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The use of geomorphological mapping and modelling for identifying land affected by metal contamination on river floodplains

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Research and Development

Final Project Report

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Project title	The use of geomorphologi affected by metal contamined by metal contamin	ical mapping and modelling nation on river floodplains	g for identifying land
DEFRA project code	SP 0525		
Contractor organisation and location	Institute of Geography and University of Wales, Abery Ceredigion, SY23 3DB		
Total DEFRA project costs	£ 20 012		
Project start date	01/02/03	Project end date	01/05/03

Executive summary (maximum 2 sides A4)

As the result of past and present mining, processing and utilisation of base metals, many river floodplains in the UK have become contaminated by metal-rich waste in concentrations that may pose a hazard to ecosystem and human health. The importance of this issue was further highlighted during the autumn 2000 floods that resulted in significant reworking of metalliferous waste, particularly in former mining and industrial areas, and widespread deposition of metals on agricultural floodplain soils. Predicted increases in flooding related to a changing climate, and growing development pressure in floodplain areas, makes R&D on this topic a high priority.

The primary goal of this scoping study was to field test geomorphological mapping and modelling techniques for assessing potential hazards arising from metal contamination in UK river floodplains. This has very important practical implications for environmental management and protection in river basins, and represents a generic, process-based framework for monitoring the movement of particulate-borne metals in rivers, and for identifying areas of potentially contaminated land on floodplains.

The main findings of the project are:

- 29.1 km² of the valley floor of the River Swale is likely to be contaminated with Pb, Zn and Cd.
- In upper Swaledale (west of Catterick), contaminated floodplain soils tend to be located up to 2 m above the present river channel.
- Pb, Zn and Cd concentrations in sub-surface samples (20-50 cm below ground level) are significantly higher than those found at the surface of the Swale floodplain.
- 91% and 94% of all surface and subsurface floodplain soil samples, respectively, have Pb concentrations that exceed background levels.

- 94% of all surface and subsurface floodplain soil samples contain Zn concentrations that exceed background levels.
- Background concentrations of Cd are exceeded by 90% of surface samples and 95% of subsurface samples.

In the light of these findings, we strongly recommend the following programme of targeted and strategic research:

- To carry out a series of spot checks on individual agricultural fields in the Swale catchment (particularly in the Vale of York, downstream of Catterick), to confirm, or refine, floodplain soil metal contamination maps.
- To investigate contaminated floodplain soil source-pathway-receptor relationships more fully in the Swale catchment and to establish the degree to which metals pose a hazard to environmental and human health.
- To further test the use of geomorphological mapping and modelling for identifying floodplain land affected by metal contamination in other catchments in England and Wales also affected by historical mining. This should include the former base metal mining areas of mid-Wales, the Northern Pennines and southwest England.
- To develop environmental quality guidelines appropriate for assessing the hazards posed by contamination on agricultural land, which can also inform compliance and implementation of the new European Union Water Framework Directive.

Scientific report (maximum 20 sides A4)

1. INTRODUCTION

Since the late 1970s it has been recognised from research carried out in both Europe and North America that the dispersal and accumulation of sediment-associated metals in the river environment can be directly related to sediment transport processes, channel and floodplain sedimentation styles, and flooding regime (Lewin *et al.*, 1977; Lewin and Macklin, 1987; Leenaers, 1989; Graf, 1994; Macklin, 1996; Miller, 1997; Coulthard and Macklin, 2003). This arises because more than 90% of metals in river systems are carried in a particulate-bound form and follow the same transport pathways as the natural sediment load of a river. A corollary of this is, if river sediment dynamics can be modelled, then so can the long-term and large-scale movement, and storage, of sediment-borne metals in river systems.

The primary goal of this scoping study was to *field* test geomorphological mapping and modelling techniques for assessing potential hazards arising from metal contamination in UK river floodplains. This was undertaken in the River Swale, northern England, which was severely contaminated by historical base-metal mining (Macklin *et al.*, 1994) and was also badly affected by the autumn 2000 floods that resulted in widespread deposition of metals on floodplain soils (Dennis *et al.*, 2003) The River Swale has been chosen for two principal reasons. First, the River Basin Dynamics and Hydrology Research Group, at the University of Wales Aberystwyth, have a comprehensive GIS database of metal concentrations in floodplain soils (surface and sub-surface) for the region. Second, the Swale catchment contains the full range of floodplain environments commonly encountered in the UK, which are likely to make the results from this study directly applicable to other similarly contaminated floodplains elsewhere in the country.

This report is divided into three sections. In the first section the methodology used for identifying land affected by metal contamination on river floodplains is described in detail. This forms a substantive part of the report as it is intended that geomorphological mapping and modelling, particularly through its use of GIS, will assist the Department for Environment, Food and Rural Affairs (DEFRA), the Environment Agency (EA) and Local Authorities (LAs) in their assessment of floodplain areas affected by sediment-borne contamination. In the second part of the report data are presented on: (i) present day flooding regime and associated metal concentrations in floodplain soils; (ii) the spatial variability of metal concentrations in floodplain soils and its relationship to past and present river sediment dynamics; and (iii) the extent of floodplain contamination in the Swale catchment. Finally, in the concluding section, the main implications of this study for environmental policy and management are summarised and a series of future research priorities are outlined.

2. METHODS

Geomorphological mapping and modelling have been undertaken to identify land affected by metal contamination in the River Swale catchment, northern England, at two complementary spatial scales. These are local, river reach studies and river corridor investigations of the entire Swale catchment.

2.1 Reach investigations

2.1.1 Study sites

The relationship between flooding regime and metal concentrations in floodplain soils has been assessed immediately south of Reeth and at a second site centred on Brompton-on-Swale (Figure 1; see Annex 2 for all figures). These were carefully selected because present day (as well as historical) patterns and rates of river channel movement, bank erosion and floodplain sedimentation at these sites are typical of those found in the upper and middle parts of the Swale valley (west of Great Langton, Figure 1), which was severely affected by base metal mining during the 19th century (Macklin *et al.*, 1994).

The study reach at Reeth (Figure 2, SE 034 988) is 1.5 km long and covers an area of 0.18 km². It is located 2.3 km downstream of Barney Beck, within which some of the largest lead mines, crushing and smelt mills in the region were located. In the Millennium Floods of autumn 2000, and in subsequent flood events, Barney

Beck has been identified as one of the principal sources of mining-related metals to the River Swale (Dennis *et al.*, 2001; Dennis *et al.*, 2003).

Metal mining and processing activities during the late 18th and 19th centuries released large quantities of mine waste into the River Swale. This caused significant and widespread long-term contamination, primarily through overbank deposition, of fine grained (< 2 mm) metal-rich sediment. High in-channel and overbank sedimentation rates during this period also resulted in valley floor aggradation of between 1.0–1.5 m, which buried earlier alluvial deposits. Metal contaminated mining age (late 18th and 19th century) alluvium at Reeth, and at many sites throughout the Swale Valley, is sedimentologically and visually distinctive, consisting of alternating light and dark layers (*c*. 0.5–5.0 cm thick) of sand and silty sand, respectively. They overlie earlier, pre-mining floodplain sediments that are usually un-bedded, have a higher proportion of silt and clay, are more cohesive and resistant to bank erosion, and frequently contain significant quantities of sub-fossil wood. A ¹⁴C date on wood from this older unit at Reeth (SE 03560 98889) gave a calibrated age of between AD 1210 and AD 1295, indicating that it was deposited during the late Mediaeval period.

In the 20th century the River Swale at Reeth continued to move at both the western end and in the central part of the study reach, laterally eroding and reworking earlier floodplain sediments. However, partly in response to a reduction in river sediment loads (following mine closure), and to some extent as the result of engineering works that attempted (unsuccessfully) to straighten the channel, the River Swale has progressively incised its bed, undermining adjacent river banks and making them more prone to erosion and collapse.

The second study reach at Brompton-on-Swale (Figure 3, SE 213 996) is 2 km long and extends over 0.29 km². It lies outside of the area directly affected by mining operations and is located 15 km downstream of the nearest major mine at Hurst (SE 045 023). In contrast to the Swale at Reeth, the position of the river channel at Brompton has changed relatively little since the middle of the 19th century. The only significant change over the last 150 years has been the stabilisation by vegetation of former lateral and point bars, principally as the result of bed incision.

2.1.2 Floodplain soil sampling protocol

A systematic sampling protocol was employed in this investigation, following guidelines produced by the Department of the Environment (1994) and the Environment Agency (2000). Sampling grids were established on a field-by-field basis, and were scaled to reflect the size of each individual parcel of land. A grid spacing of 25 m was employed in smaller fields (up to 1 ha), ranging up to 100 m in larger areas of land. Surface (0–20 cm) and subsurface (20–50 cm) soil samples were collected on a square grid pattern across each study site using a stainless steel Edelmann auger. Duplicate samples, consisting of five sets of samples collected within a 1 m radius, were taken at 10% of the sampling sites, to allow sampling uncertainty to be quantified (Ramsey, 1998). Coefficient of variation for these duplicate samples ranged from just under 11% (Zn) to just over 21% (Cd) (Table 1; see Annex 1 for all tables). All equipment was cleaned thoroughly after each sample was collected, and samples were stored in clean, wet-strength paper bags. The exact position of each sample point was surveyed using a Trimble 5700 differential GPS (horizontal resolution \pm 10 mm, vertical resolution \pm 20 mm).

2.1.3 Laboratory geochemical analytical procedures

Particle size selection: 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). Current legislation defines contamination thresholds for soil, which is generally considered to consist of material with a diameter of < 2 mm (Grimshaw, 1989). Sampling of this size-fraction has been recommended by MAFF (1986), and a considerable number of previous investigations have focussed on material of this size (*e.g.* Lewin *et al.*, 1983; Hudson-Edwards *et al.*, 1996; Macklin *et al.*, 1997; Hudson-Edwards *et al.*, 1999b). The < 2 mm size-fraction was therefore selected for use in this investigation.

The use of geomorphological mapping and modelling for identifying land affected by metal contamination on river floodplains

Initial sample preparation: Prior to analysis, all sediment samples were oven dried for 24 hours at 40°C and then thoroughly disaggregated in a porcelain mortar and pestle. All samples were then dry-sieved through stainless-steel mesh (as recommended by Grimshaw, 1989), and the < 2 mm size-fraction collected for geochemical analysis. Sieved samples were stored in sealed polythene bags to prevent contamination. Lids were used at all times to minimise dust-generation, and work surfaces were covered in clean polythene sheets, which were replaced at regular intervals. All equipment was cleaned thoroughly between sample preparations.

Digestion procedure: A variety of extraction techniques are available for the determination of metal content in soils. Standard procedures involve either the dissolution of samples and the analysis of resulting solutions, or the direct analysis of solid material (Gill, 1997). A solution method was selected for this investigation due to the ease of standardisation and comparative lack of matrix effects. Although "total" extraction techniques have been used to determine the full metal content of a sample (Chao and Sanzolone, 1992), partial metal extraction techniques are often considered a more appropriate measure of metal content for environmental studies where potentially bioavailable adsorbed contaminants are present (Totland *et al.*, 1992; Walsh *et al.*, 1997).

In this investigation, a hot nitric acid (HNO₃) digestion procedure was used to extract heavy metals from soil samples prior to geochemical analysis (Figure 4). This technique has been widely employed in investigations of fluvial contamination in the UK and overseas (*e.g.* Lewin *et al.*, 1983; Brewer and Taylor, 1997; Langedal, 1997; Hudson-Edwards *et al.*, 1999a; Dennis *et al.*, 2003; Walling *et al.*, 2003), and is particularly effective at decomposing sulphide minerals and carbonates that are present in the Swale catchment. In addition to this, HNO₃ is frequently selected in investigations involving high-precision analytical techniques because it produces fewer spectral interferences and a clearer background signal than other common extractants such as *aqua regia* (Hall, 1992; Walsh *et al.*, 1997). All glassware and plastic equipment was washed for 24 hours in 15% HNO₃ prior to use to prevent contamination (*cf.* Masse and Maessen, 1981) and AnalR grade reagents were used to prevent the introduction of contaminants (Walsh *et al.*, 1997).

ICP-MS analysis: Concentrations of Cd, Pb and Zn were measured using a VG Elemental PlasmaQuad ICP20P Inductively Coupled Plasma-Mass Spectrometer (ICP-MS). ICP-MS analysis was selected because (i) a wide range of elements can be measured simultaneously, with sample analysis typically lasting under 60 seconds (Hall, 1992); and (ii) the technique is extremely precise, with a relative standard deviation of between 2 and 10%, and highly accurate (Jarvis, 1997).

Two analytical quality control procedures were adopted: (i) samples were analysed in a random order, to minimise the effects of cross-contamination (Thompson, 1992); and (ii) a series of reagent and water blanks (solutions with zero analyte concentrations) were used during each run to allow any contamination introduced during sample preparation to be identified and subsequently removed from results (Ramsey *et al.*, 1987; Thompson, 1992).

Analytical uncertainty was quantified in three ways (Table 1): (i) samples of a synthetic solution containing known concentrations of all analytes were included in each run to correct instrumental calibration and determine *instrumental accuracy* (Ramsey *et al.*, 1987); (ii) *analytical precision* was quantified by conducting duplicate analyses of 20 field samples; and (iii) *analytical bias* was determined by analysing two Certified Reference Materials (GSS-1 and GSD-12) as an independent check on results (Ramsey, 1998). Reference materials were inserted randomly into each batch, and made up approximately 10% of all analyses (Thompson, 1992).

2.1.4 Environmental quality guidelines for metal concentrations in soil

Several sets of environmental quality guidelines for metal concentrations in soil are currently available in the UK, each applicable to different sources of contamination (Table 2). The use of DEFRA Soil Guideline Values (DEFRA, 2002) is recommended for land contaminated by former industrial activities. These are applicable to residential land (with and without plant uptake), allotments, and industrial and commercial sites. For agricultural land contaminated by sewage sludge, values from the MAFF *Code of Good Agricultural Practice*

for the Protection of Soil (MAFF, 1998) are most commonly used. The Inter-Departmental Committee on the Redevelopment of Contaminated Land (ICRCL) Guidance Note 70/90 is designed for former mine sites subsequently re-developed for agriculture (ICRCL, 1990).

Assessment of floodplains affected by historical metal mining and used for agricultural purposes is, however, problematic, since no specific guidelines presently exist. DEFRA Soil Guideline Values apply only to specific land uses where human exposure to contamination could be a problem. MAFF guideline values are only intended to regulate the application of sewage sludge to agricultural land, and may not be appropriate for use in cases where contamination is derived from other sources. The ICRCL 70/90 guideline concentrations apply to former mine sites that are being reclaimed for agricultural purposes. However, the Swale floodplain is a semi-natural system that has been receiving contaminant metals produced by mining activity for many hundreds of years. It has not been "restored", and the use of ICRCL 70/90 guidelines for the aftercare of mining sites may not be entirely appropriate. Since no suitable environmental quality guidelines for the assessment of floodplain contamination as a result of historical metal mining exist within UK legislation, an alternative approach was developed.

2.1.5 Estimating background metal concentrations

An alternative approach for assessing the environmental impact of historical metal mining on river basins is to compare metal concentrations with estimates of the pre-mining 'background' concentration in a catchment. The use of background concentrations has two principal advantages over legislated environmental quality guidelines that are presently available. First, they are specific to the area for which they are obtained, and therefore take into account local factors such as the enrichment of stream sediments with metals through natural weathering and erosion processes (*e.g.* Helgen and Moore, 1996). Second, their use avoids the present incompatibility with existing environmental quality guidelines for assessing fluvial sediments contaminated by historical metal mining.

In this investigation, a statistical technique presented by Davies (1983) was employed to determine background concentrations of Pb, Zn and Cd in the Swale 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 utilised 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; 1997b).

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 log₁₀ 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, *i.e.* the likely upper limit of a particular element within the background population (Lepeltier, 1969; Sinclair, 1974; Davies, 1983). Four stages were followed in order to derive background metal concentrations for soils in the Swale catchment:

1. All floodplain geochemical data from the Swale valley were compiled into a single data set from which background concentrations could be determined. Simple descriptive statistics indicate that the data are

highly skewed (Table 3), and following Davies (1983) were 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 was derived from the formula:

Log interval = log (maximum value / minimum value) number of class intervals

(1)

For twenty class intervals, class widths of 0.15, 0.19 and 0.11 were calculated for Pb, Zn and Cd, respectively.

- 2. The percentage frequency distribution of the data was then calculated using the Histogram function within Microsoft Excel 2003, and accumulated from the highest to lowest values (Lepeltier, 1969; Davies, 1983). The cumulative frequency data for each element were then plotted on a probability scale (Figure 5). This is easily achieved within specialist graphing packages, but a probability scale is generally unavailable in non-specialist packages such as Microsoft Excel. However, data can be simply transformed to the linear equivalents of a probability scale using the =NORMSINV() function, and plotted on a linear scale. 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 (*cf.* Davies, 1983).
- 3. Several steps are required in order 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 was 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. For the River Swale, the determination of the inflection point was relatively straightforward for Pb, where the curve clearly displays two straight-line populations (Figure 5). However, this procedure was more problematic for Zn and Cd, which plot as a straighter line on a probability scale. Nevertheless, a lower straight-line portion of the complex curve can still be readily identified (Figure 5).

The class intervals that comprise the background population were identified as those that fall below the graphical threshold. The cumulative frequency of each of these points (F) was 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), calculated using Microsoft Excel 2003. First, the geometric mean (*XM*) was calculated, which corresponds to the antilog of the 50% cumulative frequency. Second, the geometric deviation of the arithmetic data (*SM*) was calculated, that corresponds to the antilog of the standard deviation of the \log_{10} data, derived from the formula:

$$SM = \frac{1}{2}$$
 (16th percentile – 84th percentile)

(3)

4. Finally, the background threshold was calculated by the formula:

Threshold =
$$XM \times SM^3$$

The background population (*F*) was plotted, and a regression line was fitted through the data. The resulting regression equation was used to derive the 16^{th} , 50^{th} and 84^{th} percentiles, and the background concentration threshold values were then calculated using Equations 3 and 4 (Table 4). These values are lower than the environmental quality guidelines that currently exist in UK legislation (Table 2).

2.1.6 Flood inundation modelling using HEC-RAS and HEC-geoRAS

The return periods of discharges used in the flood inundation modelling at Reeth and Brompton-on-Swale were calculated using the Gumbel "peaks over threshold" analysis based on a 10-year flow record from the Catterick Bridge gauging station (SE 226993). The "peaks over threshold" method is particularly good for estimating the mean annual flood from records as short as 3 to 10 years (NERC, 1975) and for assessing the frequency of relatively frequent events.

To calculate flood return periods, maximum daily flows at Catterick Bridge exceeding 250 m³ s⁻¹ were selected and ranked from largest to smallest. The probability of each event occurring was calculated using the Weibull formula:

$$F = \frac{m}{n+1}$$
(5)

(4)

where F is the frequency, m is the rank order of the event and n is the number of years. The probability of each event was then plotted on a normal probability chart with magnitude on the y-axis and probability of occurrence on the x-axis. A straight line was then fitted to the data and return periods calculated. Flood return periods and their corresponding discharges are given in Table 5.

HEC-RAS (Hydrologic Engineering Center-River Analysis System), developed by the US Army Corps of Engineers (USACE, 2001), is a 1-dimensional flow modelling package that uses a combination of channel and floodplain cross sections to simulate flow inundation areas. In both study reaches, cross sections were derived from 3-dimensional digital elevation models (DEMs) of the valley floor created from Triangular Irregular Networks (TINs). At Reeth, the TIN was created using spot heights measured by differential GPS survey and the TIN for the Brompton-on-Swale reach was created using Environment Agency filtered LiDAR data. The precision of the modelled inundation areas at each site is related to the number, location and spacing of cross-sections. Around meander bends, cross sections were spaced every 20 m and in straight reaches every 100 m. A total of 112 cross sections were used at Brompton-on-Swale and 38 at Reeth. Once the cross sections had been created in ArcView 3.2 (using the HEC-geoRAS extension), they were imported into HEC-RAS as geometric data. These data were then edited within HEC-RAS to re-define bank positions and to add levees, where they were present.

The simulation was run for both reaches using the Steady Flow Data option within HEC-RAS using the 11 return periods given in Table 5. For each return period the boundary conditions were set to "critical depth". Once the simulation had been performed, the data were exported back into ArcView and following the HEC-geoRAS post-processing options, a set of layers were produced and draped over the valley floor TIN, to show areas and depth of inundation associated with each discharge.

The use of geomorphological mapping and modelling for identifying land affected by metal contamination on river floodplains

2.2 River corridor investigations

In engineering terms, a river corridor has been defined by the limit of the so-called "hundred-year flood" (Gardiner and Cole, 1992), shown by the Environment Agency's 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 a very useful one by emphasizing longer-term linkages (and interaction) between river channels and their floodplains. In the case of the environmental effects of historical base-metal mining in the Swale catchment, the practice of discharging fine-grained metal waste directly into the nearest watercourse, with little or no treatment, resulted in sediment-associated metal contaminants being dispersed many 10s of km from their point of origin (Lewin *et al.*, 1977).

Under low flow conditions (sub-bankfull) contaminated material was deposited within the banks of the river, on the bed of the channel and on river bars. Furthermore, because under non-flood conditions mine waste would have comprised virtually the entire particulate load, 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 the knowledge that more than 90% of most metals are carried in a particulate bound form (certainly the principal contaminant metals [Cd, Pb, Zn] in the Swale catchment) and follow the same transport pathways as the natural load of a river, modelling and mapping longer term sediment dynamics can provide important information on the geographical distribution of sediment-borne contaminants in river systems. In the Swale catchment this has been done in three stages. First, to identify patterns of planform change along the River Swale, 1st edition 1:10,560 Ordnance Survey (OS) maps (dated 1854) and 1:10,000 OS Landline data (c.1982) maps were used. These were chosen as they represent the earliest and most recent, respectively, surveys available for the entire Swale valley. All OS maps adopt a consistent definition of river bank position as "normal winter water level" (Harley, 1975), which ensures comparability between maps of different dates. For each map edition, channel boundaries, active gravel areas and vegetated areas on bar surfaces were digitised using PC ARC/INFO and transformed into National Grid Reference (NGR) coordinates. The two digitised map editions were then combined, creating a composite map of the two river channels, which was then classified to show: (i) the River Swale channel and bars in 1854, during the peak of metal mining; (ii) the area of floodplain that the river has migrated across between 1854 and 1982; and (iii) the River Swale channel and bars in 1982. As a consequence of later river movement and bed incision, river bars and segments of channel dating to the mid-19th century, contemporary with the peak of mining in the Yorkshire Dales and likely to contain sediments with high metal concentrations, have been incorporated into the Swale floodplain. These are expected to constitute some of the most important contaminant "hotspots".

The second stage required collating all published (Macklin et al., 1994; Taylor and Macklin, 1997, Sedgwick, 1998; Hudson-Edwards et al., 1999b; Dennis et al., 2003) and unpublished (Carter, 1998; Sparks, 1998; Sedgwick, 2000; this study) data on metal levels in floodplain soils within the Swale catchment (a total of 444 samples) and importing into ArcView. Using this database, the surface (0-20 cm) and subsurface (20-50 cm) distribution of Cd, Pb and Zn in the floodplain of the River Swale has been evaluated at nine reaches (including Reeth and Brompton-on-Swale), located between 5-25 km apart (Table 6), from Hartlakes downstream to Myton-on Swale, where the Rivers Swale and Ure join. Sample points at these sites (Figures 6-14) have been plotted at a scale that allows metal concentrations in individual agricultural fields to be assessed and the extent of land contamination to be mapped with some accuracy. Geochemical data on these maps have been plotted as proportional charts that reflect absolute metal concentrations at each sample site. This approach enabled the maximum distance from the present river channel that Pb levels exceeded background levels by at least 5 times to be determined (Figure 15). This value represents more than 3 times the standard deviation of uncontaminated samples, and should therefore account for 99% of uncontaminated floodplain sediments. The maximum distance of metal enrichment was found to range from 25-200 m in the upper and middle Swale valley (downstream as far as Brompton-on-Swale), while in the lower reaches floodplain land contaminated by Pb extends between 50-400 m from the present channel. These data have been used to help define the maximum extent of likely land contamination (see below). Noteworthy is the fact

that at a majority of these reaches metal contamination extends across nearly half of the valley floor mapped by the EA as Indicative Floodplain.

The third and final stage of mapping the geographical distribution of metals in the Swale valley has been to delineate the maximum likely extent of floodplain contamination along the entire river corridor, outside of the nine reaches described above. This has been done by using the break of slope between the lower lying valley bottom (inundated both during and after the mining period) and adjoining, upstanding river terraces or hill slopes, which are visible on 1:5,000 colour aerial photographs. In the higher relief and generally narrower parts of Swaledale (down as far as Brompton-on-Swale), this generally coincides with the contour line nearest the present river channel, but does not always follow the EA's Indicative Floodplain limit. Downstream of Brompton-on-Swale the valley widens and floodplain relief is more subdued. However, breaks of slope delineating river terraces are still evident on aerial photographs and the likely maximum extent of contamination has been mapped along the foot of the nearest major terrace scarp (≥ 2 m in height), adjacent to the present river channel. This has been "ground truthed", and validated, at the Great Langton, Morton Flatts, Maunby, Thornton Manor and Myton-on-Swale reaches. One unexpected result from this mapping exercise was that in the lower reaches of the River Swale (downstream of Great Langton), which have extensive embankments for flood protection, high levels of heavy metals are found in the floodplain both within and outside of the levees. These structures were constructed at the beginning of the 19th century (c.1808-1814) and postdate the first phase of large-scale metal mining that began around 1780. Thus, before they were in place floodwaters containing mine waste would have been less constrained. Periodic breaching of embankments by large floods, particularly during the 19th century, would also have contributed to the more widespread dispersal of metals across the Swale floodplain at these sites.

3. RESULTS

3.1 Relationship between flooding regime and metal concentrations on floodplain soils (scientific objective 1)

In Figures 16 and 17 the limits of floods of a 1, 1.5, 2, 5, 10, 20, 50, 100, 200, 500 and 1000-year recurrence probability are shown for the Reeth and Brompton-on-Swale study reaches; the frequency and pattern of inundation at these sites are rather different. At the lower relief site at Reeth nearly all of the reach is flooded by an event of a 2-year recurrence probability. By contrast, at Brompton-on-Swale, where valley floor relief is much greater, only floods with an estimated return period of more than 10-20 years extensively inundate the reach. In Table 7 metal concentrations in soils collected from the floodplain surface (0-20 cm) at both study reaches are compared with the estimated flood recurrence intervals. At Reeth Pb and Zn levels are generally highest on parts of the floodplain that are currently more frequently inundated but Cd concentrations show no clear trend with flooding regime. Indeed, both for Cd and Zn some of the very highest concentrations are recorded at sites that lie above the estimated limit of the "1000-year flood". A much more complex relationship between metal levels and flood recurrence probability is evident at Brompton-on-Swale (Figure 17). For all three metals the highest values are recorded at sample sites that have a wide range of flood return periods of between 1.5-50 years. These analyses suggest that only at sites such as Reeth, which are inundated most years, is there likely to be a strong relationship between metal concentrations in floodplain soils and present day flooding.

This confirms the findings of Dennis *et al.* (2003) following the Millennium Floods of autumn 2000 and can be demonstrated very clearly by plotting surface and subsurface floodplain metal concentrations against height above low-flow river level. At Reeth (Figures 18 and 19) metal values are relatively uniform up to a height of around 2 m above the present channel, above which Cd and Zn concentrations rise and Pb levels in surface samples fall. At Brompton-on-Swale, where floodplain relief is much greater, there is an overall decrease in metal values with increasing elevation above the river (Figures 20 and 21). However, similar to Reeth, metal concentrations are consistently high at floodplain sites up to 2.0-2.5 m above the River Swale but above this level metal values abruptly decrease to below 5 times background concentrations.

The use of geomorphological mapping and modelling for identifying land affected by metal contamination on river floodplains

In summary, hydraulic modelling at Reeth and at Brompton-on-Swale demonstrates that floodplain metal concentrations co-vary with inundation frequency in a complex but predictable manner. However, carrying out this type of modelling along the entire Swale river corridor may not be cost effective. A cheaper, more rapid and probably equally robust alternative method would be to use floodplain elevation above local low-flow river level as a guide to whether a site is likely to be contaminated by heavy metals. On the basis of surveys both at Reeth and Brompton-on-Swale, in the Swale Valley upstream of Catterick floodplain sites *less* than 2 m above the river channel are likely to have Pb, Zn and Cd concentrations at least 5 times above background (Table 4).

3.2 Geographic variation in floodplain soil metal concentrations in the Swale Valley (scientific objective 2)

Surface and subsurface metal concentrations in floodplain soils were investigated at nine reaches in the Swale valley (Figure 1, Table 6). The principal purpose of this was: (i) to evaluate the degree to which metal concentrations in floodplain soils vary spatially and how this relates to past and present river channel sediment dynamics; and (ii) to establish the magnitude of floodplain soil contamination by metals, measured against background metal concentrations (Table 4).

In Figures 6 to 14 Pb, Zn and Cd concentrations in floodplain surface (and the case of Reeth and Bromptonon-Swale, subsurface as well) soils are plotted at the nine floodplain study. In Table 8 minimum, maximum and mean concentrations of Pb, Zn and Cd in floodplain soils at each of the nine study reaches are presented. There is an overall decrease in metal concentrations down valley from Reeth but this trend is much stronger for Pb than for either Zn or Cd, and is stronger in surface soils than subsurface samples. One very striking feature of the geochemical data picked out in this table is the high metal concentrations recorded in subsurface (20-50 cm) floodplain soils at the four reaches (Reeth, Brompton-on-Swale, Great Langton and Maunby) where both surface and subsurface samples have been analysed. Indeed, for all three metals, concentrations in subsurface samples are significantly higher than those found at the surface of the Swale floodplain. Moreover, the maximum depth of floodplain contamination is considerably greater than 50 cm. Previous investigations at Reeth (Macklin *et al.*, 1994; Sedgwick 1998 and 2000), Brompton-on-Swale (Taylor and Macklin, 1997), Great Langton (Sedgwick, 2000) and Maunby (Carter, 1998) have demonstrated that Pb concentrations exceed background levels down to at least 1 m below present ground level.

At those floodplain reaches with higher valley floor relief (Hartlakes, Hudswell, Brompton-on-Swale, Great Langton), the most severely contaminated sites are generally located closer to the present course of the River Swale (Figures 6, 8-10). They are often located on, or very close to, former channels and bars that either date to the mid-19th century, or on parts of the floodplain that have been eroded and/or deposited during, or since, the mining period. At the flatter floodplain reaches at Reeth, Morton Flatts, Maunby, Thornton Manor and Myton-on-Swale (Figures 7, 11-14), metal concentrations are more uniform across the most severely contaminated parts of the valley floor. Although at Morton Flatts (Figure 11) a former channel of the Swale on the west side of the present river, which pre-dates both the construction of the railway and the 1854 OS map, is picked out by very high metal concentrations.

The possible environmental health implications of elevated metal concentrations in floodplain soils of the Swale catchment are assessed in Table 9, where the proportion of soils (expressed as a percentage) that exceed background concentrations are shown. The following key observations can be made:

- (a) Pb, Zn and Cd concentrations in floodplain soils greatly exceed background levels throughout the catchment.
- (b) A high proportion of floodplain soils have Pb concentrations that exceed background concentrations by at least five times. Considerable metal enrichment is apparent as far south as Maunby, nearly 40 km downstream of the nearest mine (Figure 1).
- (c) Zn and Cd concentrations exceed background values by more than five times in a high proportion of floodplain soils.

It is self evident from this analysis that metal levels (most notably Pb) in the River Swale floodplain are high even by UK standards (Macklin *et al.*, 1994). This must be of some concern because elevated metal

concentrations in the Swale floodplain may be affecting the ability of soils to support their present function or, if environmental or economic conditions change, their ability to support new functions.

3.3 Mapping the extent of contaminated floodplain land along the Swale Valley river corridor (scientific objective 3)

Employing the methodology outlined in section 2 of this report, and validated by data generated from scientific objectives one and two (sections 3.1 and 3.2), maps showing the extent of potentially contaminated land along the Swale Valley from Hoggarths (NY 871 014) to 3 km downstream of Brafferton (SE 438 701) (a total distance of 113 km) have been produced (Figure 22). These maps are colour coded as following:

- (a) All areas shaded red (comprising river channel and bars marked on the OS 1854 map, and floodplain eroded and /or deposited since 1854) denote land with a high probability of contamination.
- (b) Red stippled areas (located *outside* of the valley floor zone reworked by lateral migration of the River Swale over the last 150 years, but affected by overbank floods during and immediately after the mining period) denote zones with a likelihood of land contamination. Agricultural fields included in this category are very likely to have some soils (probably those located closest to the present river) with metal levels that exceed background Pb concentrations by at least 5 times.
- (c) Green shaded areas within the EA's Indicative Floodplain have a very low probability of land contamination and are unlikely to have soils with metal concentrations significantly above background levels.

At the nine study reaches mapping was "ground truthed", and at every site floodplain zones designated in the river corridor survey as: (i) areas with a high probability of land contamination; (ii) areas with a likelihood of land contamination; and (iii) areas with very low probability of land contamination were confirmed as being correctly classified. The proportion of samples in each area that exceed background concentrations by more than 5 times are shown in Table 10. This clearly indicates that the most highly contaminated samples occur in the zone that is classified as having a "high probability of land contamination", that a large proportion of samples from the area that is classified as having a "likelihood of land contamination" greatly exceed background concentrations, and that samples outside these zones are significantly less enriched in metals. The robustness of contamination mapping was also confirmed by comparing metal concentrations in different floodplain contamination zones using a Kruskal-Wallis H test (Table 11). In this non-parametric test, three or more groups with a single variable are tested for statistical difference. Observations are ranked across the groups and summed to give a single score for each group (Shaw and Wheeler, 1994). These scores are 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). The results of this test demonstrated highly significant differences (p < 0.005) with, as expected, both areas with a high probability of land contamination and areas with a likelihood of land contamination having the highest mean ranks.

The area of land on the Swale floodplain with a high probability of land contamination and a likelihood of land contamination is summarised in Table 12. Taking these areas together, 29.1 km² (2%) of the Swale catchment is likely to be contaminated, which constitutes over 55% of the Swale Valley floor mapped by the EA as Indicative Floodplain. This can be compared to the 47.9 km² of contaminated floodplain land previously identified by Hudson-Edwards *et al.* (1999b) and Sedgwick (2000) in the Swale, Ure, Wharfe and Nidd catchments, which suggests that these studies underestimated the extent of land contamination in the northern rivers of the Yorkshire Ouse basin.

4. CONCLUSIONS

This scoping study has successfully tested a generic, process-based procedure for monitoring the large scale and long term movement of particulate-borne metals in rivers, and for identifying areas of potentially contaminated land on floodplains. It is intended that this methodology, particularly through its use with GIS and

LiDAR, will provide a "toolkit" useable by non specialists, assisting DEFRA, the EA and LAs in their identification and management of floodplains affected by metal contaminants.

Results for the River Swale, northern England, using this approach show that over 55% of the valley floor mapped by the EA as Indicative Floodplain is likely to be contaminated, and that previous studies have underestimated both the geographical extent and degree of contamination resulting from historical metal mining. The River Swale, both in terms of the environmental legacy of mining, and scale of floodplain contamination, is by no means atypical with an estimated 12,000 km² of river catchments in northern England alone (*e.g.* Aire, Nidd, Tees, Tyne, Ure, Wear) directly affected by historical mining. In the light of this, we strongly recommend the following programme of targeted and strategic research on this problem.

- 1. To carry out a series of spot checks on individual agricultural fields in the Swale catchment (particularly in the Vale of York, downstream of Catterick), to confirm, or refine, floodplain soil metal contamination maps.
- 2. To investigate contaminated floodplain soil source-pathway-receptor relationships more fully in the Swale catchment and to establish the degree to which metals pose a hazard to environmental and human health.
- 3. To further test the use of geomorphological mapping and modelling for identifying floodplain land affected by heavy metal contamination in other catchments in England and Wales also affected by historical mining. This should include the former base metal mining areas of mid-Wales, the Northern Pennines and southwest England.
- 4. To develop environmental quality guidelines appropriate for assessing the hazards posed by contamination on agricultural land, which can also inform compliance and interpretation of the new European Union Water Framework Directive.

REFERENCES

Brewer, P. A. and Taylor, M. P. (1997) The spatial distribution of heavy metal contaminated sediment across terraced floodplains. *Catena* **30**, 229-249.

British Geological Survey (1996) Regional geochemistry of north-east England. British Geological Survey, Keyworth, Nottingham. 100pp.

Carter, J. H. (1998) *Heavy metal contamination of alluvial sediments in the middle reaches of the River Swale, North Yorkshire.* Unpublished M.Sc. Thesis, University of Leeds. 117pp.

Chao, T. T. and Sanzolone, R. F. (1992) Decomposition techniques. *Journal of Geochemical Exploration* 44, 65-106.

Coulthard, T. J. and Macklin, M. G. (2003) Modeling long-term contamination in river systems from historical metal mining. *Geology* 31, 451-454.

Davies, B. E. (1983) A graphical estimation of the normal lead content of some British soils. *Geoderma* **29**, 67-75.

Davies, B. E. and Wixson, B. G. (1985) Trace elements in surface soils from the mineralised area of Madison county, Missouri, USA. *Journal of Soil Science* **36**, 551-570.

Dennis, I.A., Coulthard, T.J., Macklin, M.G. and Brewer, P.A. (2001) *Preliminary report on the impact of autumn 2000 floods on channel and floodplain geochemistry in the River Swale catchment, north Yorkshire.* Unpublished report, River Basin Dynamics and Hydrology Research Group, University of Wales Aberystwyth, 7pp.

Dennis, I. A., Macklin, M. G., Coulthard, T. J. and Brewer, P. A. (2003) The impact of the October / November 2000 floods on contaminant metal dispersal in the River Swale catchment, North Yorkshire, UK. *Hydrological Processes* **17**, 1641-1657.

Department of the Environment (1994) Sampling strategies for contaminated land. CLR Report No.4. Department of the Environment, London. 27pp.

Department for Environment, Food and Rural Affairs and Environment Agency (2002) Assessment of risks to human health from land contamination: an overview of the development of soil guideline values and related research. Environment Agency, Bristol. 32pp.

Environment Agency (2000) Secondary model procedure for the development of appropriate soil sampling strategies for land contamination. R&D Technical Report P5-066/TR. Environment Agency, Bristol. 96pp.

Fleischhauer, H. L. and Korte, N. (1990) Formulation of cleanup standards for trace elements with probability plots. *Environmental Management* **14**, 95-105.

Förstner, U. and Wittmann, G. T. W. (1979) *Metal Pollution in the Aquatic Environment.* Springer-Verlag, Berlin. 486pp.

Gardiner, J. L. and Cole, L. (1992) Catchment Planning: The Way Forward for River Protection in the UK. [In] Boon, P.J., Calow, P. and Petts, G. E. (Eds.) *River Conservation and Management*. John Wiley, Chichester, 397-406.

Gill, R. (1997) Which method should I use? [In] Gill, R. (Ed.) *Modern Analytical Geochemistry: An introduction to quantitative chemical analysis for earth, environmental and materials scientists.* Longman, Harlow, 206-214.

Graf, W. L. (1994) *Plutonium and the Rio Grande: environmental change and contamination in the nuclear age.* Oxford University Press, New York. 329pp.

Grimshaw, H. M. (1989) Analysis of Soils. [In] Allen, S. E. (Ed.) *Chemical Analysis of Ecological Materials.* (Second ed.). Blackwell Scientific Publications, Oxford, 7-45.

Harley, J. B. (1975) Ordnance Survey Maps, A Descriptive Manual, Ordnance Survey, Southampton. 200pp.

Hall, G. E. M. (1992) Inductively coupled plasma mass spectrometry in geoanalysis. *Journal of Geochemical Exploration* **44**, 201-249.

Helgen, S. O. and Moore, J. N. (1996) Natural background determination and impact quantification in trace metal-contaminated river sediments. *Environmental Science and Technology* **30**, 129-135.

Horowitz, A. J. (1991) A Primer on Sediment-Trace Element Chemistry. (Second ed.). Lewis Publishers, Chelsea, Michigan. 136pp.

Hudson-Edwards, K. A., Macklin, M. G., Curtis, C. D. and Vaughan, D. J. (1996) Processes of formation and distribution of Pb-, Zn-, Cd- and Cu-bearing minerals in the Tyne Basin, Northeast England: implications for metal contaminated river systems. *Environmental Science and Technology* **30**, 72-80.

Hudson-Edwards, K. A., Macklin, M. G., Finlayson, R. and Passmore, D. G. (1999a) Mediaeval lead pollution in the River Ouse at York, England. *Journal of Archaeological Science* **26**, 809-819.

Hudson-Edwards, K. A., Macklin, M. G. and Taylor, M. P. (1999b) 2000 years of sediment-borne heavy metal storage in the Yorkshire Ouse basin, NE England, UK. *Hydrological Processes* **13**, 1087-1102.

Inter-Departmental Committee on the Redevelopment of Contaminated Land (1990) Notes on the restoration and aftercare of metalliferous mining sites for pasture and grazing. Guidance Note 70/90. Department of the Environment. London. 15pp.

Jarvis, K. E. (1997) Inductively coupled plasma-mass spectrometry. [In] Gill, R. (Ed.) *Modern Analytical Geochemistry: An introduction to quantitative chemical analysis for earth, environmental and materials scientists.* Longman, Harlow, 171-187.

Langedal, M. (1997) Dispersion of tailings in the Knabeåna-Kvina drainage basin, Norway, 1: evaluation of overbank sediments as sampling medium for regional geochemical mapping. *Journal of Geochemical Exploration* **58**, 157-172.

Leenaers, H. (1989) The transport of heavy metals during flood events in the polluted River Geul (The Netherlands). *Hydrological Processes* **3**, 325-338.

Lepeltier, C. (1969) A simplified statistical treatment of geochemical data by graphical representation. *Economic Geology* **64**, 538-550.

Lewin, J. and Macklin, M. G. (1987) Metal mining and floodplain sedimentation in Britain. [In] Gardiner, V. (Ed.) *International Geomorphology 1986: Proceedings of the First International Conference on Geomorphology.* Part 1. John Wiley and Sons, Chichester, 1009-1027.

Lewin, J., Davies, B. E. and Wolfenden, P. J. (1977) Interactions between channel change and historic mining sediments. [In] Gregory, K. J. (Ed.) *River Channel Changes.* John Wiley and Sons, Chichester, 353-367.

Lewin, J., Bradley, S. B. and Macklin, M. G. (1983) Historical valley alluviation in mid-Wales. *Geological Journal* **19**, 331-350.

Macklin, M. G. (1996) Fluxes and storage of sediment-associated heavy metals in floodplain systems: assessment and river basin management issues at a time of rapid environmental change. [In] Anderson, M. G., Walling, D. E. and Bates, P. D. (Eds.) *Floodplain Processes.* John Wiley and Sons, Chichester, 441-460.

Macklin, M. G., Ridgway, J., Passmore, D. G. and Rumsby, B. T. (1994) The use of overbank sediments for geochemical mapping and contamination assessment: results from selected English and Welsh floodplains. *Applied Geochemistry* **9**, 689-700.

Macklin, M. G., Hudson-Edwards, K. A. and Dawson, E. J. (1997) The significance of pollution from historic metal mining in the Pennine orefields on river sediment contaminant fluxes to the North Sea. *The Science of the Total Environment* **194/195**, 391-397.

Masse, R. and Maessen, F. J. M. J. (1981) Losses of silver, arsenic, cadmium, selenium and zinc traces from distilled water and artificial sea-water by sorption on various container surfaces. *Analytica Chimica Acta* **127**, 181-193.

McGrath, S. P. and Loveland, P. J. (1992) *The Soil Geochemical Atlas of England and Wales.* Blackie Academic and Professional, London. 101pp.

Miller, J. R. (1997) The role of fluvial geomorphic processes in the dispersal of heavy metals from mine sites. *Journal of Geochemical Exploration* **58**, 101-118.

Ministry of Agriculture, Fisheries and Food (1986) *The Analysis of Agricultural Materials: A Manual of the Analytical Methods used by the Agricultural Development and Advisory Service.* (Third ed.). Reference Book 427. HMSO, London. 248pp.

Ministry of Agriculture, Fisheries and Food (1998) *Code of Good Agricultural Practice for the Protection of Soil.* MAFF Publications, London. 66pp.

NERC (1975) Flood Studies Report, Natural Environment Research Council, London. 5 volumes.

Parslow, G. R. (1974) Determination of background and threshold in exploration geochemistry. *Journal of Geochemical Exploration* **3**, 319-336.

Ramsey, M. H. (1998) Sampling as a source of measurement uncertainty: techniques for quantification and comparison with analytical sources. *Journal of Analytical Atomic Spectrometry* **13**, 97-104.

Ramsey, M. H., Thompson, M. and Banerjee, E. K. (1987) Realistic assessment of analytical data quality from Inductively Coupled Plasma Atomic Emission Spectrometry. *Analytical Proceedings* **24**, 260-265.

Reimann, C. and de Caritat, P. (1998) Chemical Elements in the Environment. Springer-Verlag, Berlin. 398pp.

Sedgwick, C. M. (1998) Historic metal contamination at Reeth, Upper Swaledale. [In] Howard, A. J. and Macklin, M. G. (Eds.) *The Quaternary History of the Eastern Yorkshire Dales: Field Guide. The Holocene Alluvial Record*. Quaternary Research Association, London, 67-76.

Sedgwick, C. M. (2000) *Heavy metal contamination in the River Swale catchment, northern England.* Unpublished PhD Thesis, University of Leeds. 300pp.

Shaw, G. and Wheeler, D. (1994) *Statistical Techniques in Geographical Analysis.* (Second ed.). David Fulton Publishers, London. 359pp.

Sinclair, A. J. (1974) Selection of threshold values in geochemical data using probability graphs. *Journal of Geochemical Exploration* **3**, 129-149.

Sparks, H. (1998) Radiometric dating and assessment of heavy metal contamination to vertically accreted sediments of the River Swale, North-East England. Unpublished B.Sc. Dissertation, University of Lancaster. 74pp.

Taylor, M. P. and Macklin, M. G. (1997) Holocene alluvial sedimentation and valley floor development: the River Swale, Catterick, North Yorkshire, UK. *Proceedings of the Yorkshire Geological Society* **51**, 317-327.

Tennant, C. B. and White, M. L. (1959) Study of the distribution of geochemical data. *Economic Geology* **54**, 1281-1290.

Thompson, M. (1992) Data quality in applied geochemistry: the requirements, and how to achieve them. *Journal of Geochemical Exploration* **44**, 3-22.

Tobías, F. J., Bech, J. and Sánchez Algarra, P. (1997) Establishment of the background levels of some trace elements in soils of NE Spain with probability plots. *The Science of the Total Environment* **206**, 255-265.

Tobías, F. J., Bech, J. and Sánchez Algarra, P. (1997) Statistical approach to discriminate background and anthropogenic input of trace elements in soils of Catalonia, Spain. *Water, Air, and Soil Pollution* **100**, 63-78.

Totland, M., Jarvis, I. and Jarvis, K. E. (1992) An assessment of dissolution techniques for the analysis of geological samples by plasma spectrometry. *Chemical Geology* **95**, 35-62.

USACE (2001) *HEC-RAS River Analysis System, Users Manual, Version 3.0,* US Army Corps of Engineers Hydrologic Engineering Centre (HEC), Davis, CA.

Walling, D. E., Owens, P. N., Carton, J., Leeks, G. J. L., Lewis, S., Meharg, A. A. and Wright, J. (2003) Storage of sediment-associated nutrients and contaminants in river channel and floodplain systems. *Applied Geochemistry* **18**, 195-220.

Walsh, J. N., Gill, R. and Thirlwall, M. F. (1997) Dissolution procedures for geological and environmental samples. [In] Gill, R. (Ed.) *Modern Analytical Geochemistry: An introduction to quantitative chemical analysis for earth, environmental and materials scientists.* Longman, Harlow, 29-40.

Annex 1: Tables

Table 1: Sampling and analytical coefficient of variation (%) data for samples collected at Reeth and Brompton-on-Swale. See sections 2.1.2 and 2.1.3 for description of terms.

Measureme	ent uncertainty	Pb	Zn	Cd
Sampling upcortainty	Reeth	13.6	11.4	21.3
(± %)	Brompton-on-Swale	14.8	10.8	19.1
	Mean	14.2	11.1	20.2
Analytical uncortainty	Instrumental accuracy	4.7	4.1	3.1
(± %)	Analytical precision	4.7	6.4	16.4
	Analytical bias	2.8	6.2	3.7

Table 2: UK metal concentration guidelines used in this study. All values in mg kg⁻¹ dry weight soil.

	Standard	Pb	Zn	Cd
ICRCI 70/90 ¹	Threshold	300	1000	3
	Movimum for grazing livestack	1000	2000*	20*
	Maximum for grazing investock	1000	3000	30
	Maximum for crop growth	-	1000	50
MAFF ²	pH > 5.0	300	200	3
	pH > 7.0	-	300	-
CLR SGV ³	Residential with plant uptake	450	-	1-8**
	Residential without plant uptake	450	-	30
	Allotments	450	-	1-8**
	Commercial/Industrial	750	-	1400

¹ Inter-Departmental Committee on the Redevelopment of Contaminated Land (1990) Notes on the restoration and aftercare of metalliferous mining sites for pasture and grazing. Guidance Note 70/90.

² Ministry of Agriculture, Fisheries and Food (1998) *Code of Good Agricultural Practice for the Protection of Soil.*

³ Department for the Environment, Food and Rural Affairs (2002) Contaminated Land Research Programme Soil Guideline Values.

* The possibility of sub-clinical antagonistic effects on copper metabolism cannot be ruled out if concentrations of Zn and Cd in soils exceed 2000 and 15 mg kg⁻¹, respectively.

** Maximum Cd concentrations are 1 mg kg⁻¹ at pH 6, 2 mg kg⁻¹ at pH 7 and 8 mg kg⁻¹ at pH 8.

NB floodplain soil pH values in all samples cited in this report are between pH 5 and pH 9.

Tabla	A. D.			f fl		fue un the	Quala astalamant
rable	3. DE	escriptive	STATISTICS	IOF HUV	ai seaiments	from the	Swale catchment.

Statistic	Pb	Zn	Cd
Mean	1531	1127	7.0
Median	723	589	5.0
Minimum	22	2	0.4
Maximum	24767	11818	65.8
Skewness	4.18	2.97	3.71
n	799	796	419

Table 4: Background concentrations for Pb, Zn and Cd in River Swale floodplain soils, compared with metal levels in stream sediments and soils in the Swale catchment and U.K. topsoil.

	Pb	Zn	Cd
Background threshold ¹	212	105	1.0
Swale stream sediment range ²	18 - 24766	0.4 - 11818	0.3 - 48
Swale catchment soils range ³	40 - 123	62 - 108	0.7 - 1.0
Mining-affected alluvium ⁴	125	251	-
U.K. topsoil median⁵	40	82	0.7

¹ Calculated in this study using the Davies (1983) method (Section 2.1.5)

² Derived from BGS G-BASE data (British Geological Survey, 1996)

³ Derived from McGrath and Loveland (1992)

⁴ From the River Ystwyth, mid-Wales, calculated using the Davies (1983) method by Lewin *et al.* (1983)

⁵ Quoted in Reimann and de Caritat (1998)

Table 5: Discharge for selected return periods at Catterick Bridge calculated using Gumbel "peaks over threshold" analysis.

Return Period (years)	Discharge (m ³ s ⁻¹)
1	145
1.5	282
2	315
5	375
10	410
20	435
50	465
100	487
200	508
500	530
1000	545

The use of geomorphological mapping and modelling for identifying land affected by metal contamination on river floodplains

DEFRA project code

SP 0525

Table 6: Study site characteristics.

Reach	NGR	Distance downstream (km)	Reach Iength (km)	Reach area (km²)	Number of samples	Data source
Hartlakes	SD 908 003	5.6	0.25	0.02	12	Sedgwick (2000)
Reeth	SE 034 988	22.2	1.5	0.18	155	This study
Hudswell	SE 146 007	37.1	0.5	0.06	7	Sedgwick (2000)
Brompton-on-Swale	SE 213 996	47.2	2.0	0.29	168	This study
Great Langton	SE 291 961	59.0	2.2	1.14	43	Carter (1998); Sedgwick (2000)
Morton Flatts	SE 318 921	65.9	0.75	0.46	15	Sedgwick (2000)
Maunby	SE 341 864	75.4	2.5	0.49	28	Carter (1998)
Thornton Manor	SE 433 714	100.5	0.5	0.11	12	Sedgwick (2000)
Myton-on-Swale	SE 432 664	115.5	2.0	0.97	4	Hudson-Edwards <i>et al.</i> (1999); this study

Return period		Pl	o (mg kg	⁻¹)	Z	n (mg kợ	g ⁻¹)	С	d (mg kg	J ⁻¹)
(years)	n	Min	Mean	Max	Min	Mean	Мах	Min	Mean	Max
		META		CENTRA	TIONS	S AT REI	ЕТН			
1	52	1007	2369	8052	446	923	1481	3	6	13
1.5	22	1009	1980	2930	491	851	1513	3	6	10
2	2	1204	1758	2311	857	876	895	5	15	24
5	4	662	1149	1555	324	778	942	2	8	16
10	1		1256			932			9	
20	0	As ′	10 year fl	ood	As	10 year t	flood	As	10 year f	lood
50	0	As ²	10 year fl	ood	As	10 year t	flood	As	10 year f	lood
100	0	As ′	10 year fl	ood	As	10 year t	flood	As	10 year f	lood
200	0	As ′	10 year fl	ood	As	10 year t	flood	As	10 year f	lood
500	0	As ²	10 year fl	ood	As	10 year t	flood	As	10 year f	lood
1000	0	As ′	10 year fl	ood	As	10 year t	flood	As	10 year f	lood
>1000	5	1099	2352	4061	770	1587	3855	6	15	40
I	META		ENTRAT		T BRC	MPTON	-ON-SV	/ALE		
1	4	234	840	1160	226	651	894	2	4	5
1.5	17	815	1645	3054	225	652	2178	1	4	12
2	11	241	1810	3492	184	779	2516	1	5	19
5	10	896	1583	3459	224	584	1227	2	4	8
10	6	1919	2582	3484	573	1005	1882	4	7	14
20	2	1067	1431	1964	359	425	551	2	3	4
50	6	937	2184	3431	354	1358	2363	2	8	14
100	4	631	1048	1365	192	350	531	1	2	3
200	3	1389	1412	1447	367	455	584	2	3	4
500	0	As 2	00 year f	ilood	As 2	200 year	flood	As 2	200 year	flood
1000	3	1736	1821	1938	484	723	1159	3	4	6
>1000	34	105	823	2985	80	284	1248	1	2	9

Table 7: Metal concentrations in floodplain surface sediments compared with flood return periods.

Sito	P	b (mg kg	⁻¹)	Z	n (mg kg	1)	C	d (mg kg	1)
Sile	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max
		S	SURFACE	SAMPL	.ES				
Hartlakes	75	417	1000	50	553	1500	0	3	10
Reeth	662	2185	8052	324	935	3885	2	7	40
Hudswell	400	1114	3000	200	886	2300	0	5	15
Brompton-on-Swale	105	1366	3492	80	538	2516	1	4	19
Great Langton	100	1326	3024	64	805	2000	0.5	5	15
Morton Flatts	100	1640	3000	85	1146	2000	0	6	10
Maunby	192	965	2256	196	648	1403	1	3	7
Thornton Manor	150	558	1500	100	325	500	2	4	5
Myton-on-Swale	192	500	932	198	307	472	2	3	4
		SU	BSURFA	CE SAM	PLES				
Reeth	514	2932	11990	365	1070	4007	3	12	66
Brompton-on-Swale	54	1418	9052	60	694	4052	0.4	9	51
Great Langton	223	2563	4209	153	1447	3092	1	7	12
Maunby	439	1573	3206	274	788	1623	2	4	8
Myton-on-Swale	457	766	1081	165	252	383	1	3	4

Table 8: Minimum, mean and maximum metal concentrations at each study site.

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Table 9: Percentage	of samples	exceeding back	ground concentra	tions for Pb,	Zn and Cd.
0				,	

		РЬ			Zn			Cd	
Site	Above background	> 5 x above	> 10 x above	Above background	> 5 x above	> 10 x above	Above background	> 5 x above	> 10 x above
			SI	URFACE SAMPI	ES				
Hartlakes	58	0	0	29	33	25	50	25	0
Reeth	100	06	35	100	93	23	100	81	7
Hudswell	100	29	14	100	43	29	57	29	14
Brompton-on- Swale	88	67	14	92	38	10	89	24	4
Great Langton	89	46	22	26	62	24	95	38	8
Morton Flatts	89	63	21	68	62	37	89	42	0
Maunby	96	29	4	100	79	4	96	8	0
Thornton Manor	92	8	0	26	0	0	100	0	0
Myton-on-Swale	06	0	0	100	0	0	60	0	0
All samples	91	58	18	76	57	16	06	39	4
			SUB	SURFACE SAN	IPLES				
Reeth	100	96	59	100	66	39	100	72	26
Brompton-on- Swale	87	51	18	87	34	18	06	43	32
Great Langton	100	100	60	100	100	100	100	100	20
Maunby	100	100	100	100	100	75	100	100	0
Myton-on-Swale	100	83	0	100	0	0	100	0	0
All samples	94	76	40	94	99	31	95	58	27

Background concentration		High probability of land contamination	Likelihood of land contamination	Low probability of land contamination	Outside Indicative Floodplain limit
Above	Pb	100	92	75	43
background	Zn	100	95	94	43
Dackground	Cd	100	93	75	29
	Pb	88	76	25	14
> 5 x above	Zn	92	62	25	29
	Cd	84	52	33	14
	Pb	32	24	13	0
> 10 x above	Zn	32	19	13	14
	Cd	18	10	0	0

Table 10: Percentage of samples exceeding background in each floodplain zone

Table 11: Kruskal-Wallis H tests of metal concentrations and floodplain zones.

Ranks

	Group	Ν	Mean Rank
Pb	High probability of land contamination	50	151.78
	Likelihood of land contamination	191	135.75
	Very low probability of land contamination	16	74.53
	Outside Indicative Floodplain limit	7	38.57
	Total	264	
Zn	High probability of land contamination	50	179.04
	Likelihood of land contamination	191	127.70
	Very low probability of land contamination	16	78.97
	Outside Indicative Floodplain limit	7	53.43
	Total	264	
Cd	High probability of land contamination	50	171.80
	Likelihood of land contamination	191	125.59
	Very low probability of land contamination	16	91.50
	Outside Indicative Floodplain limit	7	36.36
	Total	264	

Test statistics ^{a, b}

	Pb	Zn	Cd
Chi-square	23.355	34.705	30.110
Degrees of freedom	3	3	3
Significant at 0.005?	Yes	Yes	Yes

^a Kruskal Wallis *H* Test

^b Grouping variable: floodplain zone

Critical value of χ^2 at the 0.005 confidence level: 12.838.

Table 12: Summary catchment and contamination statistics for the River Swale.

Total catchment area (km ²)	
EA Indicative Floodplain area (km ²)	
1982 channel and bar area (km ²)	2.9
High probability of land contamination (red areas on Fig. 22) (km ²)	3.7
Likelihood of land contamination (red stippled areas on Fig. 22) (km ²)	
Total area of land contamination (red and red stippled areas on Fig. 22) (km ²)	
Percentage of EA Indicative Floodplain affected by land contamination	
Percentage of total catchment affected by land contamination	

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Annex 2: Figures



Figure 1: The River Swale catchment, showing the location of intensive study reaches (1-9), floodplain core sites, formerly mined tributaries (A-G) and major Pb mines.



Figure 2: The study reach at Reeth showing geochemical sample point locations.

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Figure 3: The study reach at Brompton-on-Swale showing geochemical sample point locations.



Figure 4: Flowchart illustrating the HNO₃ digestion procedure.



Figure 5: Probability curves and recalculated background populations for Pb, Zn and Cd.

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Figure 7(a): Pb, Zn and Cd concentrations in floodplain surface soils at Reeth.

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Figure 7(b): Pb, Zn and Cd concentrations in floodplain subsurface soils at Reeth.





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Figure 11: Pb, Zn and Cd concentrations in floodplain surface soils at Morton Flatts.

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Figure 12: Pb, Zn and Cd concentrations in floodplain surface soils at Maunby.





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Figure 15: Pb concentrations in individual samples at the nine study reaches plotted against distance from the present channel of the River Swale. Red and green symbols show samples that exceed and fall below five times the background concentration for Pb, respectively.



Figure 16: Simulated flood limits at Reeth.

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Figure 17: Simulated flood limits at Brompton-on-Swale.



Figure 18: Surface metal concentrations in floodplain soils at Reeth plotted against height above low flow river level.



Figure 19: Subsurface metal concentrations in floodplain soils at Reeth plotted against height above low flow river level.



Figure 20: Surface metal concentrations in floodplain soils at Brompton-on-Swale plotted against height above low flow river level.



Figure 21: Subsurface metal concentrations in floodplain soils at Brompton-on-Swale plotted against height above low flow river level.

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Figure 22: The likely extent of metal contaminated land along the River Swale. (a) Index sheet. Inset boxes refer to subsequent pages.



Figure 22: The likely extent of metal contaminated land along the River Swale. (b) Hoggarths – Isles Bridge.

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Figure 22: The likely extent of metal contaminated land along the River Swale. (d) Downholme Bridge – Catterick Bridge.



Figure 22: The likely extent of metal contaminated land along the River Swale. (e) Catterick Bridge – Londonderry.

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Figure 22: The likely extent of metal contaminated land along the River Swale. (f) Londonderry – Topcliffe.

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Figure 22: The likely extent of metal contaminated land along the River Swale. (g) Topcliffe – Myton Grange.