

CHAPTER 3

GEOCHEMICAL CHARACTERISATION OF FLUVIAL SEDIMENTS IN THE SWALE CATCHMENT

3.1. INTRODUCTION

As the primary aim of this investigation is to identify current and long-term patterns of metal-rich sediment dispersal, transport and storage in the River Swale catchment (Section 1.3), a detailed geochemical survey of metal dispersal in fluvial sediments throughout the catchment was undertaken. This involved the collection of fluvial sediments from Gunnerside Beck, a formerly mined tributary in the headwaters of the Swale (Chapter 4), from representative floodplain reaches throughout the catchment (Chapter 5), and from channel-edge and overbank material deposited along the trunk channel during three large flood events (Chapter 6). These data were combined with existing data from the literature in order to provide a detailed picture of metal dispersal patterns throughout the Swale catchment.

The field and desk-based techniques employed in identifying and interpreting metal dispersal patterns in tributary, floodplain and flood sediments are relatively disparate, and are therefore outlined in the individual chapters where the results of the geochemical survey in each of these environments are discussed in detail (Chapters 4, 5 and 6, respectively). However, a number of the procedures involved in the geochemical survey itself are common to all the fluvial environments considered in this investigation; namely, those employed in the laboratory analysis of all sediment samples, and those employed in ensuring optimum data quality during sample collection and analysis. This chapter therefore presents a brief outline of the laboratory and analytical quality control procedures employed in the investigations described in the subsequent chapters of this thesis.

3.2. LABORATORY METHODS

3.2.1. Particle size selection

A number of studies have shown that metals are not uniformly distributed over different grain sizes, with most metals displaying a significant affinity for fine-grained sediment (Section 1.2.2, Horowitz, 1991). It is therefore extremely important that the particle size selected for geochemical investigation is standardised across all samples (Förstner and Wittmann, 1979). However, the definition of ‘fine-grained’ sediment is open to interpretation. Sampling of the <2 mm 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, 1998; Hudson-Edwards *et al.*, 1999b; Zhao *et al.*, 1999). However, it has been shown that metals are often most concentrated in material of <63 µm diameter (*e.g.* Macklin and Klimek, 1992; Liu *et al.*, 1995; Ciszewski, 2001; Walling *et al.*, 2003a). Material of this size has been identified as the most geochemically active size fraction (Horowitz, 1991, 1995), so it may therefore be appropriate for selection in studies of contamination in the fluvial environment.

In order to characterise metal dispersal patterns in active tributary and flood sediments, both the <63 µm (silt and clay) and 2000-63 µm (sand) size fractions were selected for analysis. This approach allows the comparison of metal partitioning between fine-grained material that is likely to be transported in suspension, and that that is likely to be transported as part of the bed load. However, floodplain sediment was sampled at <2 mm, in order to allow direct comparison with floodplain data from secondary sources (Section 5.2).

3.2.2. Initial sample preparation

Prior to analysis, all sediment samples were oven dried for 24 hours at 40°C, then gently disaggregated in a porcelain mortar and pestle to minimise abrasion. All samples were then dry-sieved through stainless-steel mesh (as recommended by Grimshaw, 1989). The 2000 – 63 µm (sand) and <63 µm (silt and clay) fractions from the tributary and flood sediment samples and the <2 mm fraction from the floodplain sediment samples were collected for geochemical analysis.

3.2.3. Digestion procedure

A variety of extraction techniques are available for the determination of metal content in sediment samples. Standard procedures involve either the dissolution of sediment 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 (Gill, 1997). A wide variety of partial and total dissolution techniques are available. Total extraction techniques, such as those involving hydrofluoric acid in association with another strong mineral acid, are used to determine the total metal content of a sample, including that contained within silicate minerals (Chao and Sanzalone, 1992). However, partial metal extraction techniques are often considered a more appropriate measure of metal content for environmental studies where potentially bioavailable adsorbed contaminants are of more interest than those bound within mineral grains (Totland *et al.*, 1992; Walsh *et al.*, 1997).

In this investigation, a hot nitric acid (HNO_3) partial digestion procedure was used to extract metals and trace elements from the sediment samples prior to geochemical analysis (Abrahams, 1987) (Figure 3.1). This technique is particularly effective at decomposing sulphide minerals and carbonates (Section 2.1.4, Chao and Sanzalone, 1992), and has been widely employed in investigations of fluvial contamination (*e.g.* Sedgwick, 2000; Walling *et al.*, 2003a). In addition to this, HNO_3 is frequently selected in investigations involving high-precision analytical techniques such as ICP-MS because it produces fewer spectral interferences and a clearer background signal than other common extractants such as *aqua regia* (three parts HNO_3 to one part HCl) (Hall, 1992; Walsh *et al.*, 1997).

Sufficient material must be analysed in order to ensure that each sample is adequately characterised. For the $<63 \mu\text{m}$ fraction, 0.25 g is likely to be adequate. However, the coarser nature of the 2000 – 63 μm size fraction suggests that a larger amount may be required for digestion to ensure homogeneity. The amount of sediment of this size suggested in the literature ranges from 0.25 g (Abrahams, 1987; Allen, 1989), to 2, 4 and 10 g (Harrison and Laxen, 1977; Fishman and Friedman, 1989). In order to determine the influence of increased amounts of sample on the concentrations obtained from geochemical analysis, five large samples were divided into 0.25, 0.5, 1, 2, 4, and 10 g sub-samples and analysed separately using proportional amounts of the reagents outlined in the nitric acid digestion procedure described earlier (Figure 3.1). The procedure did not show

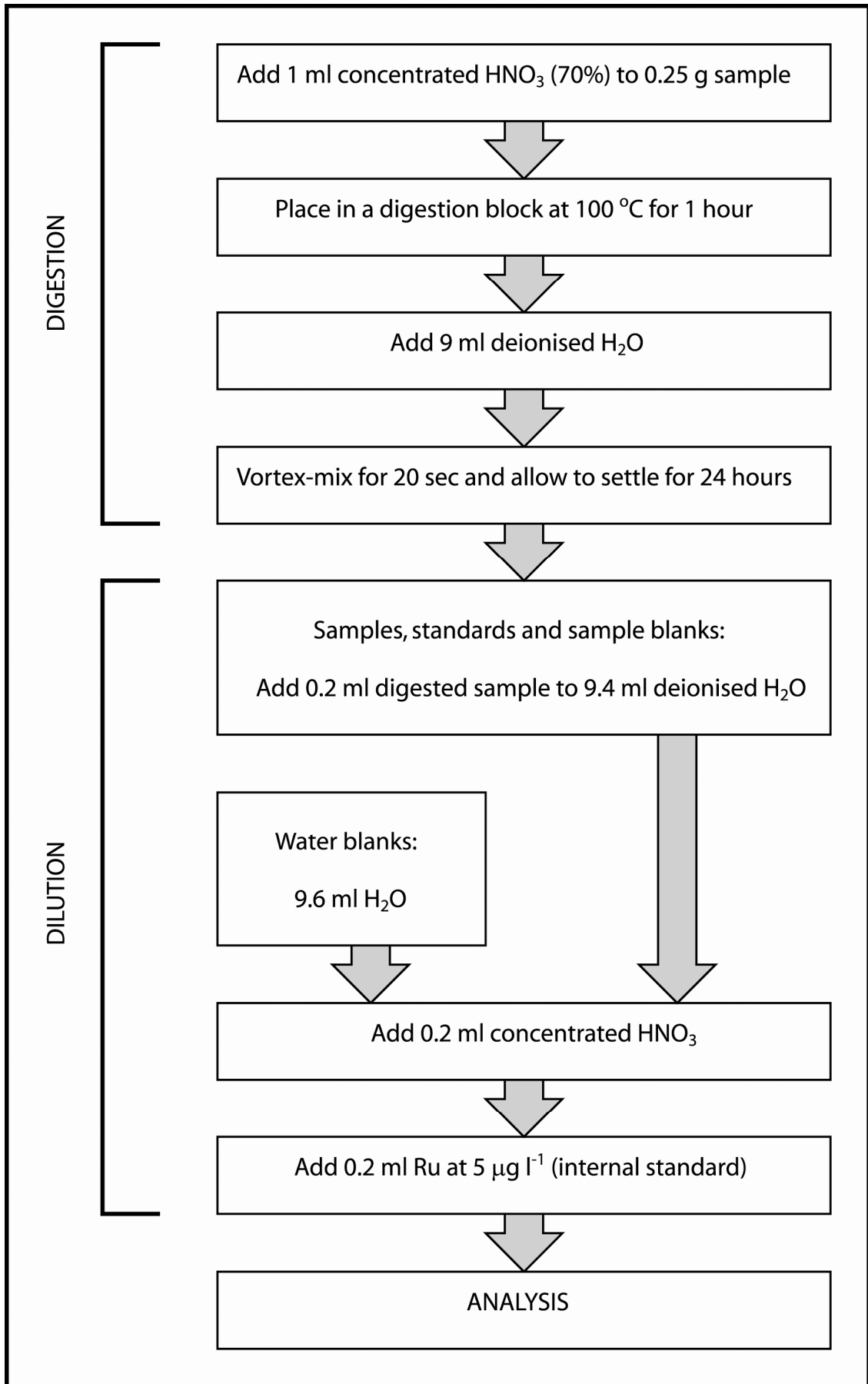


Figure 3.1: Flow chart detailing the HNO₃ digestion procedure used in this investigation

any large variation between the different sample sizes, and a Kruskal-Wallis *H*-test suggested that there were no significant differences between the results for a range of elements (*e.g.* observed χ^2 for Pb = 1.167; critical χ^2 at 0.005 significance level and 5 degrees of freedom = 16.75), indicating that there are no significant differences between the groups (*cf.* Shaw and Wheeler, 1994). As a result of this, a 0.25 g sample size was selected for analysis to ensure compatibility with the <63 μm results. This sample aliquot size was also adopted for the <2 mm fraction.

3.2.4. ICP-MS analysis

A VG Elemental Plasma Quad ICP20P Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) was used to measure the concentrations of selected elements in each sample. In this technique, a sample is sprayed through a nebuliser into a plasma flame, where it becomes ionised (Jarvis, 1997). The sample ions are then pumped through a sampling cone and skimmer, which remove uncharged atoms and molecules. The resulting beam of ions is then introduced into a quadrupole mass spectrometer, where elements are differentiated according to their mass (Jarvis and Jarvis, 1992). The number of ions of each mass is recorded by an electron multiplier, and the proportion of each element present in the sample is calculated. Inductively Coupled Plasma-Mass Spectrometry allows a wide range of elements to be measured simultaneously in a very short period of time, with sample analysis typically lasting under 60 seconds (Hall, 1992). The technique is extremely precise, with a relative standard deviation of between two and five percent. Measurements are generally highly accurate, lying within 5 % of the absolute value (Jarvis, 1997). ICP-MS detection limits for all elements are below 1 ng ml^{-1} , and can be as low as 0.01 ng ml^{-1} for elements such as Pb and Zn (Hall, 1992).

Due to the sensitivity of the ICP-MS instrument, the digested supernatant was diluted according to the procedure described in Figure 3.1. Elemental concentration data are produced in the form of counts per unit of concentration in the sample solution. An internal standard ‘spike’ of known concentration, in this case Ru, was therefore included in each sample to allow these raw counts to be converted into concentrations. Concentration data were obtained for selected trace metals (Zn, Cd, Hg, Ga, In, Tl, Sn, Pb, As, Sb and Bi), transition metals (V, Cr, Mo, Co, Ni, Cu and Ag), alkaline metals (Rb and Cs), alkaline earth metals (Be, Sr and Ba) and actinides (Th and U). These elements are measured as standard during ICP-MS analysis, in order to give as full a picture as possible

of the geochemistry of the sample material. Many of these trace elements are commonly associated with natural soils and sediments, while others are likely to be indicators of metal contamination. The nature of the mineralization in Swaledale (Sections 2.1.4 and 2.1.5) suggests that Pb, Zn and Cd are amongst the most important mining-related metals in the Swale catchment. Previous investigations (*e.g.* Macklin *et al.*, 1994; Hudson-Edwards *et al.*, 1999b; Sedgwick, 2000) indicate that these metals occur in sufficient concentrations to pose a serious hazard to environmental and ecosystem quality in many parts of the catchment. Data for these elements were therefore selected for detailed investigation in subsequent chapters.

3.3. ANALYTICAL QUALITY CONTROL

3.3.1. Approaches to AQC

Analytical Quality Control (AQC) is an essential part of any investigation that utilises geochemical data. There are two broad approaches to AQC. The first, ‘top-down’ approach involves inter-laboratory trials to estimate total measurement uncertainty (Ramsey, 1997a). The same sample is measured in different laboratories, all using the same technique. The scatter of results can then be used to estimate overall uncertainty (Thompson, 1992). The second, ‘bottom-up’ approach involves the identification and minimisation of all potential sources of uncertainty involved in the sampling and analytical procedure to be carried out in a single laboratory (Ramsey, 1997a). However, this approach is limited in that factors external to the method, for example laboratory temperature, may account for a large degree of uncertainty. Such errors can only be estimated in a multi-laboratory investigation (Ramsey, 1997a). Although the comprehensive ‘top-down’ approach to AQC is likely to provide the most satisfactory results, it is unfeasible for a small-scale investigation such as this project. Instead, a robust ‘bottom-up’ approach to analytical quality control was adopted throughout this investigation.

3.3.2. Quality control during sample collection

Sample collection has been identified as one of the largest sources of errors in the analytical process (Ramsey, 1997b; Ramsey and Argyraki, 1997; Ramsey, 1998). To minimise this error, a single-sampler single-protocol approach was adopted (Ramsey,

1997a). In the case of overbank, channel-edge and floodplain surface sediment samples, 10 randomly positioned spot samples were collected within a circle of 5 metres radius, and amalgamated to minimise the effects of small-scale heterogeneity (*cf.* Pestana *et al.*, 1997; *cf.* Ramsey and Argyraki, 1997). This method was not applied to deeper floodplain cores due to the nature of the sampling technique. Repeat samples, consisting of five sets of samples collected within a 5 metre radius, were taken at 10 % of the sampling sites, to allow any variation to be quantified (Ramsey, 1998). All sampling equipment was cleaned thoroughly after each sample was collected, and samples were stored in clean wet-strength paper bags for transportation to the laboratory for preparation and analysis.

3.3.3. Quality control during sample preparation and analysis

Several standard Good Laboratory Practice (GLP) procedures were adopted to minimise the likelihood of contamination during sample preparation (*cf.* Ramsey, 1997b). Sieved samples were stored in sealed polythene bags, and lids were used at all times to minimise dust-generation. Work surfaces were covered in clean polythene sheets, which were replaced at regular intervals, and all equipment was cleaned thoroughly between sample preparations. Metals may be sorbed onto the surface of glassware, and are often incorporated into plastic equipment during its manufacture (Scott and Ure, 1972). All glassware and plastic equipment was therefore washed for 24 hours in 15 % HNO₃ prior to use to minimise the possibility of contamination (*cf.* Masse and Maessen, 1981). In addition to this, AnalR grade reagents were used in all analyses to prevent the introduction of contaminants at this stage (Walsh *et al.*, 1997).

A number of AQC procedures were adopted during each analysis. Samples were analysed in a random order, in order to minimise the effects of cross-contamination (*cf.* Thompson, 1992). A series of reagent and water blanks (solutions with zero analyte concentrations) were employed 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). In addition to this, samples of a synthetic solution containing known concentrations of all analytes were also included at the beginning, middle and end of each run in order to allow instrumental calibration to be corrected (Ramsey *et al.*, 1987). In order to allow analytical accuracy to be evaluated, 10 % of samples were duplicated (Ramsey *et al.*, 1987). Analytical bias was estimated with the use of reference materials (Kane, 1992). Two appropriate certified reference materials (GSS-1 and GSD-12) were

included as an external check on results (Gill and Ramsey, 1997; Ramsey, 1998), although there are likely to be some differences in the digestion and analytical procedures used in this study and those employed to obtain the certified elemental values of the material. An in-house reference material (ABS-1), although lacking in certification, was therefore included because its recommended values were appropriate for the digestion method employed in this study (Thompson and Ramsey, 1995). Reference materials were inserted randomly into each batch, and made up approximately 10 % of all analyses (Thompson, 1992).

3.3.4. Data quality: AQC results

The results of the AQC procedures adopted during field sampling (Section 3.3.2) and laboratory analysis (Section 3.3.3) indicate that the primary data used in this investigation are of high quality (Table 3.1). As would be expected, the uncertainty associated with sample collection ($\pm 9 - 20$ %) is much greater than the uncertainty associated with sample analysis ($\pm 3 - 6$ %), reflecting geochemical variability in the field rather than variability introduced during sample analysis and preparation (*cf.* Ramsey, 1997a). Differences in levels of sampling uncertainty between tributary, floodplain and flood sediments are likely to reflect variations in sampling technique (spot samples for flood sediments, short cores for floodplain sediments, and a combination of the two for tributary sediments; see Sections 4.4.2, 5.2 and 6.2.2, respectively). Pb and Zn measurements generally have much lower uncertainty associated with them than Cd measurements. This is likely to strongly reflect the proportionally lower concentrations of Cd observed in the samples compared to those of Pb and Zn, in addition to small-scale spatial variability.

Table 3.1: Sampling and analytical coefficient of variation (%) data for tributary, floodplain and flood sediments

Measurement uncertainty		Pb	Zn	Cd
Sampling uncertainty (\pm %)	<i>Tributary sediments</i>	12.45	12.31	18.63
	<i>Floodplain sediments</i>	14.17	11.13	20.17
	<i>Flood sediments</i>	9.78	8.82	16.61
Analytical uncertainty (\pm %)	<i>Instrumental accuracy</i>	4.74	4.09	3.12
	<i>Analytical precision</i>	4.67	6.43	16.41
	<i>Analytical bias</i>	2.78	6.16	3.67

3.4. SUMMARY

This chapter outlines the basic geochemical and quality control techniques employed in this investigation. The full methods employed in assessing patterns of metal dispersal and storage in tributary, floodplain and flood sediments will be presented in the subsequent chapters, alongside the results of these procedures. The results of the AQC procedures adopted in this investigation indicate that the uncertainty associated with sample analysis is low. This suggests that the data employed in this investigation are of high quality. Sampling uncertainty is greater, as a result of natural variability in the field.