-55 (40)	196-**1690** (**830**)	188-**803** (451)	Hudson-Edwards *et al*., 1999a
River Aire at Beal	**125-175 (140)**	nr	81-227 (162)	130-314 (237)	206-424 (254)	Hudson-Edwards *et al*., 1999a
Ouse basin pre-2000 before present alluvial sediment, n = 120	2-38 (7)	nr	2-40 (15)	4-101 (24)	16-**450** (87)	Hudson-Edwards *et al*., 1999a
River Swale at Reeth < 2 mm overbank sediment		0-**59**	5-169	54-**13353**	65-**8224**	Sedgwick, 2000
River Swale at Reeth < 2 mm in-channel sediment		0-**32**	2-58	26-**4818**	26-**12203**	Sedgwick, 2000
Upper River Swale < 63 µm overbank sediments, n = 110	nr	nr	38-42 (49)	**361-1602** (**1230**)	**884-1094** (**1010**)	Walling *et al*., 2003
River Swale 2000 flood < 63 µm overbank sediments, n = 35		**1.2-29.1**		174-**19370**	275-**13920**	Dennis *et al*. 2003

River system	As mg/kg	Cd mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg	Reference
River Swale 2000 flood < 63 µm channel edge sediments, n = 35		0.6-**29.5**		49-**20310**	55-**6500**	Dennis *et al*. 2003
River Swale floodplain sediments: surface (0-20 cm) < 2 mm, n = 297		0-**40**		75-**8052**	50-**3885**	Brewer *et al*. 2005
River Swale floodplain sediments: surface (0-20 cm) < 2 mm, n = 147		0.4-**66**		54-**11990**	60-**4050**	Brewer *et al*. 2005
Humber Estuary						
Sediments (1996)	44	nr	55	129	316	Cave *et al*., 2005
Sediments (pre-industrial estimate)	22	nr	17	22	84	Cave *et al*., 2005
Tyne catchment						
River West Allen < 2 mm overbank sediment, n = 9	nr	5-**33** (17)	22-40 (32)	98-**3166** (**1300**)	74-**1131** (**763**)	Aspinall and Macklin, 1985
River Nent upstream of Blagill, < 2 mm overbank sediment, n = 24	nr	nr	nr	224-**15800** (**5262**)	**4360-38000** (**16320**)	Macklin, 1986
River South Tyne, floodplain sediment	nr	nr	nr	15-**10490**	130-**15270**	Macklin and Lewin 1989
South Tyne and Tyne < 2 mm overbank sediment, n = 93	nr	2.3-116.9 (14.0)	8-**384** (57)	**410-9798** (**2834**)	**590-16520** (**5504**)	Macklin and Smith, 1990
River South Tyne at Blagill < 2mm overbank sediment, n = 15	nr	1.8-**160** (**25.9**)	16.8-228 (59.2)	**2770-13,000** (**7070**)	**791-38,200** (**8270**)	Hudson-Edwards *et al*., 1998
South Tyne < 2 mm in-channel sediment, n = 21	nr	nr	nr	max **6200** (**1192)**	max **8799** (**1885**)	Passmore and Macklin, 1994
River Tyne at Prudhoe < 2 mm overbank sediment, n = 20	nr	2.6-**8.0** (**3.8**)	11.1-42.5 (18.3)	**615-2340** (**1310**)	**722-2340** (**1360**)	Macklin *et al*., 1992; Hudson-Edwards *et al*., 1998
Wear catchment						
Upper River Wear, < 150 µm channel sediment, n = 107	<10-65	nr	<10-**340**	20-**15000**	40-**1500**	Lord and Morgan, 2003
Tees catchment						
Hudeshope beck, < 2 mm overbank sediment, n = 73	nr	<0.05-**17** (**6.1**)	0.5-**388** (17)	63-**26,800** (**9690**)	190-**5180** (**1630**)	Lee, 1989
< 2 mm overbank sediment, n = 15		0.95-**5.95** (2.2)	19.5-76.9 (37)	**522-6880** (**2170**)	404-**1920** (**836**)	Hudson-Edwards *et al*., 1997
Conwy catchment						
Conwy river, active channel sediment < 63 µm				85-**10000**	**1000-10000**	Elderfield *et al*. 1979
Conwy river, active channel sediment < 63 µm				212-**523**	**1091-1187**	Brydie and Polya, 2003

River system	As mg/kg	Cd mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg	Reference
Axe catchment						
River Axe at Wookey Hole Cave, < 2 mm overbank sediment, n = 24	nr	nr	3-27 (14)	226-**25124** (**2642**)	89-**660** (245)	Macklin, 1985
Trent catchment						
Hamps and Manifold rivers < 2 mm floodplain and channel sediment, n = 61		0.25-**21.86** (2.33)	11.4-**5318** (**560.3**)	15.5-**1107.7** (**162.8**)	92-**6391** (**667**)	Bradley and Cox, 1986
River Derwent at Darley Dale, < 2 mm overbank sediment, n = 157		0.08-**12.5** (2.5)	2.9-64 (17.2)	131.4-**1179** (**620**)	9.3-**1696** (194)	Bradley and Cox, 1990
River Derwent at Ambaston, < 2 mm overbank sediment, n = 8	nr	nr	25-49 (36)	**340-1400** (**1020**)	**460-850** (**650**)	Hudson-Edwards and Howard, 2004
Middle Trent at Hoveringham, < 2 mm overbank sediment, n = 7	nr	nr	14-**230** (130)	120-**600** (**420**)	130-**930** (**640**)	Hudson-Edwards and Howard, 2004
Fowey catchment						
Fowey Estuary, < 2 mm intertidal sediments, n = 201	<10-144	nr	19-527	21-120	95-309	Pirrie *et al*., 2002
Ystwyth catchment						
River Ystwyth at Trawscoed < 2 mm overbank sediment, n = 41	nr	nr	nr	73-**4646** (**1791**)	123-**1543** (**533**)	Lewin *et al*., 1983
2 mm-250 µm in-channel sediments, n = 6	nr	nr	nr	**443-795**	190-404	Evans and Davies, 1994
Rheidol catchment						
River Rheidol at Capel Bangor < 2 mm floodplain sediment (0-15cm), n = 16	nr	0.08-3.5	21-85	**291-2098**	242-630	Davies and Lewin, 1974
Rheidol floodplain sediments, < 2 mm, n = 71	nr	0.4-4.4	28-76	**440-2520**	120-680	Swain *et al*., 2005
Severn catchment						
River Severn at Welshpool, < 2 mm overbank sediment, n = 132	nr	0.35-6.4	30-67	23-204	173-**936**	Taylor, 1996

River system	As mg/kg	Cd mg/kg	Cu mg/kg	Pb mg/kg	Zn mg/kg	Reference
Catchments elsewhere in the world						
Mining- and industrially-contaminated sites in Belgium, Germany and the Netherlands, n = 34	<5-**69** (16)	nr	<10-**736** (25)	<10-**1600** (**89**)	**378-2477** (**716**)	De Vos *et al*., 1996
River Camaquã, Brazil, n = 31-37	nr	nr	17.3-112.2 (49)	3.5-**109.5** (39)	26.5-138 (70)	Pestana *et al*., 1997
Rio Tinto, Spain, n = 14	**110-750** (**370**)	nr	75-**1500** (**300**)	**490-3100** (**2800**)	<20-**1300** (200)	Hudson-Edwards *et al*., 1999b
Upper Río Pilcomayo, Bolivia, n = 7	**210-7200** (**2500**)	**6.9-190** (**62**)	88-**1400** (**490**)	**230-1700** (**960**)	**1800-10000** (**8200**)	Hudson-Edwards *et al*., 2001
Rio Guadiamar, Spain, Reach 1, n = 37	**20-1200** (**320**)	0.5-**12** (**4.7**)	17-**490** (**260**)	50-**2700** (**990**)	140-**4600** (**1200**)	Hudson-Edwards *et al*., 2003
Someş channel sediments, NW Romania	**19-5330** (**554**)	0.8-**110** (**21**)	12-**8400** (**960**)	28-**6800** (**1400**)	64-**19600** (**3900**)	Macklin *et al*., 2003
Someş floodplain sediments, NW Romania	8.8-300 (102)	<0.1-41 (3)	11-**880** (110)	18-**2760** (439)	54-**9200** (368)	Macklin *et al*., 2003
Vişeu channel sediments, NW Romania	7-**600** (**69**)	0.6-**75** (**5.7**)	3.6-**2900** (**420**)	13-**2800** (**340**)	120-**7200** (1100)	Macklin *et al*., 2003
Vişeu floodplain sediments, NW Romania	9-260 (102)	0.5-17 (4)	32-**1000** (291)	17-850 (330)	110-**2760** (**1177**)	Macklin *et al*., 2005
Mureş channel sediments, NW Romania	3-**850** (**95**)	0.3-**500** (**21**)	0.3-**26000** (**510**)	1-**270** (**270**)	3-**50800** (**1700**)	Bird *et al*., 2005
Mureş floodplain sediments, NW Romania	4-400 (71)	0.2-7 (2.3)	21-115 (60)	14-550 (120)	50-1000 (250)	Bird *et al*., 2005
Guideline concentrations						
Environment Agency draft sediment quality guidelines: threshold effective level (TEL)	5.9	0.596	36.7	35	123	Environment Agency
Environment Agency draft sediment quality guidelines: predicted effect level (PEL)	17	3.53	197	91.3	315	Environment Agency
Livestock grazing (ICRCL 70/90) threshold trigger concentrations for mining sites	500	50	500	1000	3000	ICRCL, 1990
Crop growth for animal consumption (ICRCL 70/90) threshold trigger concentrations for mining sites	1000	**30**	250	-	1000	ICRCL, 1990

Appendix 2 – Methodology for assessment of metal mining-affected river systems in England and Wales

This appendix gives information (taken from Brewer *et al*., 2005) on constructing the Geographic Information System (GIS), carrying out sediment sampling and geochemical analysis, and constructing the probability of contamination valley floor maps.

Establishing and creating digital maps of the river corridor

The river corridor can be established by digitising the river channel and bar features on all available editions of Ordnance Survey (OS) maps and OS Landline data maps, and using air photographs for supplementary information. For English and Welsh catchments, the earliest editions of these maps date to the early-mid nineteenth century when metalliferous mining was at its peak. For each map edition, channel boundaries, active gravel areas and vegetated areas of bar surfaces should be digitised, stored and manipulated using a GIS digitising package (such as, ESRI ArcMap, Mapinfo) and transformed into National Grid Reference (NGR) coordinates. All digitised map editions should then be combined, creating a composite map of all river channels, which can then be classified to show the river corridor at all different stages of development.

Sediment sampling and analytical programme

This should follow guidelines set out by the Department of the Environment (1994) and the Environment Agency (2000), as discussed in Brewer *et al*. (2005). Sampling grids should be established on a field-by-field basis, and scaled to reflect the size of each individual parcel of land. A grid spacing appropriate to the size of the catchment and agricultural fields or other parcels of land should be employed and both surface (0-20 cm) and subsurface (20-50 cm) soil samples collected on a square grid pattern across each study site using a stainless steel auger. Appropriate measures should be taken to allow sampling uncertainty to be quantified such as duplicate samples (Ramsey, 1998). The exact position of each sample point should either be surveyed using differential GPS, or recorded on a hand-held GPS instrument.

A number of studies have shown that metals are not uniformly distributed over different grain size fractions, with most metals displaying a significant affinity for fine-grained sediment (Horowitz, 1991). It is therefore extremely important that the particle size selected for geochemical investigation is standardised (Förstner and Wittmann, 1979). Sampling of material with a diameter of less than two mm has been recommended by MAFF (1986) and Grimshaw (1989), and a considerable number of previous investigations have focussed on material of this size (*see* Lewin *et al.*, 1983; Hudson-Edwards *et al.*, 1996,1999b; Macklin *et al.*, 1997).

Sediment digestion and analytical techniques are discussed in Brewer *et al*. (2005). It is important to adopt rigorous quality assurance procedures for collection of samples in the field, and during laboratory analysis. As an alternative to laboratory-based analysis of soil and sediment samples, field techniques for analysing metal concentrations (such as portable X-ray Fluorescence [XRF]) should be considered. Currently available equipment should be able to provide rapid results with sufficient accuracy.

Estimating background sediment-borne metal concentrations

A statistical technique presented by Davies (1983) is employed to determine background concentrations of metals in a catchment. In this method, geochemical data containing normal and anomalous values are divided into contaminated and background populations using probability plots. Similar graphical techniques have been extensively used in exploration geochemistry to identify the presence of mineral deposits (Lepeltier, 1969; Parslow, 1974; Sinclair, 1974). The technique has also been employed in the determination of background Pb concentrations in British soils (Davies, 1983), and for a range of elements in Missouri, USA (Davies and Wixson, 1985; Fleischhauer and Korte, 1990) and north eastern Spain (Tobías *et al.*, 1997a, b).

Fundamental to this technique is the fact that when the cumulative frequency distribution of a normally distributed data set is plotted on a probability scale, the resulting curve takes the form of a straight line (Parslow, 1974). However, most geochemical data are not normally distributed. Instead, it is generally agreed that trace element concentrations in soils are log-normally distributed (Tennant and White, 1959; Sinclair, 1974). When these data are transformed to their $\log_{10}$ equivalents, they also plot as a straight line on a probability scale. Significant deviations from a straight line indicate that the data are not normally or log-normally distributed (Lepeltier, 1969; Parslow, 1974). In reality, most geochemical data are not normally or log-normally distributed, and their resulting probability curves consist of two straight-line segments, linked by a complex curve. These can be interpreted as representing two separate populations within the data (Tennant and White, 1959). In cases where metal enrichment has occurred, these straight lines are believed to represent the anomalous and background parts of the sample population respectively (Parslow, 1974). The background population can thus be separated from the anomalous population, and simple descriptive statistics derived from the former can be used to calculate the background threshold, that is, the likely upper limit of a particular element within the background population (Lepeltier, 1969; Sinclair, 1974; Davies, 1983). Four stages should be followed in order to derive background metal concentrations for soils in a particular catchment:

(1) All river channel and floodplain geochemical data from the catchment should be compiled into a single data set from which background concentrations can be determined. If simple descriptive statistics indicate that the data are highly skewed, following Davies (1983), they should be converted to their $\log_{10}$ equivalents. To derive a suitable class interval for compiling a frequency distribution of the data (for geochemical purposes, Lepeltier (1969) recommended the use of between 10 and 20 class intervals), the optimum class width is derived from the formula:

$$\text{Log interval} = \frac{\log(\text{maximum value / minimum value})}{\text{number of class intervals}} \quad (1)$$

(2) The percentage frequency distribution of the data can then be calculated (for example, using the Histogram function in Microsoft Excel), and accumulated from the highest to lowest values (Lepeltier, 1969; Davies, 1983). Cumulative frequency data for each element can then be plotted on a probability scale. This is easily achieved within specialist graphing packages (such as MINITAB). The data appear in the form of a complex curve, with straight line portions at the lowest and highest levels. The background population within the data is shown as the straight line on the lower part of the cumulative frequency curve, and the transition between the lower straight line and the complex section of the curve marks the point where the background population can be separated from the enriched population (Figure 13; *cf.* Davies, 1983).

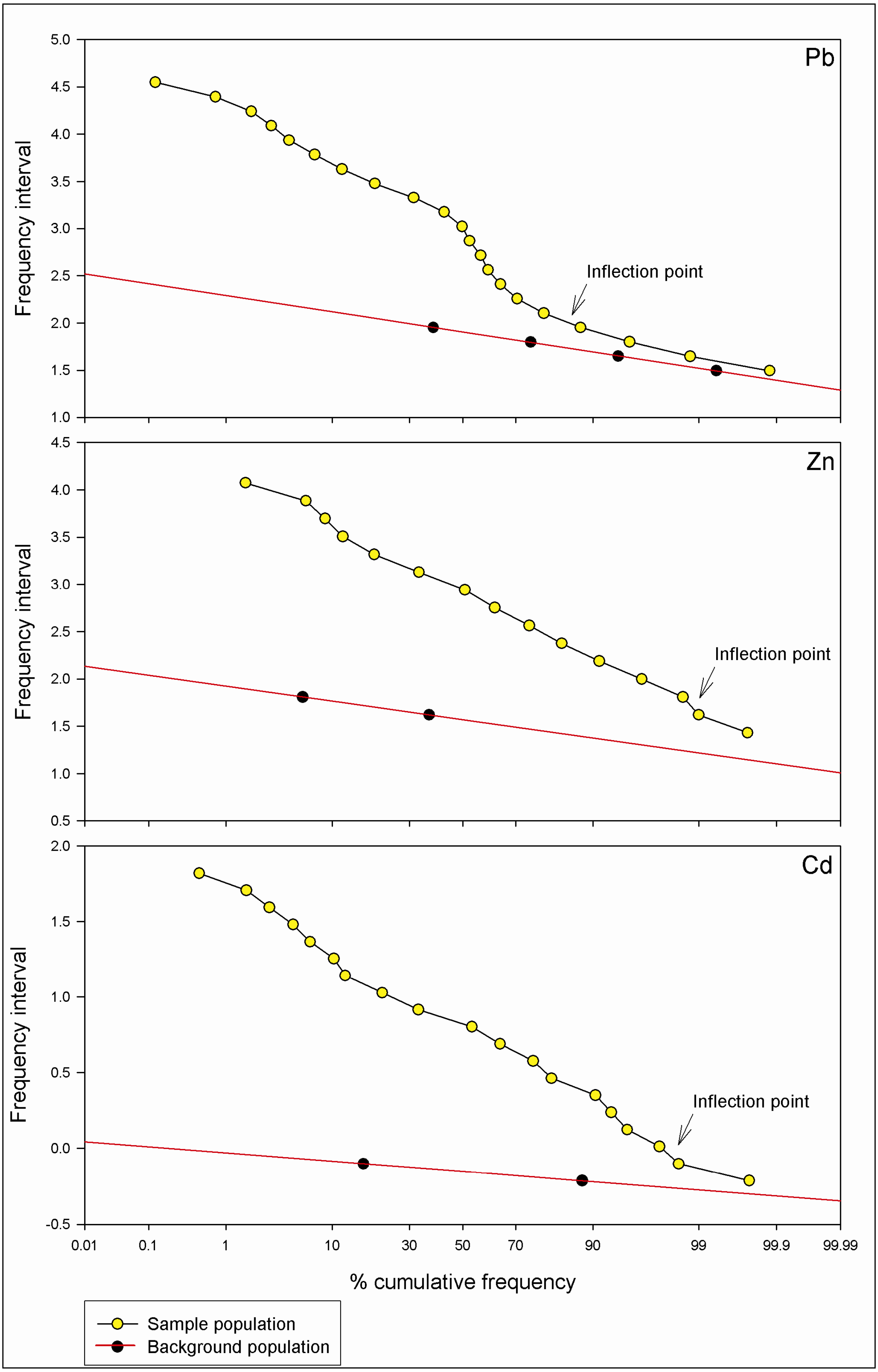

Figure A2: Probability curves and calculated background populations for Cd in the River Swale catchment.

(3) Several steps are required to separate the background population from the enriched population (Davies, 1983). Initially, the percentage cumulative frequency at which the straight line changes to a complex curve is identified. This can be estimated directly from the graph, although the procedure can be problematic in cases where there are 'elbows' in the data, and may be open to bias (Parslow, 1974; Fleischhauer and Korte, 1990). However, work by Fleischhauer and Korte (1990) has demonstrated that small variations in the estimation of the position of the inflection point on the curve are unlikely to significantly influence the resulting background concentration threshold.

The class intervals that comprise the background population can be identified as those that fall below the graphical threshold. The cumulative frequency of each of these points (F) can be recalculated using the formula:

$F' = 100 – (100-F) \times (100/c)$

(2)

where F' is the recalculated frequency and c is the cumulative frequency of the linear portion of the curve (or 100 – cumulative frequency of the inflection point). The threshold that marks the upper limit of the background population can then be derived from simple descriptive statistics of the recalculated background population (Lepeltier, 1969; Davies, 1983) using Microsoft Excel. First, the geometric mean (XM), which corresponds to the antilog of the 50 per cent cumulative frequency, can be calculated. Second, the geometric deviation of the arithmetic data (SM) can be calculated. This corresponds to the antilog of the standard deviation of the $\log_{10}$ data, derived from the formula:

$SM = ½ (16^{th}$ percentile – 84^{th} percentile)

(3)

(4) Finally, the background threshold can be calculated by the formula:

Threshold = $XM \times SM^3$

(4)

The background population (F') can be plotted, and a regression line fitted through the data. The resulting regression equation is then used to derive the 16^{th}, 50^{th} and 84^{th} percentiles, and the background concentration threshold values calculated using Equations 3 and 4.

Confirmation of robustness of contamination mapping by comparing metal concentrations in different floodplain contamination zones using a Kruskal-Wallis H test

To verify that metal concentrations in the three floodplain zones were statistically different, a non-parametric Kruskall-Wallis H test was conducted. Observations were ranked across the groups and summed to give a single score for each group (Shaw and Wheeler, 1994). These scores were then used to calculate the test statistic, H. A significant difference between the groups exists if the H statistic is greater than the critical value of χ^2 at k-1 degrees of freedom (where k is the number of groups). Both areas with a high probability of land contamination and areas with a likelihood of land contamination will have the highest mean ranks.

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