THE APPLICATION OF SEDIMENT SOURCE FINGERPRINTING TECHNIQUES TO RIVER FLOODPLAIN CORES, TO EXAMINE RECENT CHANGES IN SEDIMENT SOURCES IN SELECTED UK RIVER BASINS

Submitted by
Stephen Haley
To the University of Exeter as a thesis for the degree of
Doctor of Philosophy in Geography

I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

Stephen M. Haley
(November, 2010)

ABSTRACT

In recent years there has been an increasing awareness of the detrimental influence of diffuse sources of pollution on aquatic systems and of the integral role played by sediment in the mobilisation and transport of pollutants. The recognition of the environmental, societal and economic importance of the ecological health of aquatic environments has led to a change in emphasis regarding agricultural and environmental policy. To implement successful delivery of emerging policy requirements, there is a current need to have an enhanced understanding of the relationship between different forms of land use and sources of diffuse pollution, particularly sources of fine sediment. To understand the potential impacts of future land use changes, including environmental conservation measures on sources of sediment, it is useful to consider them within a longer-term context. This study has successfully applied the sediment source fingerprinting technique to floodplain overbank sediment cores in a retrospective study of six diverse UK river catchments with identified sediment problems. The varying estimates of relative sediment contributions from differing sources have been compared to known land use change in the study catchments over concurrent time periods, to explore any associations which might be apparent. Over the last 40 years, the increased cultivation of high erosion risk crops, such as those which are harvested late in the season (e.g. maize) and those which are sown in the autumn (e.g. winter wheat), has contributed disproportionately to the total sediment load relative to the area of land occupied by such cultivation. Increased stocking densities have resulted in increased relative sediment contributions from grassland sources, particularly intensively managed temporary grassland, but can have an even greater impact on sediment contributions derived from channel bank sources. The installation and maintenance of drainage for agriculture or for flood risk management has resulted in increased relative sediment loads from channel bank and associated sub-surface sources. Through the further development of such research, the efficacy of mitigation measures can be tested against evidence-based historic trends and those management approaches which provide identifiable improvements can be developed as best practice options for future land management targeted at reducing the negative impacts of excessive sediment ingress to river systems. The design of the source fingerprinting methodology used in this work was based on an established successful approach and this was developed further through the incorporation of a number of refinements designed to improve the robustness of the technique and expedite its implementation.

TABLE OF CONTENTS

CONTENTS

LIST OF FIGURES

CHAPTER 3

CHAPTER 4

CHAPTER 6

CHAPTER 7

CHAPTER 9

LIST OF TABLES

CHAPTER 5

CHAPTER 8

CHAPTER 9

ACKNOWLEDGEMENTS

I have been very fortunate during my PhD odyssey to have met some really great people from all over the world and to have shared many enjoyable moments in the field, in the lab, in the office and in the pub. I have to thank Dr Diane Fraser especially, for her patience and fortitude in guiding me through some tricky statistical and computing twists and turns and for her considerable contribution to the development of the refined mixing model used in this research. Her programming skills transformed the nature of the modelling experience and positively altered the trajectory of the project.

I thank Doris and Bert, the original Vision Factory Board of Directors, who were never very far from my thoughts. They started this journey with me eight years ago at the Duchy College in Cornwall and they will finish it with me now in spirit. Many thanks to my M & P for their unerring support over the last eight years of my epiphany and also the antipodean branch of the Haley family, headed by my incredibly courageous brother Mike, currently hitting a golf ball sized tumour for six in Sydney. Lots of love and gratitude to my lovely wife Rita and the little bundle that she carries within. She gave up the sunny climes of Portugal to support me in my PhD endeavour and I couldn’t have done it without her. I offer a big thank you to Gareth Thompson, for burning the midnight oil with me, to proof read and offer encouragement and to Gabriele Lamparteer for the visits with baked goods and babies.

I thought that I knew all about working the night shift from my years in the media and music industries, and then I met my erstwhile supervisor Prof Des Walling, whose late night correspondence, prompt feedback and straight talking, no nonsense approach kept me going in the wee small hours. I also thank Prof Adrian Collins and the good people of ADAS for the opportunities which they have created for me.

During my research, I have been privileged to visit some very beautiful river locations and I have enjoyed my time in the field immensely. These experiences continue to fuel my passion for water research and the desire to mess about in rivers in equal measure.

'To see a world in a grain of sand and heaven in a wild flower,
Hold infinity in the palm of your hand and eternity in an hour' - (William Blake)

CHAPTER 1 - INTRODUCTION

1.1 Background: The sediment problem

Over the last 40 years, there has been an increasing awareness of the environmental importance of the linkage between on-site soil loss through erosion and the off-site fate of suspended sediment loads transported by streams and rivers (Imeson, 1974; Wolman, 1977; Walling, 1983, 2005; Novotny and Olem, 1993; Trimble and Crosson, 2000; de Vente *et al*., 2007). On-site problems include the general degradation of soil structure, a reduction in soil depth, the decline of soil fertility and reduced agricultural crop yields (Pimental *et al*., 1995; Pagliai *et al*., 2004; Bakker *et al*., 2005; Troeh and Thompson, 2005). Off-site problems are concerned largely with the diffused pollution impacts of increased yields of suspended fine sediment on streams, lakes, reservoirs, estuaries and floodplains (Clark, 1985; Zapata, 2002). Downstream impacts of increased sediment ingress can include serious problems for sustainable water resources, the degradation of aquatic habitats including the siltation of fish spawning gravels, the loss of reservoir storage, impeded functioning of drainage and irrigation systems and hydropower production, whilst the large-scale siltation of river channels and estuarine ports can threaten the navigability of waterways (Walling, 2004). Fine sediment plays a significant role in the transport of contaminants and nutrients, including phosphorus (P), particulate organic carbon (POC), herbicides and pesticides, heavy metals, PCBs, pathogens and pharmaceuticals from various sources through fluvial systems and into lacustrine, floodplain and coastal environments (Williams, 1975; Wolman, 1977; Ohyama *et al.*, 1987; Bryan and Langston, 1992; Burgoa and Wauchope, 1995; Heberer *et al*., 1998; Johnson *et al*., 1998; Foster and Lees, 2000; Sapozhnikova, 2004; Walling *et al*., 2006; Jenkins *et al*., 2010).

Nutrients and contaminants are adsorbed onto soil and sediment particles and are transported with suspended sediment as it moves through the aquatic environment (Edwards & Withers, 1998; Kronvang *et al*., 1999). P desorption from contaminated sediment can cause eutrophication when allochthonous, enriched sediment enters receiving waters (Smol, 2002). Particular problems can occur as suspended sediment, carrying pollutants adsorbed upstream, encounter the transitional zone of tidal waters (Nixon, 1995). Contaminants and nutrients, can become desorbed in the increased saline and changing redox conditions in the water column, causing eutrophication and contamination in estuarine and coastal environments (Hopkinson *et al*., 1999; Pant and Reddy, 2001; Scoullos and Pavlidou, 2001). Certain contaminants may conversely become transformed or concentrated in sediment during transport or during periods of temporary storage in the channel system and on dynamic floodplains (Novotny *et al*., 1978; Walling, 1983; Foster and Charlesworth, 1996; Owens *et al*., 2001). Such transformations might result from changes in redox and pH conditions or from changes in water chemistry and the processes involved could include ion exchange, dissolution, microbial activity and the behaviour of particulate biofilms (Peart and Walling 1986; Schorer and Eisele, 1997; Droppo, 2001). In this manner, particles of fine sediment transported as suspended sediment or stored on the channel bed may adsorb contaminants derived from point sources such as industrial facilities and sewage treatment works or from no-point sources such as runoff from roadways and fields treated with nutrient or biocide applications (Novotny *et al*., 1978; Schorer and Eisele, 1997; Owens *et al*., 2001).

High loads of suspended sediment in rivers can create conditions of high turbidity and excessive siltation of the gravel substrate. These influences can have particularly negative impacts on aquatic invertebrates and the wider benthos (Cordone and Kelley 1961; Thorpe and Lloyd, 1999). Under high turbidity conditions, fish suffer directly through damage to gills and olfactory systems. Furthermore, excessive sedimentation can degrade spawning gravels, causing reduced fish populations, and result in changing habitats which ultimately reduce the heterogeneity of fish communities (Richards *et al*., 1993; Schleiger, 2000; Walling *et al*., 2003; Walters *et al*., 2003; O'Hare *et al.*, 2006).

High turbidity in waters creates substantially reduced light levels, which can drastically reduce the ability of submerged macrophytes to photosynthesise (Rhoads and Germano, 1986). This can have a directly detrimental effect on BOD levels (Petts *et al*., 2002). Aquatic plants can have considerable influence on sediment transport dynamics by effecting flow resistance and flow velocities (Gurnell *et al*., 2006). Macrophytic growth cycles create a heterogeneous mosaic of flow patterns resulting in the patchy deposition of fine sediment which leads to associated morphological effects on channel bed form (Green, 2005; Gurnell *et al*., 2006). In-channel vegetation loss may alter the roughness or resistance of a river channel leading to increased vulnerability during high flow rates to bank erosion and scour, ultimately creating incision and channel enlargement with inherent problems of increased sediment supply. Additional consideration might be given of the effect these fluvial responses have on the composition and condition of riparian seedbanks and propogules (Goodson *et al*, 2001; Gurnell *et al*., 2006, Brown *et al*., 2007). A reduction in aquatic primary productivity, biodiversity and biomass resultant from high turbidity represents a vital loss of both habitat and food supply for many aquatic and terrestrial species.

1.2 Policy: drivers, development and delivery

There has been extensive recognition that rates of soil erosion on agricultural land in the UK increased considerably throughout the 20th century (Speirs and Frost, 1985; Boardman, 1995; Evans, 2005; Boardman *et al*., 2009; Lang, 2010). It is considered that increased erosion has led in turn to increased colluviation and alluviation (Owens and Walling, 2002). These increases have been seen largely as a reflection of the growth in the area of land under agricultural production, the intensification of agricultural management practices and seasonal alterations in the timing of agricultural activities, such as increased stocking densities and the expansion of autumn-sown and late-harvested arable crops (e.g. winter wheat, fodder maize) (Owens and Walling, 2002; Evans, 2005; Boardman *et al*., 2009). The concern surrounding future anthropogenic influences on riverine environments and landscapes is increasingly coupled with growing recognition of the sensitivity of river basins and the coastal zone to anticipated global environmental change (Rumsby and Macklin, 1994; Owens and Walling, 2002; Walling *et al*., 2003; Palmer *et al*., 2008; Rosenzweig, 2008; Ormerod, 2009; Whitehead *et al*., 2009; Wilby and Dessai, 2010).

The period of agricultural intensification throughout the 1970s and 1980s saw significant increases in soil erosion and the incidence of runoff (Boardman, 2002; Evans, 2005). Increased erosion and runoff had negative sediment associated impacts which reduced the quality of receiving waters (Evans, 1990; Jowett, 2005; Boardman, 1995; Pretty *et al*., 2003). There has, however, been recognition of the problems associated with agricultural land management and other anthropogenic factors which lead to increased suspended sediment inputs to watercourses and river systems and associated impacts on the quality of rivers (Walling, 2005). An enhanced sense of value and understanding has been attributed to the range of ecosystem functions, ecological services and aesthetic qualities, which can be provided by healthy river systems (Gore, 1985; Haines *et al*., 1988; Richter *et al*., 1997; Biggs *et al*., 1998; Naiman *et al*., 2002;

Palmer *et al* 2005). Brierley *et al*. (2006) suggest that the health of rivers is actually a reflection on the health of the societies through which they flow and that through catchment scale consideration, river health provides a means to measure the cumulative imprint of anthropogenic actions on the environment. In conjunction with issues of water quality within riverine systems, there is also a growing recognition of the decreasing availability of suitable water supplies in many parts of the world (Poff *et al*., 2003; Brierley *et al*., 2006). In order to reflect and interpret these changing values and needs, there has been a considerable and growing shift in public policy development and implementation, designed to mitigate negative impacts and to restore the condition of rivers (Jungwirth *et al*., 2002; Wheaton *et al*., 2006; Brierley *et al*., 2006; Endsreport, 2006).

In response to this change of emphasis in policy development at the international level, on 22nd December 2000, the European Parliament adopted the Water Framework Directive, 2000/60/EC (WFD) (EC, 2000). The WFD is a significant legislative manifestation of the increased awareness of community-wide water quality issues and the requirement for an integrated water policy. Under the WFD, Member States of the European Union (EU) are required to engage in a process which will enhance, restore and protect all surface waters and groundwater, including rivers, lakes, estuaries and in-shore coastal waters and also artificial and heavily modified water bodies such as canals, reservoirs or impounded rivers (EC, 2000). The central tenet of the WFD is to achieve a nominal 'good status' for European surface waters by 2015. The assessment of water status is based on chemical and ecological indicators, which incorporate biological indicators, riverine hydrology and channel morphology (EC, 2000; UKTAG, 2006). Heavily modified and artificial water bodies are expected to achieve 'good potential' within the same timeframe (EC, 2000). Suspended sediment plays a key role in influencing many, if not all, of the indicators of water status. It is anticipated that in order to safeguard the sustainable use of water resources, it is important to consider these broader environmental standards, which are designed to protect and in certain instances, restore both the structure and function of aquatic ecosystems (Ormerod, 2004; Jowett, 2005; UKTAG, 2006; Erba *et al*., 2006; Furse *et al*., 2006; O'Hare *et al*., 2006; Staniszewski *et al*., 2006; Szoszkiewicz *et al*., 2006).

A pre-requisite in the compliance process is the requirement to establish a set of parameters with which to assess the status of the respective indicators. After considerable debate, in 2008 agreement was finally reached in the European Parliament on a directive setting out harmonised Environmental Quality Standards (EQS) for 33 priority polluting substances including various heavy metals and toxic chemicals (Europa, 2008). This legislation repealed five previous directives related to the control of the pollutants concerned. The EQS represent thresholds (e.g. pollutant concentrations) which, if exceeded, might lead to adverse effects on ecosystems (UKTAG, 2008).

> "These standards will give a high level of protection to the environment and human health by translating the concept of 'good status' into transparent numerical values based on best available science and knowledge " (EU press release)
> (Europa, 2008).

Biological status boundaries have also been established using a series of classification indices and methods to assess elements including phytobenthos, macrophytes, invertibrates and fish (e.g.in the UK, DARES, LEAFPACS, RICT and FCS) (Defra, 2010a). Final acceptance of a revised priority list and EQS, including criteria for sediment physico-chemistry and morphology, is anticipated by the end of 2010.

In recognition of the need to manage water related issues on an integrated basis and at an extended catchment scale, a central component of the WFD delivery strategy has involved the establishment of a series of River Basin Districts (RBDs) throughout the EU member states. England and Wales are divided into 11 separate RBDs, which were each required to complete individual River Basin Management Plans (RBMPs) by 2009 (EA, 2010). The RBMPs detail the main issues for the aquatic environment and the necessary measures that are required to manage them (EA, 2010). In order to maximise the improvement of environmental protection within the RBMPs, emphasis has been placed on the importance of encouraging stakeholder engagement (e.g. water companies, land-owners and competent authorities) and the widest public participation at all stages of the process (UKTAG, 2008). In addition, the RBMPs were required to be integrated with concurrent EU legislation and initiatives (e.g. Nitrates Directive 91/676/EEC, Birds Directive 79/409/EEC, Habitats Directive 92/43/EEC and Urban Waste Water Treatment Directive 91/271/EEC).

Additional measures to incorporate environmental concerns into land management at a European level have come from the various reforms to the Common Agricultural Policy (CAP) over recent years. These reforms have sought to mitigate the environmental impacts caused by intensive agricultural production and to counter the potentially negative effects of previous CAP delivery initiatives (Winter and Gaskell, 1998). Farm payments were streamlined into the Single Farm Payment (SFP) and were decoupled from previous production orientated targets and now require cross-compliance with environmentally desired land management practises (Barclay, 2010; Defra, 2010d). For example, livestock farmers no longer receive payments based on the number of animals which they own, but on the land area which they occupy. This has removed the extra incentive to increase stocking densities, which had led to considerable over-grazing in the 1990s. Additional payments are available in the UK under the Environmental Stewardship scheme, which requires land management related to specific environmental and ecological benefits (Barclay, 2010). One specific CAP reform from the 2008 CAP "Health Check" which has been seen by some as flying counter to increased environmental protection is the abolition of set-aside. Set-aside was the requirement for arable farmers to leave at least 10% of available land out of cultivation in any year. It was originally introduced to limit community-wide over-production. This requirement has now been abolished to enable farmers to maximise their production potential in the face of the perceived challenges of food security. However, in many instances set-aside land formed extended field boundaries which provided food and refuge for large numbers of plant and animal species, whilst concurrently providing enhanced buffering capacity for sediment in runoff from cultivated land (Levin, 2010; Tucker *et al*., 2010). In part recognition of the loss of these functions, some changes to the cross compliance requirements are proposed to mitigate impacts (e.g. encouraging riparian buffer strips). However, the loss of compulsory set-aside since 2008 may well prove to be an important aspect of future catchment management research into the success or otherwise of current and emerging environmental policy delivery.

An important component of the RBMPs is a programme of measures designed to remediate and mitigate pollution pressures assessed to be coming from diffuse sources. This includes the important role of protecting soil resources to thereby reduce associated diffuse pollution problems throughout river catchments. Diffuse or non-point source water pollution can originate from a wide variety of potential sources including runoff from roads and urban areas and discharges from contaminated land, from forestry operations and importantly in this study, from agricultural land (Novotny and Chesters, 1981; Robinson and Blyrh, 1982; Johnson, 1993; Defra, 2010c). Water pollution, arising from individual point sources such as sewage treatment works and industrial effluent, has become relatively simple to monitor and can be assessed through the use of EQS. Point source discharges can also be regulated with reasonable ease through the issuing of discharge consents or licenses which can control both the quantity and quality of such discharges. Consents are subject to various conditions designed to ensure that sensible discharge limits are determined using available dilution and that no pollution occurs as a consequence (D'Arcy and Frost, 2001; Defra, 2010c). However, water pollution arising from diffuse sources, particularly from agriculture is harder to both monitor and control (Young *et al.*, 1989).

Diffuse pollution sources are difficult to manage for various economic, social, technical and political reasons. Identifying diffuse sources is not always easy, as they are often located over large geographic areas. However, through successful identification and targeting of specific areas or types of land use, which have known potential to contribute relative high sediment yields and associated nutrient transfer, limited financial resources can be utilized efficiently to alleviate potential problems and protect water quality (Young *et al*., 1989).

On a national level, commensurate with the requirement to satisfy WFD compliance and to address specific concerns regarding diffuse pollution issues associated with agricultural production, the Catchment Sensitive Farming (CSF) initiative was launched in 2006 across England and Wales (Defra, 2007). Priority catchments were identified (see Figure 1.1) where diffuse pollution problems associated with agricultural activity required remediation or mitigation measures, often in the form of the modification of existing farm management practices. The development of CSF in England led to the establishment of the England Catchment Sensitive Delivery Initiative (ECSFDI), which is a working partnership between the Department of the Environment, Food and Rural Affairs (Defra), the Environment Agency (EA) and Natural England (Natural England, 2010). Under the ECSFDI, measures to improve an initial 40 priority catchments, increased since to include an additional 10 catchments, rely to a large extent on farmer engagement. This engagement is encouraged through the establishment of partnerships between farmers, farm advisers, the competent authorities, water companies and conservation organisations. Capital Grant Schemes are available to support farmers in priority catchments in England, by providing grant aid towards the improvement or installation of facilities that would benefit water quality by reducing diffuse pollution (Natural England, 2010). The work involved in identifying catchment priority issues and helping farmers to engage with the process of delivering improvements is coordinated by Catchment Sensitive Farming Officers (CSFOs) (Collins *et al.*, 2010). CSFOs who were responsible for the case study catchments featured later in this study, were particularly informative and helpful in identifying potential sediment sources and catchment specific issues related to land use change and sediment problems.

In conjunction with initiatives to encourage improved land management practices, considerable efforts have also been made at a European and national level to tighten the legislative framework surrounding damage caused to the aquatic environment. An important instrument which could have major implications particularly for sediment management is the EU Environmental Liability Directive 2004/35/EC (ELD) (Slob *et al.*, 2008). The primary aim of the ELD is,

> '...to establish a common framework for the prevention and remedying of environmental damage at a reasonable cost to society' (Slob *et al.*, 2008)

The ELD covers not only damage to people and property, but also damage to nature and natural systems, in particular those natural resources which are linked to the sustainability of biodiversity (Slob *et al.*, 2008). The directive is designed to be implemented on the 'polluter pays principle', in that any person or organisation responsible for causing environmental damage is liable for the cost of remediation. This is likely to have considerable influence on sediment management, since any public or private companies which influence the quality or quantity of sediment will have to legally and financially account for their actions.

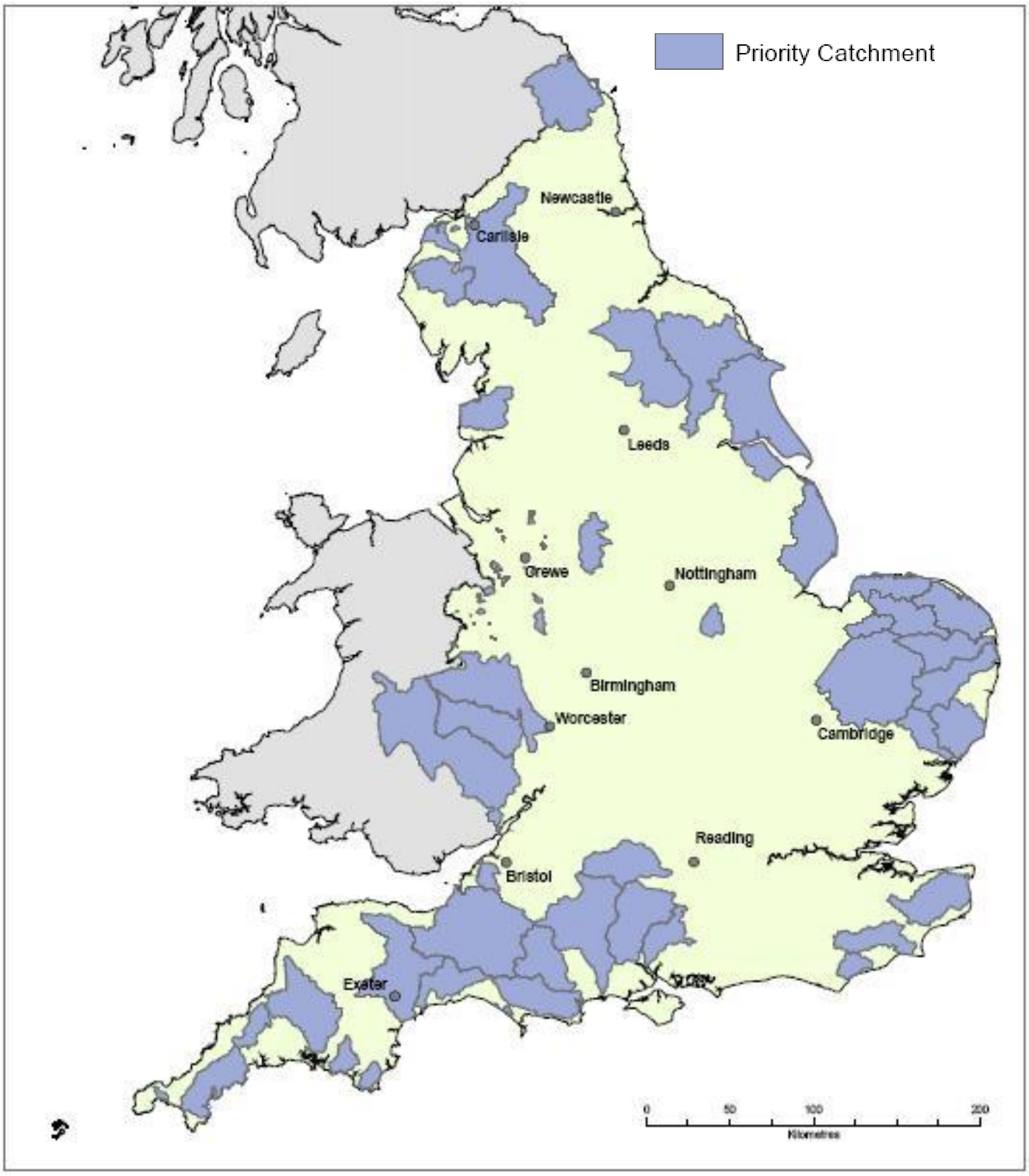

Figure 1.1 *Catchment Sensitive Farming Delivery Initiative priority catchments 2006-2008 England and Wales (Defra, 2009a)*

The ELD was transposed into English law on 1st March, 2009, through the establishment of The Environmental Damage (Prevention and Remediation) Regulations 2009. In accordance with the Directive, the Regulations are based on the polluter pays principle and hold operators financially liable for threats of or actual environmental damage (Defra, 2010e). The Regulations are designed to supplement existing environmental protection legislation such as the Environmental Protection Act 1990, the Water Resources Act 1991 or the Wildlife and Countryside Act 1981 and the Control of Major Accident Hazards Regulations 1999. Specifically the Regulations will apply in the case of environmental damage to protected species or natural habitats or a site of special scientific interest (SSSI) and also if an operator intended to cause environmental damage; or was negligent as to whether environmental damage would be caused (HMSO, 2009a). Further recent changes to UK environmental legislation to achieve compliance with the WFD include amendment to the Water Resources Act 1991, which has established the use of Water Protected Zones (WPZs) (Defra, 2010e). Activities within WPZs which may affect the quality and or quantity of water are closely regulated, particularly in respect to the hydromorphological quality element, with penalties of up to two years in prison and substantial fines for breaches (HMSO, 2009b). Significantly, the designation of WPZs has a major preventative component wherein they may be established,

> "...with a view to preventing or limiting any harm that is being or is likely to be caused to controlled waters, to regulate the carrying on in that area of activities which the appropriate national authority considers are likely to result in such harm." (HMSO, 2009b)

This enhanced environmental legislation will have major implications for damage resulting from or likely to be caused by diffuse pollution (e.g. excessive sedimentation and sediment contamination). In this respect it is essential to have robust techniques which can be used to identify with reliability the provenance of such pollution sources.

1.3 Catchment sediment sources – identification, monitoring and quantifying

In order to develop effective management strategies to satisfy current legislative requirements and to meet current and future environmental challenges, it is important to understand the effects which previous land use change has had on the sources and delivery of fluvial suspended sediment to the aquatic environment. Until relatively recently, lack of long-term data on the sources of suspended sediment has hitherto restricted the ability to properly consider the effects of changing land use on the provenance of suspended sediment (Collins *et al*, 1997a; Collins and Walling, 2004). However, the application of the sediment source fingerprinting technique can be useful in providing an informed view of the influence of past land-use on the relative sediment contributions from of different sources (Walling and He, 1994, 1999; Rumsby and Macklin, 1994; Collins *et al.*, 1997b; Owens *et al.*, 1999; Owens and Walling, 2002; Walling, 2005).

An understanding of the sources of sediment within a river system is an intrinsic component of any effective catchment management strategy (Walling *et al*., 1999). In order to establish the significance of any information on present sediment sources, it is useful to establish a context for such information, based on the variation of sediment source contributions in the past (Owens *et al*., 1999). It may then be possible to compare any temporal variations or trends in the sources of sediment against variations in other environmental factors, to thereby improve both knowledge and understanding of the processes involved, but also to target more effectively any remedial strategies and mitigation measures. However, the compilation of reliable information on sediment sources over varying temporal and spatial scales remains a challenging prospect (Walling, 2005). Traditional indirect monitoring techniques such as those with methodologies designed to estimate soil loss through the use of erosion pins, erosion plots, aerial and satellite imagery, are subject to various operational and economic constraints (Collins, 1997a; Walling, 2005).

Traditionally, indirect measurement and monitoring techniques have been employed in the assessment of the relative importance of sediment contributions from individual source types. These indirect techniques involve measurements of erosion activity or visual observations, which are subsequently used to infer sediment provenance and associated relative contributions. However, catchment-scale sediment monitoring programs running over long time periods are usually prohibitively expensive and are also often limited by problems of spatial and temporal sampling and operational difficulties (Peart and Walling, 1988; Loughran, 1989; Loughran and Cambell, 1995; Collins and Walling 2004; Walling, 2005; Walling and Collins, 2008). Consequently, indirect monitoring programs are frequently of relatively short-duration, often measured in years rather than decades (Collins and Walling, 2004). This can lead to discontinuous data records that of insufficient temporal and spatial resolution for reconstructing continuous historical patterns of suspended sediment provenance.

There are a variety of indirect techniques which have been used to assemble data related to sediment sources. Erosion pins and erosion plots have been employed to measure the rate of soil loss by recording surface lowering or the morphology of fluvial features such as channel banks or gully sides (Fanning, 1994; Lawler *et al*., 1997; Stott, 1999). However, these involve many operational problems and are difficult to apply to anything other than small catchments, due to spatial sampling constraints (Walling *et* *al*., 1993). Aerial photographs have been used to determine soil redistribution patterns, channel bank and gully erosion erosion and sedimentation patterns (Sharma and Singh, 1995; Vandaele *et al*., 1996; Ries and Marzolff, 1997; Planer-Friedrich, 2008). However, indirect measurements based on aerial imagery are known to be limited by factors like image resolution, effects of shadows, quality of ground control, vegetation cover and image evaluation techniques, which strongly influence the measurement accuracy (Giménez, 2009; Winter and Lobley, 2009). In recent years substantial improvements have been made in the use of remote sensing from satellite imagery (Basnyat *et al*., 2000; Ning *et al*., 2006; Goetz *et al*., 2008). At present, however, such studies fall considerably short of the requirement for continuous longer-term information on catchment suspended sediment sources.

Exceptions to the generally limited duration of monitoring programs include the investigation reported by Vollmer and Goelz (2006) on the River Rhine. In this longer term monitoring programme, daily records of suspended sediment flux from 11 permanent sampling stations along the River Rhine for a period of over 35 years have produced data of considerable research value. These data provide information on the influence of sediment inputs from the main tributaries and the retention effect of the impoundment-chain of the Upper Rhine on the suspended sediment budget, whilst concurrently allowing interpretation of the catchment response to high magnitude rainfall and flooding events (Vollmer and Goelz, 2006). Datasets covering such temporal and spatial scales, are however, rare and alternative techniques are required which can provide reliable historic data in a more expedient and economic manner than long term monitoring programmes.

1.4 Sediment source fingerprinting

The sediment source fingerprinting technique provides for the direct quantitative determination of sediment provenance, whereby the relative contribution of different sediment sources (e.g. land use types, channel banks and road verges) and spatial provenance (e.g. tributary sub-catchments or differing catchment geologies) can be reliably determined across a range of spatial and temporal scales (Collins *et al*., 1997a; Walling and Collins, 2000; Small *et al*., 2004; Collins *et al*., 2010a). The technique requires the initial selection of suitable physical or chemical properties which can reliably discriminate potential source materials, followed by the comparison of values measured for the selected properties in source materials against measured values for the same properties in suspended or deposited sediment in order to identify the likely sediment source (Walling *et al*., 1993).

1.4.1 Development of the sediment source fingerprinting technique

The sediment source fingerprinting technique has been used successfully to provide reliable information on suspended sediment sources in a wide range of studies over the last 30 years (Klages and Hsieh, 1975; Wall and Wilding, 1976; Lewin and Wolfenden, 1978; Walling *et al*., 1979; Grimshaw and Lewin, 1980; Oldfield *et al*., 1985; Foster *et al*., 1986; Peart and Walling, 1986; Dearing and Foster, 1986; Foster and Walling 1994; Slattery *et al*., 1995; Collins *et al*., 1997a,b; Wallbrink *et al*., 1998; Owens *et al*., 1999; Botterill *et al*., 2000; Kim *et al*., 2001; Gruszowski *et al*., 2003; Carter *et al*., 2003; Collins *et al*., 2010a,b). The technique has been applied to suspended sediment, bed sediment and estuarine sediment to determine contemporary sediment provenance. Changes in the primary sediment sources within river catchments over time have been estimated by employing sediment cores from lakes, and floodplains (e.g. Yu and Oldfield, 1989; Foster and Walling 1994; Collins *et al.*, 1997b; Owens *et al*, 1999; Duck *et al*., 2001; Foster *et al*., 2003; Foster, 2010).

Many earlier investigations which applied the sediment fingerprinting approach achieved some success using single-component fingerprints (e.g. Oldfield *et al.*, 1979; Peart and Walling, 1986, Stott, 1986; Wasson *et al*., 1987; Burch *et al*, 1988; Garrad and Hey, 1989, Oldfield & Clark, 1990; Jones and Smock, 1991; Wallbrink and Murray, 1990; Walling and Woodward, 1992). However their ability to provide robust quantitative results was confounded by a number of difficulties. These include firstly, the spatial variability of any potential sediment sources within a river catchment; secondly, the highly complex sediment routing and delivery process; thirdly, the invariable need to discriminate between various potential sources (Walling and Collins, 2000). In addition, spurious source-sediment associations can result from the use of single-component sediment fingerprints, consequently no individual diagnostic property can distinguish reliably between different source types (Yu and Oldfield, 1989; Molinaroli *et al*., 1991; Walling *et al*., 1993). Whilst the concentration of a single fingerprint property measured in a sediment sample could resemble that of a particular source, such a value might also result from the mixing of various combinations of other sources within the catchment (Walling and Collins, 2000). Consequently, it is now common for investigations employing the sediment source fingerprinting approach to use multi-component (composite) fingerprint signatures incorporating various physical and chemical properties (e.g. geochemistry, radioisotopes, mineral magnetism, particle size and shape, organic elements, colour) (Oldfield and Clark, 1990; Foster and Walling, 1994; Walling *et al*., 1993; He and Owens, 1995; Walden *et al*., 1997; Collins *et al*., 1997a,b; Wallbrink *et al*., 1998; Owens *et al*., 1999; Collins *et al*., 2001; Gruszowski *et al*., 2003; Walling *et al*., 2008; Martínez-Carreras *et al*., 2010).

Important advances in the development of the source fingerprinting technique have included the incorporation of quantitative mixing model (also referred to as unmixing model) algorithms, which allowed the quantitative estimation of relative contributions from different sources (Yu and Oldfield, 1989; Walling *et al*., 1993). The development of these mixing models has tended to be based around optimised linear regression incorporating the iterative solving of a series of sum of least squares equations (Collins *et al*., 1996; Collins *et al*., 1997a,b,c; Walden *et al*., 1997). The increased reliability of estimates provided by use of quantitative mixing models was further enhanced by the use of rigorous statistical procedures to test the ability of properties to adequately discriminate source types, including cluster analysis and multivariate discriminant function analysis (Walling and Woodward, 1995; Collins *et al*., 1996, Collins *et al*., 1997a,b,c). Additional aspects of development work have included studies incorporating the influence of particle size and organic matter content on property concentration values (He and Walling, 1996; Collins *et al*., 1997a,b,c; Russell *at al*., 2001; Motha *et al*., 2003). More recent work has focussed on aspects of uncertainty within the technique, including that associated with the number and type of tracers included in the mixing model, the spatial variability of the tracer signatures of individual sources, the within-source variability and discriminatory power of individual tracer properties and the equifinality of derived mixing model solutions (Bevan, 1996; Rowan *et al*., 2000; Franks and Rowan, 2000; Small *et al*., 2002; Martínez-Carreras *et al*., 2008; Collins *et al*., 2010a,b,c). Various refinements to minimise aspects of uncertainty have been suggested including the use of Baysian Monte Carlo frameworks, weighting factors and the use of prior information (Rowan *et al*., 2000; Small *et al*., 2002; Collins *et al*., 2010b).

1.4.2 Sediment source fingerprinting of historical sedimentation

Sediment source fingerprinting has proved to be a useful technique for addressing the temporal limitations of more conventional sediment source monitoring programmes through the use of sediment profiles preserved in various types of depositional sinks, such as lakes, reservoirs and floodplains (Foster *et al*., 1986; Foster and Dearing, 1987; Foster *et al*., 1991; Collins *et al*., 1997b; Owens *et al*., 1999; Ahn *et al*., 2009). The information stored in such depositional sinks can serve as an integrated record of proxy historical suspended sediment data. Horowitz (1991) stated:

> "An undisturbed sediment sink contains an historical record of chemical conditions. If a sufficiently large and stable sink can be located and studied, it will allow an investigator to evaluate chemical changes over time and possibly to establish area baseline levels against which current conditions can be compared and contrasted" (Horowitz, 1991).

Similarly, by employing geochemical fingerprint properties which discriminate differing catchment sources and are conservative, following sediment mobilisation, deposition and storage, the sediment fingerprinting technique can establish historical trends in relative sediment yields for comparison against concurrent land use changes. This information can also provide baseline conditions for comparison with any subsequent changes in relative sediment contributions from catchment sources in response to future land use change.

The investigation of variation in sediment yields and sources over different time periods using lacustrine sediment cores has become well established (Foster *et al*., 1985; O'Hara e*t al.*, 1993; Foster and Walling, 1994; Heathwaite, 1994; Owens and Slaymaker, 1994; Page and Trustrum, 1997; Zolitschka, 1998; Owens *et al*., 1999; Owens and Walling, 2002; Foster *et al*., 2003). Similarly, although to a lesser extent, floodplain sediment, deposited during overbank flooding, has been used in retrospective investigation of changing sediment sources (Passmore and Macklin, 1994; Collins, 1995; Foster *et al*., 1996; Collins *et al*., 1997b; Foster *et al*., 1998; Bottrill *et al*., 1999; Owens *et al*., 1999; Nicholls, 2000; Owens and Walling, 2002) and to estimate historical variations in suspended sediment fluxes (Walling and He, 1994; Owens *et al*., 1999). Throughout upland areas of the UK, there are many river catchments draining into lakes and reservoirs which can be used to investigate historical changes in the sediment response, however, floodplain overbank sediment often represents the most readily available source of information for lowland environments (Owens *et al*., 1999).

The temporally orientated application of the sediment source fingerprinting technique is based on a comparison between fingerprint properties of historical sediment deposits and contemporary catchment source material. Although floodplain sediment, by definition, is limited to that which is deposited overbank during flooding events, suspended sediment transport is generally episodic and occurs primarily during storm events (Walling and Webb, 1987). Consequently, the record of sedimentation resulting from high magnitude storm events contained in floodplain sediment deposits can be considered to be generally representative of the total suspended sediment flux within a catchment over time (Collins and Walling, 2004). A thorough description and application of the sediment fingerprinting technique to overbank floodplain sediment is detailed in the following chapters.

1.5 Land use change

In order to inform river and land management planning for future changes in land use, it is important to gather relevant information on the influence and impacts of historic land use and management changes. Over the last century, land use in the UK has undergone considerable changes.

After the "Golden Age" of British agriculture in the 1860s and 1870s, the subsequent period up to the First World War was heavily influenced by rising agricultural prices and increasing completion from abroad (Stamp, 1940). This led to a general decline and the abandonment of many tracts of marginal land, particularly in the uplands and the concentration of farming into the most productive areas of land (Stamp, 1940). During the First World War there was an increase in the area of land used for arable cultivation in response to the 1917-1918 ploughing-up campaign, designed to improve food security. The area of cultivated land increased from 3,468,000 ha in 1914 to 4,055,500 ha in 1919 (Sheail, 1973). The increase in arable cultivation was encouraged through the high prices achieved for arable crops through price protection for farmers, introduced by the War Cabinet in 1917 (Riley and Harvey, 2007; Sheail, 1976). The instigation of the plough-up campaign met with mixed results, as land that was poorly suited for arable production was often included in the effort. In common with the wider economy, the period between the wars saw a great depression in agriculture following the Agriculture Act of 1921 (Grigg, 1965). Land use began to polarise as labour costs rose, arable cultivation decreased and grassland farming became more productive with larger herds, particularly in the West of the country. With the outbreak of the Second World War in 1939, grassland was once again put under the plough as agricultural policy was taken over by the Ministry of Food and farms were encouraged to become self-contained mixed units once again (Stamp, 1940). In the aftermath of the Second World War, national agricultural policies in the UK ushered in a huge productivity drive with the Agriculture Act of 1947 (Robinson and Sutherland, 2002). The privations of the war years and the continued rationing of food stuffs, coupled with an unaffordable reliance on imports, created a strong national desire for improved food security based on increased production and productivity (Self and Storing, 1962). Price guarantees were introduced to encourage stability and confidence in the agricultural industry (Winter *et al*., 1998). The push to improve productivity and increase output was boosted further following the UK entry into the Common Market in 1973 (Potter, 1997; Robinson *et al*., 2000). The European Common Agricultural Policy (CAP), based around production led subsidies, dominated the economics and methods of agricultural production in the UK (Evans, 2005). The implementation of these policies led to substantial changes in agricultural practises and forms of land management. The amount of inputs (e.g. fertilizers) and treatments (e.g. pesticides and herbicides) increased, whilst advances in genetics led to higher yielding cultivars and larger livestock breeds (Robinson and Sutherland, 2002; Tscharntke *et al*., 2005). The intensification of agricultural production practices resulted in considerable changes in land use with concurrent consequences for terrestrial and aquatic environments (Owens and Walling, 2002; Benton *et al*., 2003).

Agriculture covers over 70 per cent of the land area of England and common farming practices represent major sources of diffuse pollution of aquatic systems, including soil erosion, nutrients from fertilisers, herbicides and insecticides, faecal contamination, pharmaceuticals and organic material from livestock (Novotny and Chesters, 1981; Young *et al*., 1989; Trimble and Mendel, 1995; Kim and Carlson, 2005; Ghosh and La Para, 2007; Defra, 2010a). Eutrophication resulting from allochthonous nutrient inputs to rivers can result in toxic algal blooms with consequent adverse impacts on the food chain affecting vegetation, insects, fish, mammals and birds (Smith, 2009). Whilst agriculture is not the single cause of these problems it has been identified as a major cause and is estimated to contribute approximately 60 per cent of nitrates, 25 per cent of phosphorus and 70 per cent of sediments entering surface waters, amongst other pollutants (Defra, 2010a).

Production based livestock subsidies incorporated within the European CAP led to increased stocking densities, which often became associated with over-grazing (Winter *et al*., 1998). The occurrence of such practises in upland areas of rough grazing lowers sward height, reduces surface roughness and increases soil exposure which leads to increased vulnerability of soils to erosion and runoff (Evans, 2005). High stocking densities can also be ecologically detrimental in areas containing sensitive habitats (Milsom *et al.,* 2003). Lowland over-grazing can result in excessive trampling, compaction and puddling (poaching) of soils, whilst unfenced riparian zones are vulnerable to increased stream bank erosion by thirsty livestock (Collins *et al*., 1997a; Russell *et al*., 2001, Walling *et al*., 2003). Increased bank erosion generates direct sediment inputs to river waters and can create channel widening. Increases in channel width can result in flow velocity being reduced, thereby enhancing the potential for fine sediment deposition and associated deleterious effects on aquatic flora and fauna (Walling *et al*., 2003; Owens *et al*., 2005).

Due to various factors, the numbers of cattle and sheep in the UK have generally declined over the last decade, as illustrated in Figure 1.1 (Defra, 2007). The impact of foot and mouth disease in 2001 had a devastating effect in many parts of the UK. CAP reforms in 2003, which severed the link between subsidy and production, combined with the introduction of the single farm payment in 2005 to removethe incentive to maintain livestock numbers to receive subsidy payments (Gohin, 2006). However, whilst overall livestock numbers may have declined, intensive production techniques can concentrate livestock in smaller areas of grassland leading to increased stocking densities, thereby compounding livestock environmental impacts. The effects of trampling in these focused conditions leads to soil poaching, which can in turn result in increased surface runoff and sediment mobilisation during high magnitude rainfall events. Many farmers who left the dairy industry switched to beef production (Burrell, 2004). The relative live weight of a beef herd is considerably higher than that of a dairy herd and this also increases consequent pressure on grassland (Vickery *et al*., 2001).

However, if the reduction in overall livestock numbers in the UK results in increasing imports of meat and meat products, then this will simply lead to the translocation of the associated environmental problems to other parts of the world (Williams *et al*., 2006).

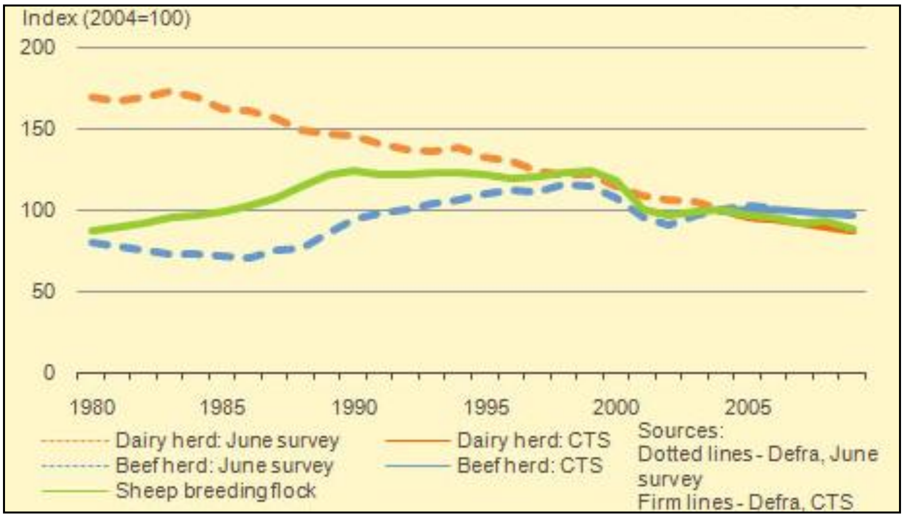

Figure 1.2 *Changes in the English dairy herd, beef herd and sheep breeding flock since 1980. The data are expressed as indices with 2004 (as the reference year before CAP reform) set at 100 (Defra, 2007)*

The intensification of livestock production practices has also caused a growth in the demand for suitable fodder crops, such as sugar beet, field beans, turnips, swedes, mangolds and maize. These crops are generally harvested late in the year, leaving fields bare during the autumn and winter months and thereby subject to increased erosion risk from winter storms (Robinson *et al*., 2000; Holman *et al*., 2003). The development of cultivars better suited to UK climatic conditions, has led to a major expansion in maize cultivation since the late 1980s, often in areas traditionally associated with permanent pasture, as livestock farmers seek to reduce winter feed bills (Jafaar, 2010). Maize row cropping patterns create a lack of vegetative cover and the use of heavy machinery results in compacted bare soils which are a major sediment source. The cropped maize fields often remain without substantial cover over several months and can represent important sediment sources throughout the entire late-autumn and winter period. In addition, weed control herbicidal practices associated with intensive maize cultivation expose inter-row soils to increased vulnerability to both erosion and runoff (James, 2004). Grassland systems and thereby livestock production in the UK are generally established in areas receiving high rates of rainfall, such as the South West and North West of England. The increased vulnerability of soils to erosion caused by maize production in these areas can be further exacerbated when coupled with frequent high magnitude rainfall (Robinson and Sutherland, 2002; Wagner *et al*., 2009).

Arable cultivation has been transformed over the last 50 years. Field sizes have been enlarged in response to requirements for ever increasing intensification. Fuelled by CAP grants in the 1970's for the grubbing out of hedges to maximize the potential for mechanisation, it is estimated that there has been a 50% loss of UK hedgerow stock (Robinson and Sutherland, 2002). There has been a substantial increase in the area of land cultivated with autumn sown cereals and oil seed rape (Robinson and Sutherland, 2002). These practices leave tilled soils bare and vulnerable during the winter months. Such soils can more easily become saturated and prone to runoff and erosion, causing increased sediment inputs to the river system (Walling and Amos, 1999; Evans, 2005). Increased mechanisation and the requirement to access the land during the wetter months of the year, due to autumn sowing, can lead to increased soil compaction. This problem can be compounded when it occurs as bare tractor wheelings orientated down hillslopes (Withers *et al.*, 2006). Compacted wheelings not only increase runoff and can lead to erosion but can also serve to deliver such runoff and associated sediment more quickly to water courses, by increasing connectivity between fields and receiving waters (Silgram, 2010).

Connectivity between potential sources of sediment and water courses has been substantially increased in many areas by the large-scale installation of field drainage, particularly during the 1970s and early 1980s (Robinson and Armstrong, 1988; Foster *et al.*, 2003). Such drainage was often installed on marginal land with heavy soils, prone to saturation and flooding, but it was also installed widely on improved grassland and intensive arable areas in an attempt to increase productivity (Chapman *et al.*, 2005). Increased connectivity can lead to problems of flooding downstream as the time to peak of the flood hydrograph is reduced, thereby increasing the potential and magnitude of medium and large river floods (Robinson and Blackman, 1990). Further, following historical precedent, large wetland areas of high ecological value have been drained for agricultural production (Holden *et al.*, 2004). The effects of drainage on hydrological contact across the water-land ecotone combined with the decrease in water transfer times can considerably reduce the nutrient retention capacity within field systems (Fleischer *et al.*, 1991; Vought, 1995; Kronvang *et al.*, 1998). The removal of field boundaries such as hedges and walls to increase field sizes are further factors which increased the connectivity between land under agricultural production and watercourses. Increased connectivity raises the potential for more efficient suspended sediment delivery to receiving waters, with the accompanying potential to transport substantial amounts of nutrients and contaminants (Chapman *et al*., 2003).

In the period immediately following the Second World War, extensive areas of forest plantations were established, both through the state Forestry Commission and private forestry incentivised through financial subsidies and tax concessions (Robinson and Sutherland, 2002). Over recent years, a large proportion of these forests have reached felling age. Forestry operations are heavily mechanised and can often cause considerable soil mobilisation through the effects of surface disturbance and soil compaction combined with track and drain construction on steep slopes (Newson, 1980). The impacts on water quality in the UK resulting from increased sediment loads linked to afforestation have been widely recognised (Burt *et al*., 1984; Duck, 1985: Stott. 1989; Leeks, 1992; Nisbet, 2001; Stott and Mount, 2004).

1.6 Emerging issues for future land use change

Land that is suitable for agricultural production is subject to changes in management practices as a consequence of the choice of crop type and instigation of differing cropping land-use patterns, crop rotations and livestock requirements. Political policy and agri-economics can influence the increased cultivation of crop types which were previously only grown over limited areas and can also lead to the introduction of entirely novel crops (Haughton *et al*., 2009). This type of land use change has occurred throughout history, but, growing concerns over energy and food security combined with climate change are likely to result in major land-use change, which could occur over relatively short time-scales and affect considerably large areas of land (Schulp, 2008; Von Braun, 2009; Winter and Lobley, 2009; Dayan *et al*., 2009; Haughton *et al*., 2009).

1.6.1 Food security

Recent spikes in the worldwide price of certain foods, related largely to uncertainties in commodity markets and oil prices, have led to renewed concerns over food security both globally and nationally (Naylor *et al.*, 2008). UK agriculture already has relatively high rates of productivity, and in order to increase agricultural output significantly, land which has been previously taken out of agricultural production may be required to revert to its former use. The potential environmental impact of any increase in the area of land under cultivation or further intensification will need careful consideration and information on the effects of previous changes could be particularly useful in guiding management decisions.

1.6.2 Bioenergy

In response to increasing demands for renewable sources of energy and the requirement for climate change mitigation measures there is substantial interest in the cultivation of crops for bioenergy and biofuel generation (Rowe *et al*., 2009; Baka and Roland-Holst, 2009). In order to cultivate sufficient biomass for large-scale bio-energy generation substantial land use conversion is likely to be required. Aside from any conflicts related to competition between crops for energy and increasing food security issues, there are also important potential environmental impacts to be considered (Schmidhuber, 2006; Ogg, 2009; Petrou and Pappis, 2009). In addressing concerns related to the use of prime agricultural land for the cultivation of crops for bioenergy, such cultivation is increasingly being considered on more marginal land. Whilst this option might reduce potential impacts on food production, the impacts on terrestrial and aquatic environments resulting from converting large areas of marginal land will need careful consideration. Assessment of potential physical impacts, loss of ecosystem services and also implications for existing legally binding international commitments to environmental protection will be required (Howard *et al*., 2009; Lovett *et al*., 2009; Rowe *et al*., 2009).

1.6.3 Carbon sequestration

As part of the emerging climate change strategies, carbon capture and storage are important aspects which can have impacts on both water quality and quantity. Carbon sequestration through the expansion of plantations planted with fast-growing species such as poplar and willow, typified by high leaf area index and the rapid development of a closed uniform canopy can lead to the lowering of the water table through the impact of evapotranspiration rates well in excess of those associated with arable cultivation (Finch *et al*., 2004; Tricker *et al*, 2009). Planting trees on land which has previously been under-drained can lead to the destruction of existing field drains causing localised flooding and reduced flow rates to the lower catchment (Sherrington, 2008). Conversely, preparation of marginal wet land areas for plantations through extensive under-drainage can lead to greatly increased sediment delivery (Ramchunder *et al*., 2009). Impacts on runoff rates and erosion can be particularly acute with forestry operations, during periods of both planting and harvesting (Tricker *et al*, 2009).

Over the coming decades, patterns of land use in the UK are highly likely to change in response to various pressures, both established and emerging. Although the exact form of any potential changes and their associated impacts cannot be predicted with any certainty, important information may be identified by establishing general trends and associated consequences related to land use change in the recent past.

1.7 Summary

It has been demonstrated that land use can influence the behaviour of soil erosion and mobilisation processes which contribute sediment to aquatic systems. Greater understanding of the relationship between land use and the relative sediment contributions from differing contributory sources remains an important research need for informed holistic catchment management and land use planning.

Through the use of the sediment source fingerprinting technique applied to floodplain overbank sediment cores, it is possible to estimate relative sediment contributions from differing sources over the recent past ca. 100years. The fluctuations in relative sediment contributions from differing sources over time can be compared to any known land use changes which occurred within the catchment over the same time period to consider possible associations. Floodplain overbank sediment cores have been successfully used in such a context in previous studies. However, these studies have not been particularly numerous and it is hoped that by applying the technique to a range of six differing catchment types with histories of identified sediment related problems, further insight into catchment interdependencies might be achieved.

Since the early development of the source fingerprinting technique it has undergone various refinements to improve its robustness and minimise areas of uncertainty. It is hoped that this study can make a useful, if modest, contribution to the continued refinement of the technique which can improve its resolution and expedite its application.

1.8 Aim and objectives

1.8.1 Aim

The aim of the study reported in this thesis is to consider the impacts and influence of known land use changes in the recent past (ca. 100 years) on sources of sediment in six different UK river catchments by using the sediment source fingerprinting technique applied to floodplain overbank sediment cores. It is anticipated that any information derived regarding sediment sources could be used in the development of subsequent policy which addresses the requirements of the EU Water Framework Directive.

1.8.2 Objectives

1. To identify six suitable geographically disparate UK case study catchments which have experienced clearly identified sediment related problems and for which documented land use histories are available.

2. To identify optimum composite fingerprints for discriminating the potential sources using appropriate statistical tests and to quantify relative sediment contributions from individual sources over the time period represented by individual sediment cores using appropriate numerical modelling.

3. To refine aspects of the fingerprint property selection procedure to thereby improve the ability of the composite fingerprint to discriminate between source types and also to ensure that the mixing model provides robust apportionment estimates as reflected by the resultant goodness of fit.

4. To redesign the configuration of the mixing model to expedite performance and improve its ease of operation.

5. To recognise explicitly aspects of uncertainty by incorporating Monte Carlo frameworks and fingerprint property discrimination based weightings into the mixing model.

1.9 Thesis structure

The thesis is divided into 10 chapters. Chapter 1 (this chapter) provides an introduction to the work by outlining the background to changes in land use in the UK over recent history. The development of methods to study the impacts of these changes on sediment sources, particularly in the context of water quality policy and practice is also presented. In addition, the requirement for continued development and the research application of the fingerprinting technique is outlined. Chapter 2 describes the field and laboratory methods which were applied during the catchment case studies presented in Chapters 4-9. Similarly, Chapter 3 describes the statistical methods, data processing and refinements of the sediment source fingerprinting technique which were applied to the respective case studies. The case study chapters present the application of the sediment source fingerprinting technique to cored sections of floodplain overbank sediment from 6 different case study river catchments with varying sediment related land use issues. Chapter 4 features the River Torridge catchment, in Devon, UK and specifically considers the potential effects of land drainage on sources of fine sediment, whilst additionally analysing the potential effects of other land use changes in the catchment over the last 100 years. Radioisotope geochronology estimates are compared using ^{137}Cs and ^{210}Pb techniques. Chapter 5 presents a case study from the River Axe catchment in South West UK and specifically considers the potential impact of fodder maize cultivation and intensive livestock production practices on sediment sources. Chapter 6 examines the effects of land use change on sediment sources in the River Arrow catchment in Herefordshire, UK, with particular reference to the impact of the increased area of intensive potato production and the reduction of livestock numbers over the study period. In Chapter 7, the re-profiling and maintenance of river channels for flood risk management are specifically considered in the context of sediment impacts within the River Waver catchment, Cumbria, UK. Chapter 8 presents a case study of the River Rye catchment in North Yorkshire, UK and examines the potential impacts on sediment sources of an expansion of arable cultivation into inappropriate areas and considers issues of catchment scale in relation to localised high magnitude impacts. The case study presented in Chapter 9 investigates the effects of land use changes within the River Wensum catchment in Norfolk, UK and specifically considers the impacts of intensification of arable production systems on sediment sources. In addition, the potential for historical in-channel engineering structures to temporarily buffer the transport of suspended sediment storage is considered. Finally, Chapter 10 provides a brief discussion of the main conclusions from the case studies, including some of the problems and limitations encountered during the research programme and some suggestions for future work.

CHAPTER 2 FIELD AND LABORATORY METHODS

2.1 Introduction

This chapter details the field and laboratory methods used in this study. The methods described include the approach used for selecting suitable study catchments; the techniques used for collecting source material and floodplain sediment samples and the laboratory protocols and procedures applied during sample preparation and analysis.

Figure 2.1 presents a basic conceptual model of sediment source fingerprinting by comparing floodplain sediment deposits with a series of potential sources defined in terms of source types (Collins and Walling, 2000). Land use practices can leave soils vulnerable to high magnitude storm events, which can lead to the erosion and mobilisation of sediment from various sources. These sources could include topsoils from cultivated land, uncultivated grassland or woodland respectively and also material from eroding channel banks or similar sub-surface sources such as ditches and open field drains. The sediment mobilised from the various individual sources within a catchment is mixed during transport and delivery to the floodplain. Individual source types can be discriminated by a statistically-verified combination of properties which form a composite fingerprint. Comparison of source and floodplain material using the concentration values of the composite fingerprint properties incorporated into an optimised numerical mass balance mixing model permits the apportionment of the relative contributions (%) of sediment from the respective sources.

Comparison of floodplain samples and source soils necessarily limits assessment of sediment provenance to the sediment transported by flood events resulting in overbank inundation, as opposed to all sediment transporting events. However, since overbank flood events are likely to account for a large proportion of sediment transport per unit time, the results obtained can provide representative information on sediment source contributions in the various study catchments.

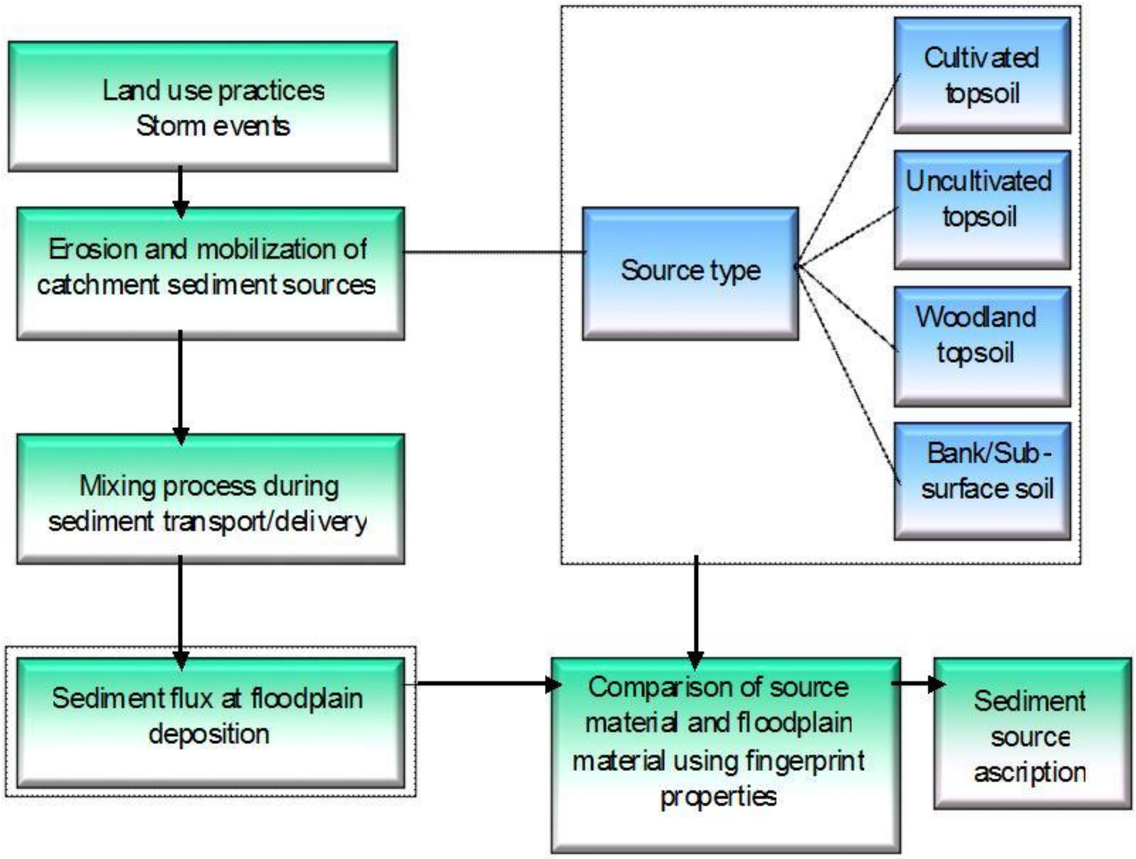

Figure 2.1 *Conceptual model of floodplain sediment source fingerprinting (From: Collins and Walling, 2002)*

2.2 Study catchment selection

Catchments which were suitable for inclusion in the study were selected using five basic criteria. The first requirement was that any potential study catchment should have an identified sediment-related problem. Second, candidate catchments required reasonable records of land use history from the recent past in order to compare documented changes in land use with any estimated changes in the relative sediment contributions derived from individual source types. Third, catchment sizes would have to be large enough to be representative of catchment-scale processes and yet small enough to be adequately characterised within the resource limitations of the study. Fourth, in order to consider the efficacy of applying the technique to varying catchment types, the catchments were required to be geographically diverse and representative of differing river types. Fifth, any prospective study floodplain was required to be reasonably well developed in order to provide an acceptable sediment sink.

Under the England Catchment Sensitive Farming Delivery Initiative (ECSFDI) a total of fifty priority catchments were identified as being the focus of targeted advice and support (DEFRA, 2010). The ECSFDI priority catchments were selected from data which had been collated for purposes related to the delivery of the EU Water Framework Directive (WFD). The drivers for the designation of priority catchments included concerns over sediment-related issues. The study catchments and their respective sediment and land use issues are listed in Table 2.1.

Table 2.1 *Study catchments and reported associated sediment problems*

Catchment	**Problem**
Wensum	SSSI is considered to be under the condition ‘unfavorable and declining’ mainly because of sediment deposition, bank poaching and diffuse water pollution. Designated a Special Area of Conservation (SAC) under the EU Habitats Directive.
Axe	SAC in unfavorable condition due, in part, to unacceptable sedimentation. Fisheries staff concerned for salmonid survival due to high sedimentation. Expanding maize cultivation cited as a potential problem, particularly in the upper catchment. Intensive grassland management associated with dairy farming throughout the entire catchment.
Arrow	Expansion of intensive potato cultivation since the late 1970s. Fine tills prepared in lateral rows on hill slopes, in conjunction with potentially high connectivity to watercourses. Infilling of field ditches with accumulated sediment. Excessive sediment impacts on downstream River Lugg.
Waver	High connectivity between intensively farmed land and water courses due to extensively re-profiled surface drainage. Ground in many areas still remains saturated for long periods of time, resulting in severe poaching from livestock and structural damage from trafficking. Maize cultivation reportedly increasingly prevalent on inappropriate high erosion risk land.
Rye	Large-scale land slip and mass sediment mobilization reported by the catchment officer. High rainfall, combined with steep gradients can result in agricultural land generating high runoff rates, delivering large volumes of sediment into the River Rye and the downstream River Derwent River system. Extensive areas of winter wheat, maize, potatoes and other high risk arable crops established on a variety of gradients, including steeply sloping land.
Torridge	Identified increases in sediment loads, negative effects reported on salmonid habitats possibly related to large scale land drainage improvements. Recent increase in fodder maize cultivation.

(Environment Agency, 2008; DEFRA, 2010a; Walling, 1999, 2005)

Five regionally diverse ECSFDI priority catchments, which had been identified as having sediment-related problems, were selected for inclusion in this study. The catchments which were selected included the River Wensum, Norfolk; the River Waver, Cumbria; the River Axe, Dorset; the River Rye (tributary of the River Derwent), Yorkshire and the River Arrow (tributary of the River Lugg), Herefordshire. A sixth catchment, the River Torridge, in Devon, was included based on sediment issues identified in the existing literature and on the basis of anecdotal evidence (Walling, 1999; Walling, 2000, 2005). In certain cases it was necessary to focus upon the upper reaches or, in the case of larger catchments, to select specific priority tributaries. The locations of the study catchments are shown in Figure 2.2.

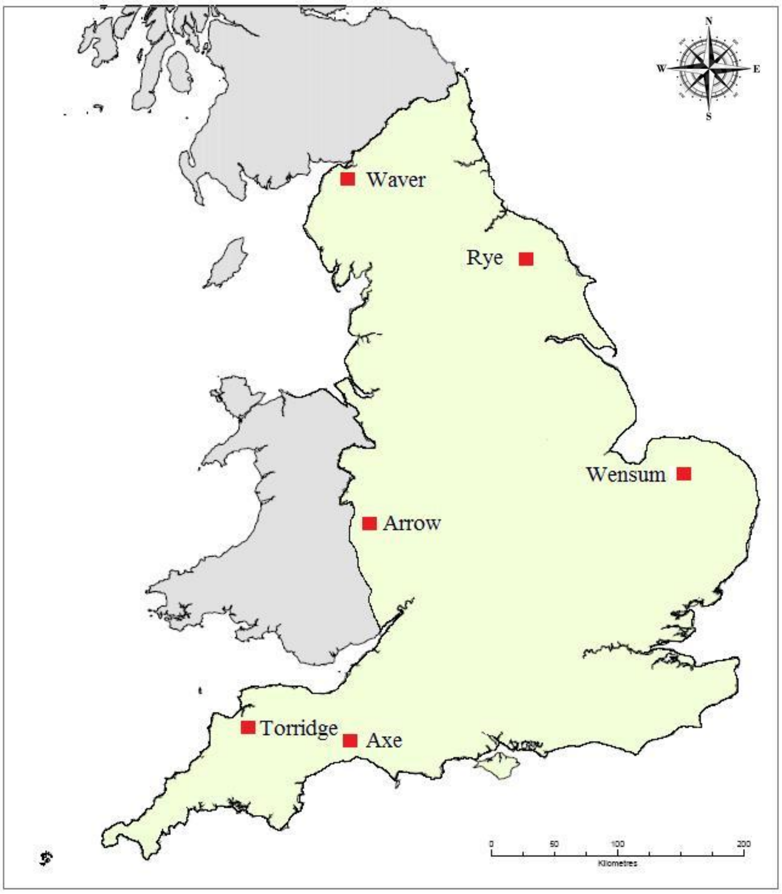

Figure 2.2 *Map showing locations of the study catchments*

2.3 The field programme

The sampling of the six study catchments was broken down into two phases, with each phase concentrating on three specific catchments. Phase one sampling encompassing the first three catchments commenced in the first quarter of 2007 and included the upper and mid catchments of the Rivers Torridge, Axe and Arrow. Phase two, comprising the sampling of the River Waver and the upper and mid catchments of the Rivers Rye and Wensum began in the first quarter of 2008.

2.3.1 The collection of representative catchment source material samples

Source material sampling was carried out throughout the catchments to facilitate the characterisation of potential source types associated with particular land-uses and water course channel banks. Precautions were taken to ensure that source material samples were representative of soil or subsurface material which was likely to be eroded (i.e. < 2 cm depth for surface samples or geological and colluvial material from actively eroding channel banks). Similarly, care was taken to consider the potential connectivity of sample sites to neighbouring watercourses, including via drains, ditches, roads and tracks or via other potential overland flow pathways. In order to collect material which could adequately represent each of the designated source types, a minimum of 30 samples (~500g–800g wet weight) were collected for each source type from throughout each catchment. Individual samples comprised sub-samples from within the immediate sample site vicinity (~0.5 km^2). The sub-samples were composited, to ensure that each sample was as representative of the individual site as possible. Samples were collected using a hand trowel and placed in labeled polythene bags, which were transported to the laboratory. Basic field notes were recorded for each sampling site including, sample number, source type, a brief description of the sample site and the OS grid reference obtained using a Magellan eXplorist 300 handheld GPS instrument.

In order to ensure that tributaries were proportionally represented in a robust manner, it was often necessary to walk cross-country for some substantial distance, particularly where road or public foot-path access was limited. In wet weather, it was necessary to ensure that survey vehicles were parked on a hard standing, a requirement which is not always readily met in remote rural areas serviced by narrow lanes. Public footpaths were utilised for land access, where available and care was taken, wherever possible, to obtain permission from landowners for access to sampling sites. It became apparent that in certain catchments, particularly the River Torridge, River Axe and River Arrow, many holdings are tenanted farms. The land was often tenanted or rented by individuals working across various sites, often living some distance from the land they work. However, where interaction occurred with land owners or those farming the land, it often provided a positive opportunity to obtain useful additional background information on local land-use history.

2.3.2 The collection of representative floodplain sediment

In order to assess potential historical changes in the key sediment sources of the study catchments, sediment cores were collected from floodplain sites representing the study catchment outlets. The floodplain cores served as an effective proxy for historical flood event suspended sediment records.

Suitable floodplain sampling sites were identified for the collection of overbank sediment cores using topographic maps, satellite imagery, ground observation and anecdotal evidence. These techniques were combined with interrogation of Environment Agency flood risk maps, an example of which is shown in Figure 2.3 (Environment Agency, 2010). This process pinpointed representative sites which were regularly inundated by overbank flooding, with corresponding propensity to receive and store sediment mobilized from upstream areas. The potential of a site to experience regular overbank flooding was further confirmed by field observations such as, the location of flood trash lines and evidence of sediment deposited on plant leaves, together with anecdotal recollections of flood extent from landowners.

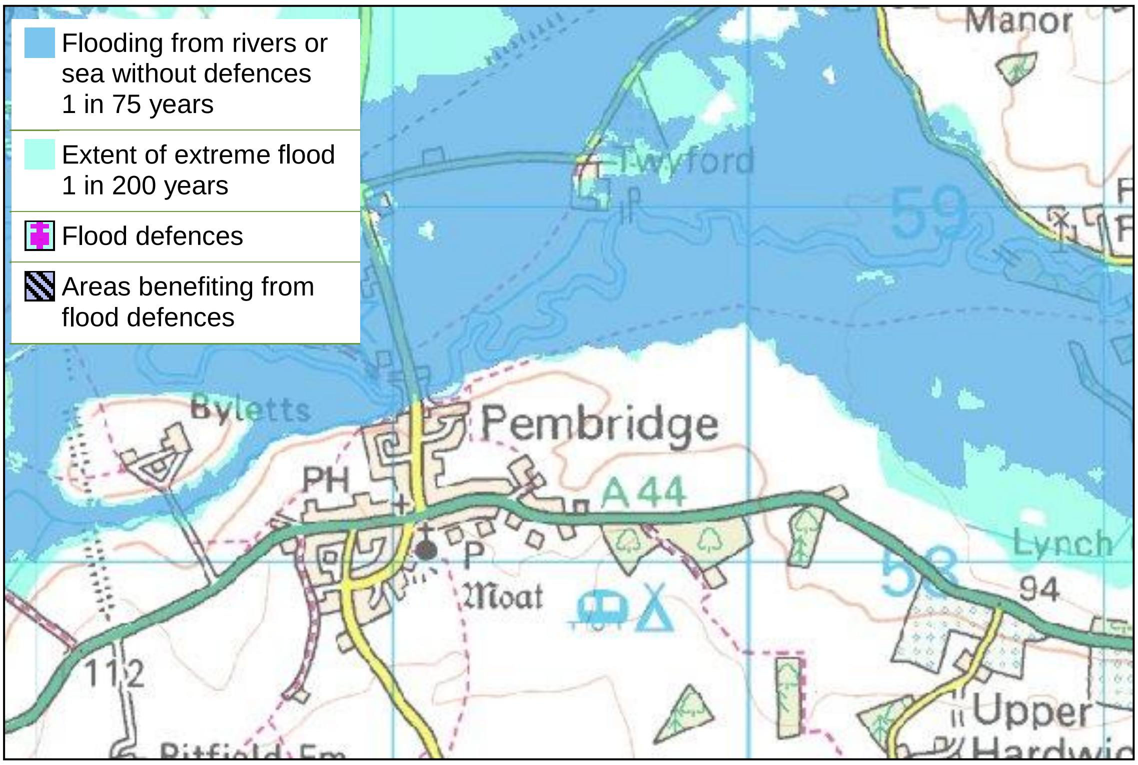

Figure 2.3 *Example of Environment Agency flood risk map (Environment Agency, 2010)*

All floodplain-coring sites had to be located on uncultivated land to minimize the possibility of sediment disturbance and post-deposition mixing by ploughing. This was an important factor, to ensure that the cores represented a continuous record of deposited sediment over the study period. In order to confirm the undisturbed nature of coring sites, basic observations were made of the floodplain plant ecology. Species richness and composition of the sward was observed, as were indicator species. A sward containing a fairly uniform ratio of a single grass species, for example Rye, with clover, was considered likely to be indicative of an improved intensive grass ley (Rodwell, 1998; Price, 2003). In contrast, a sward composition containing various grasses, with mixed herb, flower or rush species could be considered as unlikely to have been cultivated, at least not for several decades (Stevenson *et al.,* 1997; Pywell *et al.*, 2002; Price, 2003). An example of an undisturbed floodplain site, displaying a diverse sward including established rush and wet grassland species is shown in Figure 2.4.

Floodplain ecology observations were cross referenced with anecdotal evidence from land owners wherever possible. In several cases, older family members had personal recollections of the land use of particular floodplain sites going back over fifty years. The above methods for identifying undisturbed floodplain sites were subject to certain limitations. A relatively high degree of understanding of grassland ecology would be required to identify definitively that a site had not been cultivated at any time over a period of several decades from relatively brief field observations. Similarly, anecdotal recollections can involve unquantifiable uncertainty. However, in combination, these approaches appeared to offer the best solution available for identifying undisturbed floodplains within the scope of this study and proved in practice to be acceptably reliable.

Figure 2.4 *Undisturbed floodplain site displaying a diverse sward including well established rush and wet grassland species*

Two types of cores were collected as pairs from the floodplain sampling sites, as illustrated in Figure 2.5. The first core (Core A) was used for bulk ^{137}Cs analysis; to assess the likely magnitude of deposition at individual sampling points and this bulk sample was collected in a 6 cm diameter steel coring tube. The second paired core (Core B) was collected for sectioning into 1 cm horizons, for use in subsequent geochemical analysis and radionuclide geochronology. The cores for sectioning were collected in 10 cm diameter plastic coring tubes. The larger diameter tubes were used to reduce core compaction and to provide adequate material for the subsequent geochemical and radionuclide analysis (Benoit and Rozan, 2001). Bulk cores were also collected from selected reference sites in proximity to each of the floodplain sampling sites. The reference sites were required to be undisturbed, level areas with no soil erosion nor sediment deposition since the onset of ^{137}Cs fallout and to have full vegetation cover all year (Walling and Quine, 1993). These sites could therefore be considered to have received a full complement of atmospheric fallout and not to have lost or gained any ^{137}Cs by erosion or deposition. The measured ^{137}Cs inventories at the reference sites, therefore, represent the accumulated atmospheric input per unit surface area, adjusted for radioactive decay and were used as control references for the nearby floodplain sampling areas during subsequent radionuclide inventory analysis and comparison (De Jong *et al*, 1983). If the measured inventory value from floodplain cores are compared to measured inventory values from control reference sites then depletion could represent erosion, conversely enhanced levels of ^{137}Cs would indicate deposition (Walling and Bradley, 1990).

For the construction of the plastic coring tubes, heavy-duty 10 cm diameter plastic drainage pipe was cut into 1 m lengths. A graded chamfer was applied to the outer edge around one end of the tube to improve the ground penetration (see Figure 2.6). Parallel holes were drilled at 5 cm from the unchamfered end of the tube to facilitate the insertion of a steel lifting pin, from which a hook, chain and ratchet system could be attached to a jig for core extraction.

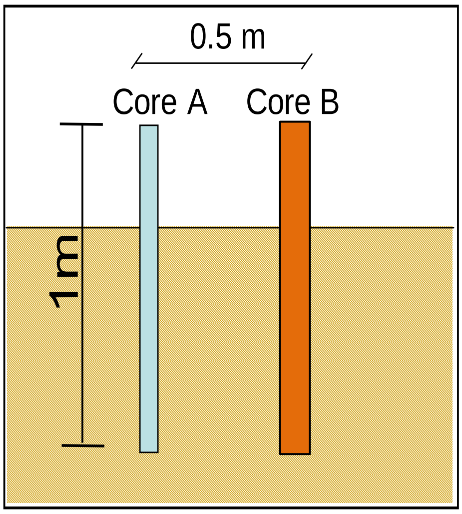

Figure 2.5 *Illustration of the paired core approach*

Figure 2.6 *Details of the prepared plastic coring tube*

The field equipment required for the collection of soil and sediment cores is shown in Figure 2.7.

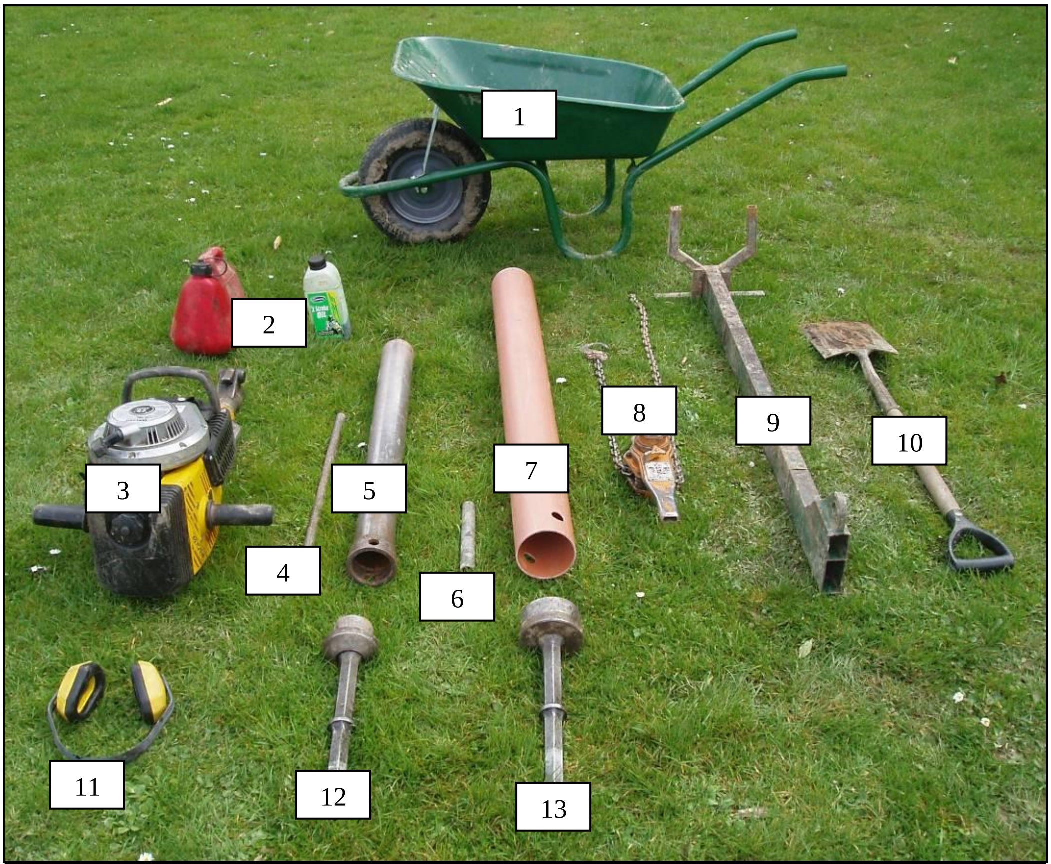

Figure 2.7 *Field equipment required for the collection of soil and sediment cores*

1. Wheel Barrow	8. Winch, hook and chain
2. Petrol and 2-stroke oil	9. Winch jig (3 section)
3. Wacker percussion hammer	10. Spade (heavy duty)
4. 10mm steel lifting pin	11. Ear defenders
5. Steel bulk coring tube	12. 6mm coring bit
6. 15mm steel lifting pin	13. 10mm coring bit

A Wacker, petrol driven percussion hammer, fitted with an appropriate coring bit, was used to insert each coring tube into the ground. A steel lifting pin was then inserted through the parallel lifting holes in the top of the tube and a hook, which was connected to a chain and winch suspended from the lifting jig, was attached under the lifting pin. A spade was positioned under the front of the jig base to prevent it being forced into the ground as tension was applied to the lifting chain from the winch. Operation of the winch facilitated the extraction of the core as shown in Figure 2.8.

Figure 2.8 *Floodplain core extraction*

Problems associated with floodplain coring included encountering pebbles, stones, tree roots and buried debris, which could disrupt the continuity of the profile, damage the plastic coring tubes and in some instances limit the depth of the core. This effect was minimized by selecting sampling sites which were sufficiently distant from the bank so that larger bed load sediment, which may have been transported onto the floodplain during peak flows, was unlikely to be present. Similarly, coring sites were chosen to be sufficiently distant from hedges and trees to minimize the likelihood of encountering tree roots. Voids can occur within the core sample during extraction of the core tube under certain circumstances, such as situations where a floodplain site is at or near field saturation. A vacuum can develop within the cored hole when extracting the core tube and this can draw material out of the bottom of the tube back into the hole as the tube is extracted. Under these circumstances an alternative core would have to be collected. Where the floodplain sediment contained a substantial proportion of clay, it was possible for the resistance of the clay to cause the lifting pin to tear through the plastic tubing when under tension from the winch, requiring that the tube be dug out by hand with a spade. This eventuality was not only time consuming, but could cause increased disturbance of the sampling site. This recurring problem was significantly alleviated by using a redesigned lifting pin which closely matched the diameter of the holes in the coring tube and thereby dissipated the upward force on the tube holes sufficiently to allow subsequent careful extraction.

Extracted cores were appropriately labeled and sealed at either end with plastic bags retained by elastic bands to prevent them from drying out during transport and subsequent storage in the laboratory cold store.

2.4 Laboratory preparation procedures

Source material samples were oven dried at 40 °C and then disaggregated and homogenised using a pestle and mortar. Samples which consisted of a high percentage of clay material were freeze dried to aid disaggregation. Element property concentrations in sediments have been identified in various studies as being significantly dependent on the sediment grain size distribution (Förstner and Wittman, 1981; Horowitz and Elrick, 1987; Walling and Morehead, 1989; Horowitz, 1991; Tanizaki, 1992, Walling and He, 1993; Foster *et al*., 1998; Walling *et al*., 1999; De Vos *et al*., 2006). This potentially introduces problems when attempting to compare the properties of sediment and source material samples of contrasting grain size composition. In order to minimise the influence of the grain size effect, all samples were dry sieved through a 63 µm mesh as recommended by Horowitz and Elrick (1988). This facilitated the direct comparison of source samples with the often finer floodplain sediment samples (Forstner, 1990; Ntekim *et al*., 1993; Mantei and Sappington, 1994; Wallbrink *et al*., 1998; Datta and Subramanian, 1998; Wang and Chen, 2000; Whiting *et al*., 2005; Stutter *et al*., 2009). The potential for direct comparison of source and floodplain sediment samples, i.e. without the requirement for applying particle-size effect correction factors, was assessed for each catchment using a statistical correlation test to examine the relationship between the specific surface area (SSA) of samples and their associated geochemical concentrations, detailed below. Floodplain cores retrieved for bulk analysis were disaggregated and sieved to 2 mm using an automated mechanical grinder to ensure constant detection geometry. Floodplain cores collected for depth-incremental analysis were sectioned into 1 cm slices, which were subsequently freeze dried to aid disaggregation. The floodplain samples were then disaggregated and homogenized using a pestle and mortar and initially sieved to 2 mm for radionuclide determination. Following this, the floodplain samples were re-sieved through a 63 µm mesh prior to geochemical concentration and particle size determination, to ensure compatibility for comparison with the fine fraction of source material samples as detailed below. Bulk density was calculated for individual core sections to allow comparison of ^{137}Cs inventory mass depth reference chronologies with ^{137}Cs inventory peak extrapolated chronology estimations.

Floodplain sediment samples and source soil material samples were analysed for a range of 48 potential diagnostic geochemical properties. Geochemical property values were determined by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). The suite of geochemical properties analysed was selected to include a variety of determinands with differing environmental behaviour and which might therefore exhibit a degree of independence, thereby facilitating source discrimination (Collins and Walling, 2002). The geochemical suite included properties which have proved successful for discriminating sediment sources in previous studies (Walling, 2005; Collins and Walling, 2007a; Collins and Walling 2007b; Collins *et al*., 2010) and past experience in source fingerprting at the University of Exeter. The suite included a range of alkaline metals, alkaline earths, transition metals, basic metals, semi-metals, lanthanides and actinides as shown in Table 2.2.

Table 2.2 *Analytes determined for the study by ICP-MS*

Alkaline Metal	Li	Na	K	Rb	Cs											
Alkaline Earth	Mg	Sr	Ba													
Transition Metals	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Y	Zr	Mo	Pd	Cd	Hf
Basic Metal	Al	Ga	Sn	Tl	^{206}Pb	^{207}Pb	^{208}Pb	Bi								
Semi-Metals	Ge	As	Sb													
Lanthanides	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Yb				
Actinides	U															

Use of historically deposited floodplain sediment for source ascription required that only geochemical analytes which were conservative during mobilization, transport, deposition and in the post-deposition environment could be considered for use as fingerprint properties. A method for confirming this criterion by explicitly comparing property concentration ranges between source samples and floodplain samples (The Property Concentration Range Test) was devised and applied to property concentration values from the analytical suite (see Chapter 3).

Certain types of tracer properties which have been used in other fingerprinting studies, such as those considering suspended or bed sediment, were excluded for consideration here due to the specific requirements for historic floodplain sediment fingerprinting. Organic properties, such as C, N and P, which can be useful tracers when fingerprinting contemporary suspended sediment sources (Hasholt, 1988; Peart, 1993; Collins *et al*., 1997a; Walling *et al*., 1999), are not appropriate for use in floodplain sediment fingerprinting studies as these properties are likely to be non-conservative, particularly in the post-deposition environment being highly susceptible to mineralization and pedogenic processes (Collins *et al*., 1997b; Lees,1997; Owens *et al*., 1999; Walling, 2005). In addition, mineral magnetic properties which have also been used in contemporary suspended sediment fingerprinting (Caitcheon, 1993; Walden *et al*., 1997; Caitcheon, 1998) are not considered appropriate for use here as they are not reliably linearly additive (Lees, 1997). Similarly, certain fallout radionuclides such as ^{137}Cs have been particularly useful as fingerprint properties in various suspended sediment fingerprinting studies (Walling and Woodward, 1992; Wallbrink and Murray, 1993; Walling and Quine, 1995; Ormerod, 1998; Nagle and Ritchie, 2004; Collins and Walling, 2007a). However, fallout radionuclides are not appropriate for use as sediment provenance tracers in floodplain core fingerprinting studies. Despite generally being conservative, down-profile fluctuations in fallout radionuclide concentrations within floodplain sediments will reflect the pattern of fallout, sediment deposition and radioactive decay, rather than reflecting temporal variations in spatially disparate sediment sources (Collins *et al*., 1997c; Owens *et al*., 1999). The temporal dependence of fallout radionuclide activity, when considered within the floodplain profile, can be particularly useful for the geochronological dating of sediment cores and is covered in greater detail below.

2.5 Laboratory analytical procedures

2.5.1 Elemental property analysis by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS)

Elemental property concentrations of source and floodplain sediment samples were measured using a Thermo Elemental X series Quadrupole ICP-MS (Figure 2.9), after sample preparation by acid digestion. ICP-MS is capable of determining multiple analytes per sample in just a few minutes and achieves this by counting the number of ions present at a specific mass of each element. Following the analysis of a set of standards (Glen Spectra CLMS-2 and Rh^{103}), a calibration curve is internally generated and this is compared to the signals from the study samples to determine the concentration of individual elemental properties within the samples.

Figure 2.9 *The Thermo Elemental X Series Quadrapole ICP-MS*

2.5.2 Preparation of sediment samples for ICP-MS analysis

Between 0.5 g and 1.0 g of sediment sample was accurately weighed into a 100ml glass beaker and the mass was recorded. 3 ml of concentrated HNO_3 was then added to the weighed sample. The contents of the beaker were then evaporated to dryness on a hotplate placed under a fume hood. The beaker was then removed from the hotplate and a further 3 ml of concentrated HNO_3 and 0.5 ml of concentrated HCl was added. The beaker was returned to the hotplate and warmed until brown NO_2 fumes were observed. At this point the beaker was removed from the hotplate and allowed to cool. The remaining contents of the beaker were flushed with a small amount of distilled water into a 50 ml centrifuge tube. The tube was subsequently centrifuged at 2500 rpm for 20 minutes. The resultant supernatant was then decanted into a 25 ml volumetric flask. The residue remaining in the centrifuge tube was resuspended and washed in a small amount of distilled water using a vortex mixer. The tube was centrifuged for a further 20 minutes at 2500 rpm and the supernatant was then added to the volumetric flask. The volume in the flask was made up to 50 ml using distilled water.

The quantitation range of the ICP-MS is 1000 ppb to 50 ppt. As it is essentially a trace element technique, dilutions had to be made to bring more concentrated analytes into this range. Therefore, prepared digestates were diluted 1:100 (0.25ml-25ml) prior to analysis.

2.5.3 ICP-MS analysis

During the operation of the ICP-MS instrument, the sample is introduced through a nebulizer and spray chamber system. The liquid samples are converted into fine droplets by the nebulizer. The droplets are then propelled through a spray chamber and into an injector tube, which is the central channel of the torch. From the injector tube the droplets pass into the plasma. As the sample passes through the plasma it changes from an aerosol into a vapour. The vapour is atomized by the plasma at an optimum between 7500k and 10000k at which temperature elements within the vapor are instantly ionized. The resultant ions are passed through an interface to the ion lens which focuses them. Following focusing, the ions were separated in the Quadrapole mass spectrometer according to their mass-to-charge (m/z) ratio. The separated ions are then transmitted to the detector and measured. The measured signal intensities were converted into individual elemental concentrations (ppm) of solution and a report of the results was generated. The concentration value for elemental properties in sediment (ppm) was then calculated from the concentration value in solution, viz.:

$$\text{ppm in sediment} = \frac{\text{volume of solution} \times \text{ppm of solution}}{\text{mass of original sediment sample}} \tag{2.1}$$

2.5.4 Particle size analysis by laser diffraction spectroscopy

Previous studies have established that particle size can exert an influence on sediment-associated elemental property concentrations (Walling and Morehead, 1989; Horowitz, 1991; He and Owens, 1995; He and Walling, 1996; Foster *et al*., 1998; Motha *et al*., 2002; Chapman *et al*., 2005). Therefore, in order to take account of this influence, it was necessary to determine the particle size distribution and specific surface area of all sediment and source material samples considered in the study. There are a variety of analytical techniques available for the determination of particle size composition. These include techniques based on settling, particle counting, sieving, photon-correlation spectroscopy and laser or light diffraction spectroscopy. No individual analytical technique is ideal for sizing all materials, applications and operational requirements. The factors to be considered include the size ranges being considered, the physical and chemical properties of the sample material, the throughput requirements of the analysis, the precision and resolution required, combined with consideration of the environment in which the technique is to be applied. For the purpose of this study a technique was required which would produce accurate, reproducible, high resolution results, within an expedient timeframe. Consequently, particle size characteristics were determined using a Micromeritics Saturn DigiSizer 5200 high definition digital laser particle size analyzer, shown in Figure 3.10. The Saturn DigiSizer operates in the range of 0.1 µm to 1000 µm and can analyse up to 10 samples per hour.

2.4.5 Sample preparation for particle size analysis

Prior to analysis, between 1 g and 2 g of the previously dried and sieved (<63 µm) sample material was put into a clean, dry beaker. 10 ml of water was then added to each sample, followed by 5 ml of H_2O_2. The samples were then observed for a period of around 5 minutes for any signs of over-active effervescence. If over-active effervescence did occur, it was controlled by the addition of a few drops of Industrial Methylated Spirit (IMS) (99%). After 2 hours, providing any frothing had ceased, an additional 5 ml of H_2O_2 was added and the sample was left to stand overnight at room temperature. Watch glasses were then placed on the beakers to minimize evaporation and they were warmed on a hotplate, starting at 80°C and gradually increasing the temperature up to 100°C. This warming process continued until the reaction was complete and there was a clear supernatant above the sample. It was sometimes necessary to add a small amount of water to the beakers during the warming process to avoid the sample drying out, as this could lead to the re-aggregation of particles within the sample and could also result in the cracking of the beaker. When the reaction was complete, the entire contents of the beaker were carefully transferred to a centrifuge tube. A policeman on a glass rod was used with a little water to clean any residue from the sides of the beaker. The tubes were then centrifuged at 2500 rpm for 1 hour. After being centrifuged, the supernatant was discarded. Approximately 30 ml of 0.4% $[(NaPO_3)_6]$ solution was then added to each tube to aid disaggregation. The solution was stirred with a spatula and each tube was then agitated for 10 seconds using a vortex mixer. The suspension was then transferred to a beaker and placed into a MasterTech 052 Autosampler, also shown in Figure 2.10, which allowed automated delivery of up to 18 samples in succession to the MasterTech Saturn DigiSizer. Samples were further disaggregated and mixed immediately prior to analysis by being subject to automated ultrasonic dispersion for 30 seconds, combined with high speed automated stirring. Both the ultrasonic probe and the stirrer were attached to the head of the sampling arm on the MasterTech 052 Autosampler.

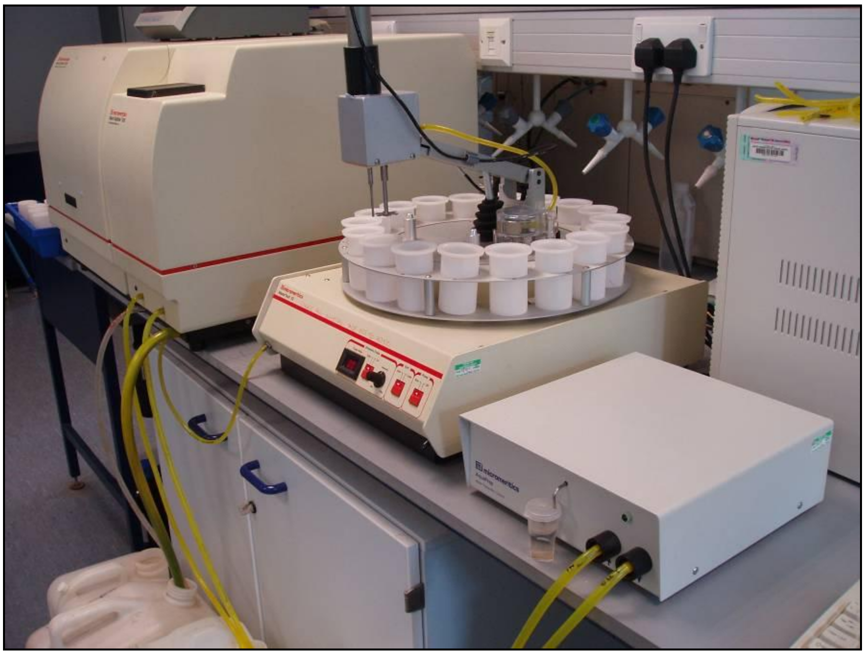

Figure 2.10 *The Micromeritics Saturn DigiSizer 5200, MasterTech 052 Autosampler and AquaPrep*

Samples were then delivered via the Autosampler to the DigiSizer analysis chamber. During the process of laser diffraction particle size analysis, the forward diffraction of the laser beam by the sample particles is used to determine their size distribution. The angle of diffraction is inversely proportional to particle size and the intensity of the diffracted beam, at any angle, is a measurement of the number of particles with a specific cross-sectional area within the path of the beam.

The particle size estimation performed by the Saturn DigiSizer used multiple-angle laser light scattering based on Mie theory, which predicts the angle versus intensity relationship as a function of size for spherical scattering particles when other system variables are known and constant (Bohren and Huffman, 1983). The variables concerned are the relative refractive index of the sample material and suspension fluid and the wavelength of incident light. The particle size distribution was thereby calculated from the angle distribution of the scattered light collected by the charge-coupled device (CCD) light detectors within the DigiSizer (Micromeritics, 2002). The specific surface area (SSA) of individual samples was automatically estimated based on results from the particle size distribution analysis. In common with other light diffraction based particle analyzers, the estimation of SSA is based on an initial assumption that particles are spherical. However, within the Saturn DigiSizer these results are subsequently corrected for variations in particle type using the calculation of logarithms from based on values for particle material density and suspension medium density. In this way an approximation of varying particle SSA based on material density was accounted for. It was therefore important to check that the values being used were suitable for the material being analysed. Accordingly, sample material properties were used which were based on experience at The University of Exeter for soil in water. The material refractive index used was 1.55 for the real part and 0.1 for the imaginary part. The material density value used was 2.8 g cm^{-3}. The analysis liquid refractive index was 1.331, with a viscosity setting of 0.798 cp and a density of 0.996 g cm^{-3}. Obscuration values were set at minimum 5.0% and maximum 30% respectively, with auto-dilution maintained at 15%.

When water is used as the dispersing liquid for light diffraction particle size analysis, misleading or even incorrect data can result due to the presence of air bubbles which might occur in solution. Failure to remove any such air bubbles could lead to the particle size analyzer sensing them and incorrectly reporting them within the measured distribution. To overcome this difficulty, it was necessary to remove any air bubbles which may have been present in the dispersing water using a Micromeritics AquaPrep, as shown in Figure 2.10. The AquaPrep circulates water through a hydrophobic capsule consisting of multiple thin-walled capillaries. A vacuum pump then provides suction on the outside of the capillaries. In this manner dissolved air is diffused from the water through the capillary walls and into the vacuum pump. The air removed from the water is exhausted through a small tube at the front of the instrument. The Autosampler and the DigiSizer were rinsed with water after each analysis with 2 rinse cycles.

Replicates of 3 tests were performed per sample and displayed in the form of Frequency Graph Reports, as illustrated in Figure 2.11. Mean values obtained from the 3 tests were copied as text from the Digisizer reports and pasted to a pre-prepared Microsoft Excel spreadsheet. Specific surface area information was contained within in a Summary Report and similarly transferred to the Excel spreadsheet. The spreadsheet was used for statistical particle size fractional analysis and SSA comparison.

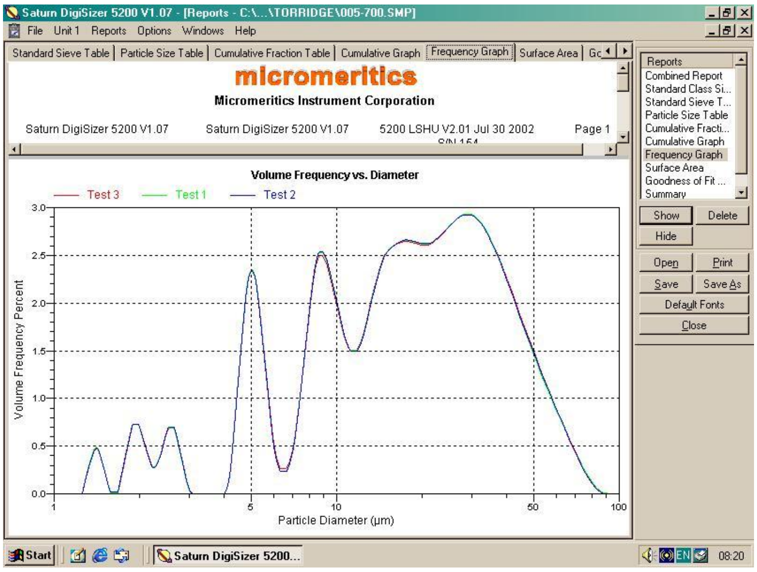

Figure 2.11 *An example of the Frequency Distribution Report from the Saturn DigiSizer (Micromeritics, 2002)*

2.5.6 Radionuclide assay

For successful temporal sediment core investigation it is essential to establish a reliable core chronology and this can be achieved through the use of radioisotope geochronology techniques (Goldberg, 1963; Robbins and Edgington, 1975; Appleby and Oldfield, 1978). The principal radioisotope for establishing chronologies of between 100-150 years is ^{210}Pb (half-life 22.2 years). Whilst more recent chronologies (ca. 35 years) are usually established using the artificial radioisotope ^{137}Cs (half-life 30.17 years) (Appleby *et al*., 1990). The use of ^{137}Cs and ^{210}Pb for establishing geochronology has been widely documented (Pennington *et al*., 1973; Ritchie *et al*., 1973; Robbins and Edgington, 1975; Matsumoto, 1975; Appleby and Oldfield, 1978; Livingstone and Cambray, 1978; Longmore, 1982; Appleby *et al*., 1986; Charles and Hites, 1987; Walling and He, 1992; Foster and Walling, 1994; Horowitz *et al*., 1995; Collins *et al*., 1997b; Benoit and Rozan, 2001).

γ spectrometry was used to make measurements of ^{137}Cs and excess (or unsupported) ^{210}Pb ($^{210}Pb_{ex}$) activity in the floodplain sediment cores to provide data for comparing sedimentation rates and for dating sediment horizons. Caesium-137 is an artificial radionuclide which is produced during nuclear fission reaction. It has been present in the environment since the advent of nuclear weapons testing in the early 1950s. The ^{137}Cs fallout from weapons testing increased gradually throughout the 1950s and reached a maximum in 1963. Thereafter, following the nuclear test ban treaty between the United States and the Soviet Union, ^{137}Cs fallout from weapons testing declined sharply. ^{137}Cs is also present in the environment at generally low levels from discharges of nuclear power stations. However, significant ^{137}Cs fallout occurred over many areas of Europe and throughout the Northern Hemisphere in 1986 as a result of the Chernobyl nuclear accident (ApSimon, 1986; Cambray *et al*., 1987).

Caesium-137 has been used frequently to provide information on sediment behaviour and sediment dating in fluvial systems and on floodplains. The use of ^{137}Cs in this context is based on a premise, as stated by Walling and He (1993), that ^{137}Cs is readily adsorbed by the fine fractions of soils and sediment, also that ^{137}Cs in floodplain sediment is derived from two primary sources. These two distinct sources represent direct atmospheric fallout and the deposition of sediment-associated ^{137}Cs mobilised from the upstream catchment by erosion during overbank flood events (Walling and He, 1993). Consequently, both the total inventory and the vertical distribution of ^{137}Cs in floodplain sediment profiles will differ to those found in soils from surrounding areas above the inundation extent of the floodplain. The shape of the floodplain sediment ^{137}Cs profile will reflect the temporal pattern of atmospheric fallout during the period when weapons testing began in 1955 to the present and the horizon represented by the subsurface peak can usually be tentatively dated to the year of maximum fallout in 1963 (Walling and He, 1993). However, whilst ^{137}Cs fallout from weapons testing is generally assumed to be reasonably uniformly distributed, due to the height to which artificial radionuclides were propelled and the extended period over which it was deposited, ^{137}Cs fallout derived from the accident at Chernobyl was more spatially variable as it was associated with a single event which propelled radioactive debris to a lower atmospheric height (Appleby, 2001). Therefore in certain regions which received particularly high levels of Chernobyl derived ^{137}Cs fallout the floodplain subsurface peak may represent 1986. In such cases and in other areas which received lesser yet still substantial Chernobyl derived fallout, twin peaks (1963 and 1986) may be observable in the depth profile (Foster and Lees, 1999; Foster, 2006).

Thus, the general rates of ^{137}Cs fallout since the early 1950s can be interpreted in vertical sediment profiles obtained from floodplain sample cores. The known peaks in ^{137}Cs fallout, e.g. 1963, 1986, can be used as markers to provide chronological reference points down a sediment profile from which, assuming constant sedimentation rates, it is possible to extrapolate estimated dates for sediment horizons which lie within or close to the period since ^{137}Cs fallout began to occur.

Caesium-137 is created when the nucleus of a heavy element (e.g. ^{235}U, ^{233}U or ^{239}PU) is split into two daughter nuclei by a neutron (Owens, 1994). Although the majority of the resultant daughter nuclides have extremely short lives, certain nuclides such as ^{134}Cs and ^{137}Cs have relatively longer lives. ^{134}Cs and ^{137}Cs possess half lives of 2.2 years and 30.17 years respectively, which make them ideal for interpreting sediment dates in the recent past. Following atomic transformation many nuclear fission products, including ^{137}Cs, have an excess of energy in the nucleus. This energy is dispersed through the emission of γ-ray photons. Therefore, ^{137}Cs activity in a sample can be detected through measurement of the electromagnetic energy in the emitted γ-rays. The γ-ray which is emitted by the ^{137}Cs daughter isomer ^{137m}Ba has energy of 661.6 keV and this has been shown to be particularly well separated from other peaks in the energy spectrum (Campbell *et al.*, 1988). The ^{137}Cs content for all floodplain samples and reference samples was determined by its γ emissions at 661.6 keV.

Lead-210 is a radionuclide from the ^{238}U series which occurs naturally in the environment and is derived from the decay of ^{222}Rn in the gaseous phase. A proportion of ^{222}Rn is diffused from soil and rocks into the atmosphere where it decays to ^{210}Pb. Subsequential fallout of ^{210}Pb to land surfaces contributes an input which is out of equilibrium with its parent ^{226}Ra (Robbins, 1978). When fallout ^{210}Pb is incorporated into sediments or soils, it is often termed excess or unsupported ^{210}Pb ($^{210}Pb_{ex}$). In this way $^{210}Pb_{ex}$ can be distinguished from supported ^{210}Pb produced in situ in soils through the decay of ^{226}Ra. The ^{210}Pb method for dating sediment or soil profiles relies on estimation of the residual radioactivity arising from the presence in the soils or sediments of fallout derived $^{210}Pb_{ex}$. An estimate of $^{210}Pb_{ex}$ at each depth can be obtained by subtracting supported ^{210}Pb determined by establishing the ^{226}Ra content of the sample from the total ^{210}Pb (Appleby and Oldfield, 1978).

For the determination of ^{210}Pb, plastic pots were filled and sealed then left for an equilibration period of 21 days, to allow equilibrium between ^{226}Ra and ^{222}Rn. ^{222}Rn decays to ^{214}Pb through a series of short-lived processes. Therefore, the activity of ^{214}Pb equates to that of ^{226}Ra and ^{222}Rn and reflects the supported ^{210}Pb activity which was determined via γ emissions at 351.9 keV. ^{210}Pb decays to ^{210}Bi which was then determined via its γ emissions at 46.5 keV.

Radionuclide activities were analysed using ORTEC LO-AX Hyperpure Ge co-axial γ-detectors (EG&G ORTEC LO-AX HPGe), coupled to multi-channel analysers, shown in Figure 2.12. Ge detectors are semiconductor diodes which have a structure such that the intrinsic region is particularly sensitive to ionizing radiation from γ-rays and x-rays. An electric field extends across the intrinsic or depleted region under reverse bias. Consequently, when photons interact with a material within the depleted volume of the detector, charge carriers in the form of holes and electrons, are produced. These charge carriers are swept by the electric field to P and N electrodes. The amount of charge is in proportion to the energy deposited in the detector by the incoming photon and is converted into a voltage pulse by an integral charge sensitive preamplifier. The pulses are amplified and sent to the multichannel analysers, where they are sorted by height and output from the respective channels into the counting system within which the counts are processed and displayed on the systems controller VDU using ORTEC Maestro II software.

Figure 2.12 *ORTEC LO-AX Hyperpure Ge co-axial γ-detector (EG&G ORTEC LO-AX HPGe), coupled to a multi-channel analyser and computer control device*

Ge has relatively low band gap, therefore the detector requires cooling to reduce the thermal generation of charge carriers to an acceptable level. Without cooling, leakage current induced noise would destroy the energy resolution of the Ge detector. The cooling medium used for the detectors is LN_2, at 77 °K. The sensitive Ge detector is mounted in a protective vacuum chamber which is attached to a LN_2 Dewar. The sensitive detector surfaces are thus ants. The detector chamber is Cu-Cd shielded to prevent anomalous determination which could be caused by ambient background radiation. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known activity. Count times were typically ca. 85,000s to ensure an analytical precision of *ca*. ±5-10% at the 95% level of confidence (Walling and Collins, 2000).

Cores which were being processed for bulk analysis, including those collected from reference sites, were weighed then ground and sieved to <2 mm using an automated rotary grinder-sieve. Marinelli pots (0.50 L) were then filled with material from individual bulk cores and sealed prior to determination.

Following determination, the bulk ^{137}Cs inventories from the catchment floodplain sites were compared with those of the respective reference sites (see Figure 2.13). The floodplain sampling point which was associated with the greatest depth of sediment deposition was identified as that which had the highest bulk ^{137}Cs inventory. The corresponding paired core was accordingly selected for sectioning. The plastic tube was cut on opposite sides of the circumference along the tube length using a circular saw set to the thickness of the plastic. The two parts of the tube were then separated. This allowed the core to be exposed in a manner which avoided any compaction effects which might have occurred if the core had been removed by extrusion. The exposed core was then sectioned into 1 cm horizons, dried, disaggregated, sieved to <2 mm and placed into sealed plastic pots for ^{137}Cs determination. All activities were decay corrected to the date of core collection.

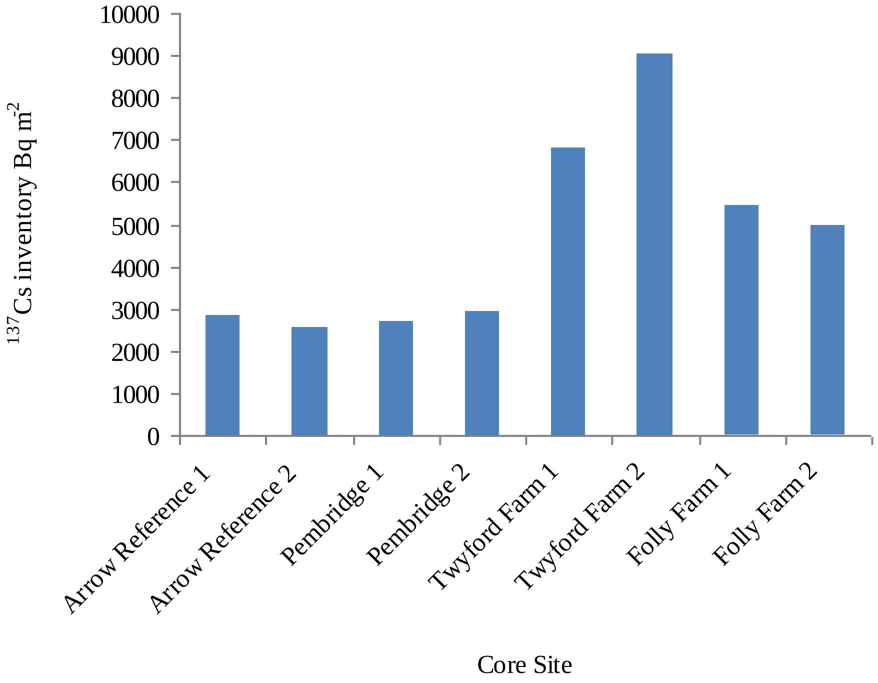

Figure 2.13 *^{137}Cs inventories for the floodplain sediment cores and local reference cores collected from the River Arrow catchment*

Only the core samples from the Torridge catchment were also analysed for ^{210}Pb. Analysis of the ^{210}Pb vertical distribution profile allowed assessment of the general uniformity of deposition and continuity of supply of sediment to the floodplain over the previous 100 years. Analytical uncertainty might account for some minor short term fluctuations in activity concentration. A chronology was estimated based on the age-depth relationship for floodplain sediment using the Constant Flux: Constant Sedimentation (CF:CS) model (Robbins, 1978; Oldfield and Appleby, 1984). In the application of the CF:CS model, it was assumed that the top 1 cm layer of sediment in the core profile was deposited in the sampling year and therefore the $^{210}Pb_{ex}$ concentration in this layer represented the initial concentration; also that annual deposition over the previous 100 years had been essentially uniform and quasi-constant. Based on the initial $^{210}Pb_{ex}$ activity concentration within the top 1 cm layer and the decay half-life for ^{210}Pb of 22.3 years, an expected concentration for year 1963 was estimated by solving the equation produced by an exponential curve fitted to the down-core variation of $^{210}Pb_{ex}$ for the target concentration. The depth of the ^{137}Cs peak marker for 1963 was then compared to the depth estimation for 1963 based on the $^{210}Pb_{ex}$ CF:CS model for validation of the estimated chronology.

2.6 Summary

This chapter has described both the field and laboratory methods used in this study. These methods included the criteria and approach used for selecting suitable study catchments, followed by the techniques used for the representative collection of source material and floodplain sediment samples. In addition, the laboratory protocols and procedures applied during sample preparation and analysis have been detailed. These laboratory analytical procedures produced a wide range of representative data for use in the quantitative statistical determination of relative historical sediment contributions from across the study catchments. The following chapter details the statistical analysis of the data for this purpose and includes some suggestions for novel refinements of the fingerprinting technique.

CHAPTER 3 - STATISTICAL METHODS AND REFINEMENT OF THE FINGERPRINTING TECHNIQUE

3.1 Introduction

This chapter details the statistical processes used in the application of the sediment source fingerprinting technique to overbank floodplain sediment. The methods described below include the statistical analysis used in the identification of the optimum composite fingerprint. In addition, this chapter also incorporates various novel refinements to aspects of the sediment source fingerprinting technique. These refinements involved a number of check-tests and a redesigned approach to the functionality of a mass-balance mixing-model for sediment source apportionment. The additional steps represent an attempt to ensure explicitly that the data being analysed remain as robustly representative of their source environments as possible and to thereby aid the minimisation of specific areas of recognized uncertainty. The functionality of the mixing-model has been designed here to consider both potential global and boundary solutions in a manner which reliably expedites the source apportionment algorithm whilst concurrently offering an easy to use interface and practical statistical output format. In addition, this chapter details the approach used for interrogation of land-use database records derived from the Agricultural Census (Agcensus) database (Defra/EDINA, 2009). The method of compilation of this land-use data for comparison with historical sediment source apportionment is presented in order to consider the relationship between land-use change and the sources of floodplain overbank sediment.

3.2 Statistical methods: approach outline

Foster and Lees (2000) identified a series of key assumptions in sediment provenance studies (Table 3.1). The assumptions 1-3 are broadly applicable to all tracer studies, whilst assumptions 4-5 are related specifically to deposited (floodplain; lacustrine) sediment, rather than actively transported sediment. Assumption 5 relates to the validity of mixing models (also referred to as un-mixing models) used to apportion the respective sediment source contributions from either suspended or deposited sediment. The statistical process followed in this study seeks to confirm whether various aspects of these assumptions are met.

Table 3.1 *Assumptions in fine sediment provenance studies (from Foster and Lees, 2000)*

1. The tracer can distinguish between at least two different sources in the catchment (e.g. topsoils and subsoils, different land-use units or different lithologies) of relevance to the research problem
2. The tracer is transported and deposited in the same way as the medium of interest (i.e. in association with fine sediment.
3. Selective erosion does not change the properties of the tracer or, if it does, only in a way that can be measured and modeled
4. Differences between source properties have not changed over the period of sediment deposition
5. Once deposited, the tracer undergoes no transformation (enrichment, dilution or depletion in its new environment
6. The un-mixing models used to reconstruct sediment source changes through time are able to deal with inherent variability in source properties and provide estimates of source contributions within known or predictable tolerances

The steps involved in the application of the sediment source fingerprinting technique, as employed within this study, are illustrated as a process decision tree in Figure 3.1. A brief summary of the process involved follows, with a more detailed explanation of the individual methodologies featured further below.

Following completion of the laboratory analysis of catchment source material and floodplain sediment, the geochemical property concentration data measured for individual source types were first statistically analysed for correlation with particle size, based on specific surface area (SSA) through the application of a particle size effect correlation test using Spearman's rho. In instances where significant correlation was observed between SSA and property concentration, property concentration values were corrected to account for any particle size dependencies, to allow robust comparison of source and sediment samples. Source property concentration ranges and floodplain sediment concentration ranges were then compared in the property range test to assess both the conservative and representative qualities of the properties being considered. This test also ensured that source and sediment input values to the mixing model were compatible. Testing of source group discrimination to ascertain the optimum composite fingerprint followed next. The first stage involved the application of the Kruskal Wallis *H*-test to identify properties which could effectively detect inter-group contrasts. The second stage in identifying which of these properties offered the optimum source discrimination involved the application of multivariate discrimination function analysis (MDFA). The application of MDFA initially involved the commonly used stepwise approach based on the minimization of Wilks' Lambda (Λ). Providing an acceptable level of discrimination was achieved following stepwise MDFA ca. >85%, then those properties thereby selected to constitute the composite fingerprint could be utilized in the next stage of the fingerprint process. However, if further discrimination analysis was required in order to attempt to improve source discrimination, then the additional option of simultaneous entry MDFA, also based on the minimization of Λ, was applied. The optimum composite set of fingerprint properties which produced the maximum source group discrimination, based on comparison of output from both stepwise and simultaneous entry MDFA was selected. The discriminatory power afforded by individual source properties comprising the final composite signature was determined by single entry MDFA, in order to produce appropriate discrimination weighting factors for subsequent inclusion in the mixing model. A Monte Carlo framework, based on composite fingerprint input values derived from the source group mean property concentration values and associated standard deviations was used in conjunction with the mixing model. The mixing model, based on the constrained sum of least squares method, utilized the optimum composite fingerprint input values and discrimination weightings to establish the relative sediment contributions from the respective source groups. The goodness-of-fit afforded by the mixing model solutions was assessed by considering the relative error associated with the model estimates. A goodness-of-fit ca. >85% indicated that the mixing model had provided an acceptable prediction of the fingerprint property concentrations measured in floodplain sediment from a given study catchment (Walling and Collins, 2000). If the goodness-of-fit was not considered acceptable, it would be necessary to return to MDFA to consider alternative combinations of fingerprint properties through variations of simultaneous entry. Although the resultant composite fingerprint might have a slightly reduced power to discriminate sources, it might afford improved goodness-of-fit. Ultimately, the optimal solution will be achieved by balancing acceptable source discrimination with acceptable goodness-of-fit, as the two are not necessarily synonymous.

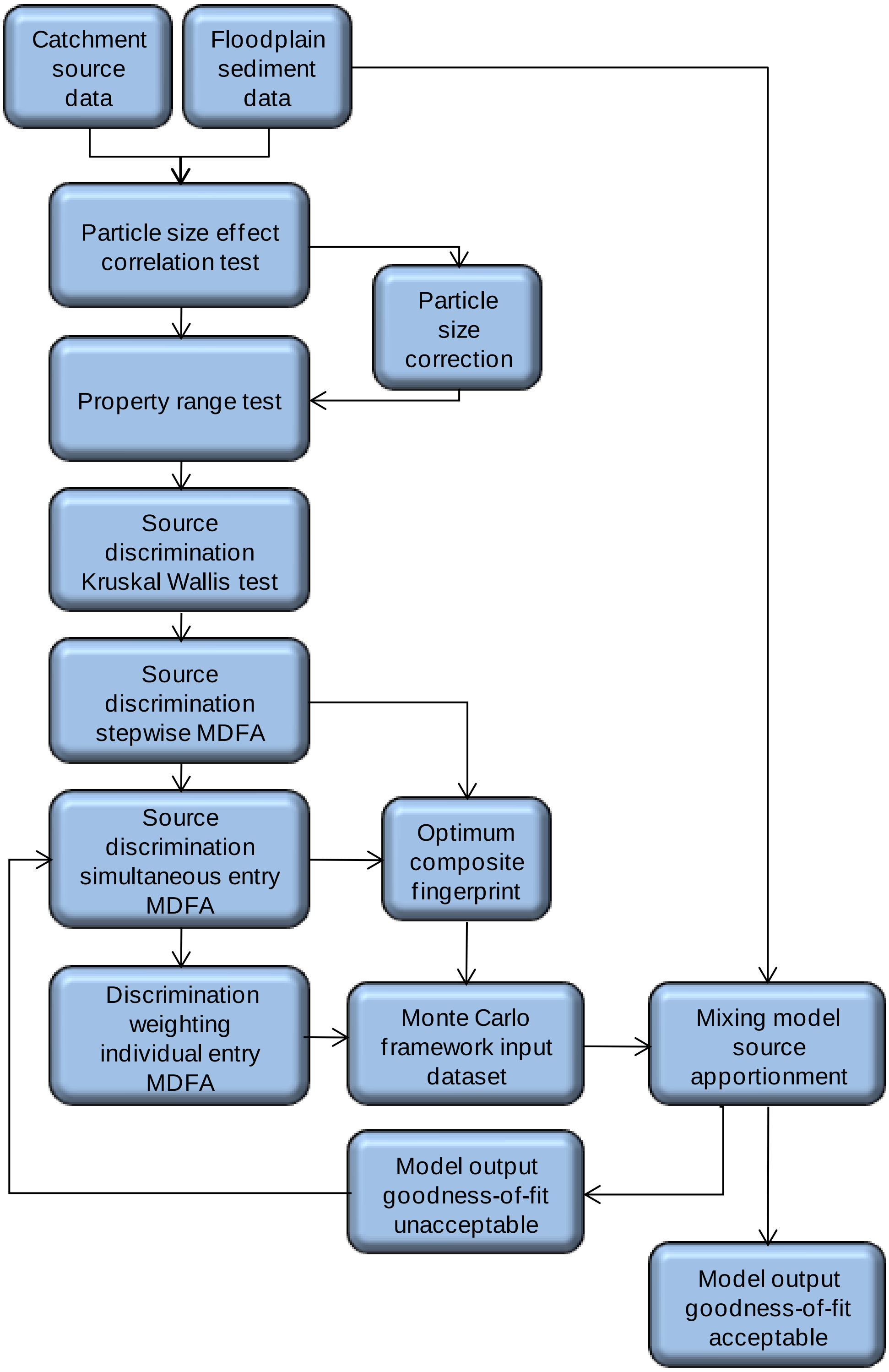

***Figure 3.1** Floodplain sediment source fingerprinting data processing decision tree*

3.3 The particle size effect correlation test

The first stage in applying the fingerprinting technique was to examine the extent of the particle-size effect for the catchment source material and floodplain sediment. Previous studies have established that particle-size can exert a strong influence on associated geochemical concentrations (Horowitz and Elrick, 1987; Horowitz, 1991; He and Owens, 1995; He and Walling, 1996; Foster *et al*., 1998; Motha *et al*., 2002; Chapman *et al*., 2005; Rawlins *et al.*, 2010). This influence occurs largely as a function of the increase in specific surface area (SSA) associated with decreasing particle-size and the availability of exchange sites on certain mineral substrates often associated with fine sediment such as Fe-oxides and expansive clay (Peterson, 1996). This is an important factor in the adsorption and desorption reactions between dissolved ions and mineral particle surfaces in soil pore water and stream beds (Rawlins *et al*., 2010). Consequently, it has become common in many sediment fingerprinting studies for the effect of particle-size dependencies to be accounted for by the application of some form of particle-size correction factor based on SSA ratios. However, many correction factors assume particle-size dependencies to be uniformly significant in all catchment types (geology, hydrology, metrology, land use), across all geochemical properties and throughout all sampled populations. However, there are various sediment characteristics in addition to particle-size with complex inter-dependencies which may also affect property concentrations in differing ways under varying environmental conditions. The internal mineral matrix of sediment particles and associated soil organic matter, contribute to the complex relationship between soil and sediment particles, including aggregation and geochemical property adsorption, transformation and desorption (Weber *et al*., 1992; Pignatello and Xing, 1996; Stutter *et al*., 2009; Rawlins *et al*., 2010). Substrates including clay, iron oxyhydroxide (FeOOH), manganese oxyhydroxide (MnOOH), carbonates and organic matter can affect the sorption of chemical properties by sediment (Balistrieri, 1986; Stone and Droppo, 1996; Wang and Chen, 2000) Variations in Eh, pH, and temperature can also significantly influence the sediment-water distribution of a wide range of geochemical properties (Prosromou and Pavlatou, 1998; Yaro and Buckney, 2000; Foster and Lees, 2000). These attributes are often extremely complex, diverse and thereby highly likely to be site specific. Within fluvial environments, property concentrations may often increase with decreasing grain size, however, this relationship is not necessarily linear and the highest concentrations are not universally associated with the finest particles (Whitney, 1975; Tessier *et al*., 1982; Brook and Moore, 1988; Martinic *et al*., 1990; Vaithiyanathan *et al*, 1993; Droppo and Jaskot, 1995; Stone and Droppo, 1996). Floodplain deposited sediment can be enriched with coarser particle-size fractions than sediment in transport, due to selective settling resulting from varied flow patterns and stream velocities during overbank flood events, combined with variations in micro-topography, ground cover and distance from the stream channel (Middlekoop and Asselman, 1998; Walling and He, 1998; Hupp, 2000; Steiger and Gurnell, 2003; Noe and Hupp, 2005; Piegay *et al*., 2008; Cabezas, 2010) Therefore, the potential significance of the variation in the proportion of the finer fractions between source and floodplain sediment may not be as acute as in comparative studies relating sources to suspended sediment. In-depth analysis of the behaviour of the available suite of geochemical properties across various fractionated ranges of particle size and chemistry for individual samples was deemed prohibitive in this study due to resource limitations. It was considered however, that the influence of particle-size on geochemical property concentrations within the individual source types should be tested statistically to inform the decision of when to apply particle size correction.

Initial experimental correlation analysis of the association between geochemical property concentration values and SSA for individual source types from catchments within this study, indicated that particle size influence was highly variable across the suite of geochemical properties and source types concerned, and that any effect was often non-linear within individual property ranges. Although time and resource constraints limited the scope of the analysis, it was appropriate, nonetheless, to analyze statistically the basic relationship between sample SSA and geochemical property concentration values before committing to the application of particle size correction.

Consequently, the available suite of 48 properties was tested for correlation between sample SSA and property concentration within the individual source types using Spearman’s rho. A non-parametric analysis was used as both geochemical property concentration data and SSA data were not necessarily Normally distributed. An example of results for correlation between property concentration and sample SSA is shown in Table 3.2.

In the example from the Arrow catchment featured in Table 3.2, correlation coefficients and significance were calculated for property concentrations from the surface soils of source types (grassland, cultivated land, woodland) and eroding material from channel banks, versus SSA. Significant correlation, $p < 0.05$, was observed in 8%, 10%, 2% and 29% of cases respectively. Importantly, no single property concentration exhibited significant correlation with SSA across all four source types, possibly indicating the influence of alternative processes within differing environments. Consequently, the blanket application of linear correction factors was deemed to be inappropriate in such instances, on the basis that it could over-simplify the relationship between certain property concentrations and SSA, thereby potentially leading to over-correction.

Where correlation between property concentration and SSA was not significant across all source types for a majority of properties, it was assumed that by disaggregating and sieving source and floodplain samples to <63 µm during processing, sufficient account had already been taken of any nominal grain size dependencies and thereby an acceptable direct comparison of concentration values could be undertaken without the requirement for additional correction (Forstner, 1990; Klamer *et al*., 1990; Ntekim *et al*., 1993; Mantei and Sappington, 1994; Dyer, 1998; Wallbrink *et al*., 1998; Datta and Subramanian, 1998; Whang and Chen, 2000; Ciszewski and Malik, 2004; Whiting *et al*., 2005; Stutter *et al*., 2009). However, where the particle size effect correlation test indicated that a majority of property concentrations are significantly correlated with SSA, then particle size correction was considered appropriate. This approach offered a pragmatic solution to an area of recognised uncertainty, although more robust analysis of the relationships between property concentrations and particle size using fractionated samples would be preferable in future work.

***Table 3.2** An example of Spearman's rho correlation coefficients and significance for property concentration versus specific surface area (SSA) from grassland, cultivated land, woodland and channel bank source groups in the River Arrow catchment*

Property	Grassland Coefficient	Grassland Significance	Cultivated Coefficient	Cultivated Significance	Woodland Coefficient	Woodland Significance	Channel Banks Coefficient	Channel Banks Significance
Mg	-0.187	0.305	-0.212	0.229	0.145	0.454	0.201	0.27
Al	0.141	0.442	0.104	0.558	0.2	0.299	0.337	0.059
K	-0.362(*)	0.042	-0.079	0.658	0.234	0.222	0.319	0.076
Mn	-0.15	0.413	-0.076	0.669	0.285	0.134	0.283	0.116
Fe	-0.089	0.628	-0.001	0.994	0.188	0.328	0.527(**)	0.002
Li	0.224	0.217	-0.271	0.121	0.176	0.361	0.256	0.157
Na	-0.426(*)	0.015	-0.362(*)	0.036	0.351	0.062	0.176	0.336
Sc	-0.205	0.261	-0.21	0.234	0.298	0.117	0.168	0.358
Ti	-0.19	0.297	-0.291	0.095	-0.249	0.192	-0.287	0.112
V	0.047	0.796	0.133	0.454	0.21	0.275	0.405(*)	0.022
Cr	0.065	0.723	0	0.998	0.201	0.295	0.304	0.091
Co	-0.102	0.577	-0.339(*)	0.05	0.28	0.142	0.464(**)	0.008
Ni	-0.058	0.752	-0.226	0.198	0.261	0.171	0.398(*)	0.024
Cu	-0.146	0.426	-0.09	0.612	-0.141	0.464	0.18	0.324
Zn	-0.390(*)	0.027	-0.139	0.432	0.091	0.64	0.308	0.087
Ga	-0.038	0.837	-0.145	0.415	0.1	0.608	0.218	0.231
Ge	-0.173	0.343	-0.133	0.454	0.157	0.417	0.572(**)	0.001
As	0.307	0.087	0.187	0.29	0.085	0.66	0.488(**)	0.005
Rb	0.478(**)	0.006	0.202	0.252	0.405(*)	0.029	0.408(*)	0.02
Sr	-0.308	0.086	-0.16	0.366	-0.06	0.757	0.262	0.147
Y	-0.039	0.83	-0.315	0.07	-0.223	0.246	-0.317	0.077
Zr	-0.188	0.302	-0.179	0.312	0.258	0.176	-0.146	0.425
Mo	-0.054	0.767	-0.306	0.079	0.048	0.804	-0.019	0.917
Pd	-0.253	0.163	-0.094	0.597	-0.121	0.533	0.477(**)	0.006
Cd	-0.015	0.936	0.052	0.769	0.126	0.514	0.434(*)	0.013
In	-0.188	0.304	-0.17	0.335	0.12	0.536	0.532(**)	0.002
Sn	0.074	0.687	-0.322	0.063	0.132	0.495	-0.045	0.806
Sb	-0.138	0.453	-0.201	0.255	0.14	0.468	-0.17	0.353
Cs	0.037	0.841	0.035	0.845	0.223	0.246	0.274	0.13
Ba	-0.113	0.538	-0.159	0.37	-0.088	0.649	0.244	0.179
La	0	1	-0.340(*)	0.049	-0.252	0.187	-0.489(**)	0.005
Ce	0.055	0.766	-0.294	0.092	-0.096	0.622	-0.440(*)	0.012
Pr	-0.006	0.972	-0.331	0.056	-0.169	0.381	-0.347	0.052
Nd	-0.019	0.92	-0.372(*)	0.03	-0.169	0.38	-0.333	0.063
Sm	-0.137	0.454	-0.294	0.092	-0.151	0.434	-0.205	0.261
Eu	-0.12	0.511	-0.318	0.067	-0.172	0.371	-0.093	0.611
Gd	-0.166	0.364	-0.343(*)	0.047	-0.19	0.324	0.011	0.954
Tb	-0.127	0.488	-0.318	0.067	-0.141	0.464	-0.205	0.26
Dy	-0.158	0.389	-0.32	0.065	-0.121	0.531	-0.073	0.691
Ho	-0.164	0.37	-0.331	0.056	-0.143	0.46	-0.067	0.714
Er	-0.18	0.324	-0.32	0.065	-0.144	0.457	-0.063	0.73
Yb	-0.2	0.272	-0.303	0.082	-0.148	0.444	-0.042	0.821
Hf	-0.225	0.215	-0.157	0.375	0.331	0.079	-0.023	0.902
Tl	0.175	0.339	0.118	0.506	0.222	0.248	0.486(**)	0.005
Pb	-0.025	0.891	-0.025	0.887	0.15	0.438	0.226	0.213
^{207}Pb	-0.051	0.783	-0.094	0.598	0.111	0.567	0.205	0.261
^{208}Pb	-0.019	0.917	-0.021	0.905	0.162	0.402	0.211	0.247
Bi	0.16	0.383	-0.033	0.854	0.198	0.303	0.392(*)	0.026
U	0.036	0.846	-0.279	0.111	0.002	0.99	0.213	0.242

* Correlation is significant at p = 0.05

** Correlation is significant at p = 0.01

Consideration was also given to the complex relationships between soil and sediment geochemical concentrations and organic matter content. These relationships can be associated with, but not limited to, particle size and surface micro-topography (Horowitz and Elrick, 1987; Mayer, 1994; Galy *et al.*, 2008) and are strongly influenced by a wide variety of site specific environmental factors and alternative dependencies e.g. soil type, temperature, pore-water chemistry, soil bacteria (Elliott, 1991; Ter Lack *et al*., 2006; Davidson and Janssens, 2006; Hartman *et al*., 2008). The sorption behaviour of soils and sediment can differ according to the composition and provenance of the organic material (Chen *et al.,* 1995; Flemming *et al,* 1996). The organic constituents of a particle may reflect matrix-bound matter, surface associated bio-films or other algal formations on the particle surface (Elliott, 1991; Schorer, 1997). Differing forms of organic constituents will have varying influences on geochemical property dependencies and concentrations. The influence is further complicated within the floodplain environment by factors such as post-depositional diagenesis and Eh variations related to fluctuating floodplain water-tables (Fiedler, 2007). Seasonal influences, both natural and anthropogenic, may affect organic matter properties and geochemical property concentration dependencies for surface soils (Walling *et al*., 2003; Hartman, 2008). In view of the highly complex nature of the relationship between geochemical property concentration and particulate organic matter content, it was considered that without further in-depth analysis, the application of a linear, ratio based correction factor might over-simplify the dependent relationship and could lead to over-correction of the source sample fingerprint property values. The resources available to this study did not allow for such in-depth analysis, therefore, source and sediment geochemical property concentration values were not corrected to account for any possible organic matter dependencies (Collins *et al*., 1997a,b, 1998; Motha *et al*., 2003).

3.4 Particle-size effect correction

The application of a particle-size correction factor can alter the resultant property value and therefore, any particle-size correction which was required was undertaken prior to testing the data for compatibility of concentration ranges and source discrimination. Logically, any particle-size correction applied to data which have been previously tested (e.g. for source/sediment concentration range comparability and source discrimination), could render any such testing unreliable, due to the correction factor altering the values which predicate the test results. Any such correction could clearly significantly alter the values and assumptions upon which the selection of the resulting composite fingerprint has been based and would consequently lead to the application of a composite fingerprint within the mixing model of effectively unknown discrimination capabilities and untested range boundaries. The approach applied here was based broadly on that utilized by Gruszowski *et al*. (2003) and ensures that the property values which are used in the subsequent range test and source discrimination analysis are the same property values which are used to provide the mean values for inputs into the mixing model. Further, by correcting to the median SSA of all samples being considered, rather than the mean, the effect of any skew within each source group may be reduced.

As noted above, source samples collected from throughout a catchment can vary considerably in basic mineral and geochemical composition. Similarly, SSA values can potentially vary considerably within individual source groups and also to a lesser extent within floodplain sediment. This variability can be logically taken into consideration by individually correcting property concentrations of all source and floodplain sediment samples, to a standard SSA corresponding to the median SSA value of all samples being considered, viz.:

$$C_{si} = C_{so}\left(\frac{M_{SSA-ref}}{SSA_s}\right) \tag{3.1}$$

where: C_{si} is the particle-size-corrected concentration of tracer property *i* of sample *s*, C_{so} is the original concentration of tracer property *i* of sample *s*, $M_{SSA-ref}$ is the median SSA ($m^2\ cm^{-3}$) of all source and floodplain samples, and SSA_s is the SSA ($m^2\ cm^{-3}$) of individual sample *s*. Without determination of a more precise relationship between SSA and property concentration for individual fingerprint properties (He and Walling, 1996; Russell *et al*, 2001), this method offered a simple method of correcting all fingerprint properties for each individual sample in a manner which maintained the property relationships inherent within the original data.

3.5 The property concentration range test

The next stage in the selection of the optimum composite fingerprint was to apply a property concentration range test to the data. This test might be considered as a test of the general conservative nature of given properties following erosion, transport and deposition, which has been noted as an important factor in this type of work (Horowitz, 1991; Foster and Lees, 2000). The test also provided a general guide as to whether all potential major sources had been included in the catchment sampling programme.

In addition, the property concentration range test also ensured that any properties being considered for inclusion within the optimum composite fingerprint met the basic assumption on which the mixing model is founded; that the concentrations of the properties which comprise the composite fingerprint, measured in the floodplain sediment core sections, represent the product of the corresponding concentrations in the catchment sources and the relative inputs contributed by those sources (Collins *et al.*, 2007). Failure to meet this requirement could lead to the inclusion of properties within the composite fingerprint with concentration values which could not be accurately compared within the mixing model. The mixing model used in this work incorporated a Monte Carlo framework (detailed below), wherein the inputs for the model were based on the source property mean concentration values and their associated standard deviation. Therefore these parameters were also used to bound the source range values in this test.

The source range spanned the minimum mean property concentration value minus the associated standard deviation, to the maximum mean property concentration value plus the corresponding standard deviation. Microsoft Excel spreadsheet conditional formulae were used to compare the variation in property concentration ranges between source material and floodplain sediment, to ensure that sediment concentration ranges fell within the source concentration ranges. Properties which failed the range test might have been exhibiting non-conservative behavior or enrichment and may therefore have been subject to transformation during erosion and transport or as a result of post-depositional processes (Tanizaki, 1992; Foster and Lees, 2000; Motha, 2002; Small *et al.*, 2002; De Vos *et al.*, 2006; Gordev *et al.*, 2004). An example of results from application of the property range test to property concentration data from the River Axe catchment is shown in Table 3.3.

Table 3.3 *An example of the property range test results for property concentrations from the River Axe catchment*

Core range within source range	**Core range overlaps source range min**	**Core range overlaps source range max**	**Source range within core range**
Mg	Na	Zr	Al
Mn	Sc	Mo	K
Li	Ti	Cd	Fe
Zn	V	Sb	Rb
Ga	Cr		
Ge	Co		
As	Ni		
Sr	Cu		
Y	Tl		
Pd	^{206}Pb		
Sn	^{207}Pb		
Cs	^{208}Pb		
Ba			
La			
Ce			
Pr			
Nd			
Sm			
Eu			
Gd			
Tb			
Dy			
Ho			
Er			
Yb			
Hf			
Bi			
U			

.

Core range = Min to Max downcore property concentration values

Source range = Min Mean – Std Dev to Max Mean + Std Dev of mean source group property values

It is important to perform the range test for each catchment independently of any previous analysis of the conservative nature of the properties being considered as differing catchment-specific environmental factors may influence property behaviour (Birch *et al*., 2000). For example, whilst Al is generally considered to be a ‘conservative’ element and has been used in previous studies for trace element normalisation purposes (Piper, 1973; Bruland, *et al*., 1974; Horowitz, 1991), it may be subject to release from sediment resulting from the formation of Al-phosphate complexes or precipitates following the field application of phosphate based fertilizers (Chiang *et al*, 2008). Such nutrient applications are likely to vary according to land use within any given catchment, potentially leading to associated variation in any Al transformation. Conversely, it is well known that trace metals can be taken up and concentrated by sediment and suspended particulate matter in aquatic systems.

Therefore, heavy metal properties, such as Pb and Cd, could become concentrated in sediment during transport following introduction of Pb and Cd contaminants to the river corridor via road runoff or from the drainage systems of urban centers (Baeckstroem *et al*., 2004).

3.6 Source discrimination: the Kruskal-Wallis *H*-test

The next stage in identifying the optimum combination of tracer properties to provide the composite fingerprint involved testing which properties differed significantly between source types. The existence of such differences was initially tested using the non-parametric Kruskal-Wallis *H*-test applied to the source sample property value data using the SPSS 15.0 for Windows (Collins *et al*., 1997a). A non-parametric test was utilized because the property data for soils and sediments can often be of non-Normal distribution and unequal variances (Collins *et al*., 1997a). The Kruskal-Wallis *H*-test is suitable when the study incorporates two or more potential source groups and the number of observations per group exceeds the total number of groups (Walling and Collins, 2000). Greater *H*-values are produced as the significance of inter-group contrasts increases. Consequently, a statistically significant output is indicative of source inter-group contrasts, rather than confirming differences between all possible pairs of source groups (Fowler and Cohen, 1990, Collins *et al*., 2010a).

Following application of the Kruskal-Wallis *H*-test, the resultant values of *H* and asymptotic significance were analysed to ascertain which properties differed significantly between source types. An example of the output from the Kruskal-Wallis *H*-test as applied to source data from the River Waver catchment is shown in Table 3.4. The test statistic was distributed as the Chi-Square with K-1 degrees of freedom (*df*) (where K = number of potential source groups e.g. 4). Thereafter, in the example, the critical value of 7.81 for 3 *df* of the Chi-Square distribution was used at $p = 0.05$. Properties with an *H*-value <7.81 were subsequently removed from consideration as viable fingerprint properties.

Table 3.4 *H-values and asymptotic significance from the Kruskal-Wallis H-test utilized to ascertain the ability of individual tracer properties to distinguish between the source groups within the River Waver catchment.*

Property	*H*-value	Asymptotic
Mg	8.88	0.01
Al	4.27	0.12*
Mn	3.93	0.14*
Sc	25.24	0.00
Ti	3.08	0.21*
V	20.81	0.00
Cr	8.78	0.01
Co	25.04	0.00
Ni	27.05	0.00
Cu	5.18	0.07
Zn	0.05	0.97*
Ga	8.29	0.02
As	4.08	0.13
Sr	4.69	0.10
Y	19.77	0.00
Mo	2.88	0.24*
Sb	2.69	0.26*
Cs	8.83	0.01
Ba	7.57	0.02
La	8.61	0.01
Ce	14.56	0.00
Pr	26.08	0.00
Nd	28.14	0.00
Sm	33.06	0.00
Eu	30.64	0.00
Gd	30.46	0.00
Tb	29.97	0.00
Dy	25.74	0.00
Ho	25.42	0.00
Er	22.76	0.00
Yb	22.83	0.00
Tl	3.42	0.18*
^{206}Pb	10.43	0.01
^{207}Pb	9.43	0.01
^{208}Pb	10.31	0.01

Critical value = 7.81

* Not Significant at p = 0.05

3.7 Source discrimination: Multivariate Discriminant Function Analysis

Those properties which had satisfied the previous tests were subject to Multivariate Discriminant Function Analysis (MDFA), which tested the ability of the geochemical properties to classify correctly the source samples into the appropriate source groups and identified the optimum fingerprint, for this purpose. MDFA was based on the minimization of Wilks' Lambda (Λ) (Collins *et al*., 1997a). Using this approach, the statistical significance of each discriminant function is assessed, based on eigen values (Klecka, 1980). Each eigen value is a relative measure of how much of the total discriminating power an individual discriminant function has and indicates the relative strength of each discriminant function. Consequently, Λ provides a multivariate measure of group differences over several independent variables. However, rather than testing a discriminant function directly, Λ examines the residual discrimination present in the system *a priori* deriving of that function. Λ can be interpreted as an inverse indicator of how great the discrimination is among the groups. Thereby establishing to what extent the groups differ in terms of the pool of independent variables (Klecka, 1980). A lower Λ indicates greater discrimination between groups. Initially, MDFA applied in this study to identify the optimum composite fingerprint used the stepwise entry method, (Collins *et al*., 1997a). In this approach, the optimum fingerprint refers to the smallest number of combined properties which can provide adequate discrimination, thereby potentially minimizing the possibility of over-parameterization. The explanatory power of individual fingerprint properties was indicated by the discriminant function coefficients estimated by MDFA. At each step, the property which produced the greatest minimization of Λ was entered, i.e. that which afforded the greatest relative power to discriminate between source groups. After the inclusion of the second property, each property already included was also tested at each step to see if it could be dropped from the analysis without a significant decrease in discrimination. Maximum significance of F to enter a property was 0.05. Minimum significance of F to remove a property was 0.10. Prior probabilities were computed from source group sizes and the best fit of the data was based on high inter-group variability relative to low intra-group variability utilizing a covariance matrix. Stepwise selection proceeded until all source samples were classified correctly, or until discrimination could not be improved by including any of the remaining properties.

Whilst stepwise MDFA provided a fingerprint which appeared to represent the best discrimination that could be achieved by the lowest number of properties, often this approach did not yield an acceptable level of discrimination. Therefore, an alternative approach of simultaneous entry MDFA was applied to all properties which had passed the previous assessment tests. A default minimum tolerance level of 0.001 was used and properties passing this tolerance criterion were then simultaneously entered into the

MDFA. Similarly to the application of the stepwise MDFA, prior probabilities were computed from source group sizes and the best fit of the data was based on high inter-group variability relative to low intra-group variability, utilizing a covariance matrix.

The simultaneous entry MDFA approach generally produced a composite fingerprint with a greater number of properties, which afforded a higher degree of discrimination, based on a lower Λ value. This would seem to indicate that the stepwise entry MDFA often failed to indicate correctly all the properties which had an influence on group discrimination and therefore did not necessarily produce the fingerprint with the best discrimination between sources. Similar limitations for stepwise entry discriminant analysis have been noted in variety of other studies across differing disciplines (Whittingham, 2006; Mundry and Nunn, 2009, Steyerberg, 1999). Consequently, the alternative approach offered by simultaneous entry MDFA was always considered before proceeding to the mixing model stage.

3.8 Application of the mixing model

In order to quantify the relative contributions from the potential sediment sources within the study catchments to the individual sections of the floodplain sediment core, a linear numerical mixing model, based on that described by Collins *et al.*, (1997b), was utilized in combination with the identified composite fingerprint and discrimination weightings. The mixing model calculates the optimal solution of an objective function through the minimization of the sum of the squares of the weighted relative errors.

The model must satisfy linear boundary constraints represented by the two following equations. Firstly, the relative contributions (P_s) from the individual source types cannot be negative (Eq. 3.3).

$$0 \leq P_s \tag{3.2}$$

Secondly, the combined contributions from the individual source types must sum to unity (Eq. 3.3).

$$\sum_{s=1}^{n} P_s = 1 \tag{3.3}$$

The mixing model solves a set of linear equations by comparing the concentration value of each fingerprint property in a given floodplain sediment section with the property concentration value predicted for a given set of source contributions (Eq. 3.5). The set of equations associated with the composite signature is generally over-determined, in that, usually $m \geq n$ (where m is the number of fingerprint properties and n is the number of source groups). Consequently, the apportionment of contributions from each source type is calculated by minimizing the sum of the squares of the weighted relative errors, viz.:

$$\sum_{i=1}^{n}\left(\left(C_i - \left(\sum_{s=1}^{m} P_s S_{si}\right)\right)/C_i\right)^2 W_i \tag{3.4}$$

where: C_i = concentration value of fingerprint property (i) in the floodplain sediment horizon; P_s = the optimised percentage contribution from source category (s); S_{si} = concentration value of fingerprint property (i) in source category (s); n = number of fingerprint properties; m = number of potential sediment source types; W_i = property discriminatory weighting.

The mixing model incorporated property-specific weightings to account for the variable individual discriminatory power of respective properties within the composite fingerprint. This was particularly useful in the case of composite fingerprints which incorporated larger numbers of properties, as these fingerprints often incorporated wider ranges of individual property discrimination. The weightings were based on the discriminatory power of individual fingerprint properties which were established by introducing each property individually into MDFA (Collins *et al*., 2010a). The individual weighting factors were then calculated, viz.:

$$W_l = \left(\frac{d_1}{d_2}\right) \tag{3.6}$$

where: W_l is the property-specific discrimination weighting factor, d_1 is individual property discrimination percentage and d_2 is the lowest individual property discrimination percentage. Since the discrimination of the source samples collected from any catchment will vary for each property in the corresponding optimum signature, it is logical to weight the optimised mixing model solutions on this basis

(Collins *et al.*, 2010a). For illustrative purposes, weightings calculated for fingerprint properties from the River Arrow catchment are shown in Table 3.5.

Table 3.5 *An example of mixing model property-specific discrimination weightings for the Arrow catchment*

Property	Individual discrimination (%)	Weighting
Cr	49.60	1.555
Sm	47.90	1.502
Ga	46.20	1.448
Pd	45.40	1.423
Mg	43.70	1.370
Gd	42.90	1.345
Li	42.00	1.317
Eu	42.00	1.317
Er	41.20	1.292
Tb	40.30	1.263
Sr	39.50	1.238
Fe	38.70	1.213
La	38.70	1.213
Hf	38.70	1.213
K	37.80	1.185
Ba	37.80	1.185
As	37.00	1.160
Mn	36.10	1.132
Y	36.10	1.132
Pr	36.10	1.132
Ti	34.50	1.082
Ce	34.50	1.082
Co	32.80	1.028
Ni	32.80	1.028
Nd	32.80	1.028
Zn	31.90	1.000

An important source of uncertainty when using the fingerprinting approach to apportion contributions from numerous sediment sources, is the extent to which the mean concentration values of the sediment properties for a given source type actually reflect the true character of the source type being considered. This is important as the mean concentration values are often based on a relatively small number of source material samples. Consequently, a Monte-Carlo framework, based on that proposed by Collins and Walling (2007), was incorporated into the mixing model to improve representative uncertainty related to source sampling. The application of the approach involved performing 5000 solutions of the mixing model applied to simulated input data sets to compute ranges in relative source proportions and 95% confidence limits for the 50^{th} percentiles. The simulated input data sets were based on Normal distributions constructed using a random number generator from fingerprint property mean concentration values from each source group bounded by associated standard deviations. The calculation of the simulated input data sets was constrained to ensure that the values generated were positive. Use of the mean concentration value to represent each respective source was justified on a physical basis in that the sediment collected from the floodplain will inevitably represent a mixture of material which has been mobilised and delivered from a wide variety of upstream locations. Therefore, the collection of source samples from a representative range of locations throughout the catchment and the use of these samples to derive mean fingerprint property concentrations can be assumed to be analogous to the process of natural sediment mixing which takes place during the mobilization, transport and delivery of sediment onto the floodplain (Collins *et al*., 1998).

Hitherto, in various sediment fingerprinting studies the solving of linear least squares equations within the mixing model has commonly been based on the use of the Solver function within Microsoft Excel (Walling and Collins, 2000; Walling *et al*, 2003). In this process the Solver works by changing a cell value on the spreadsheet (e.g. property value). The spreadsheet then calculates updates for all related figures including, importantly, the target cell. The Solver then compares the new target cell value to the previous target cell value to determine which parameters to alter to improve (lower) the target cell output. This sequence is repeated iteratively until the target cell value cannot be reduced further, or until a predetermined number of iterations have been performed. During the process outlined above, the Solver is constantly transferring data between macro and spreadsheet, which can be extremely time-consuming. Specifically, during the development phase of this work, the determination of a single floodplain core section required ca. 45-60 minutes processing time on a Hewlett Packard PC, running an Intel ®Core™2Duo CPU T5800 at 2.00GHz with 3.00GB RAM, with additional time required to input the core property values onto the spreadsheet for each section; to construct the Monte Carlo input dataset; to collate the output results and to calculate the associated relative errors. After research and development experience gained from running the mixing model algorithm in this manner for numerous cores, it was considered that the entire process was likely to be prohibitively slow for the purposes of this study. Further, that the configuration of the model might be limiting its ability to identify a reliable optimum solution.

Therefore, it was essential to devise an alternative method, which could expedite the solution of the least squares equations and thereby enhance the application of the mixing model. The method proposed here essentially divides the solution process into two. As the solution to a constrained set of least squares equations must be either the global unconstrained solution to the equations, or it must lie on the boundary of the parameter space defined by the constraints, where the boundaries are defined by the constraints in 3.3 and 3.4 above, we solve the unconstrained set of equations and then check to see if the solution falls within the constraints. If it does then the solution is also the solution to the constrained set of equations. If it does not, then the target solution must alternatively lie on the boundary of the parameter space defined by the constraints. To obtain the boundary solution, each combination of constraints is considered and the equations are solved for each combination. The small number of boundaries creates well-defined equations, which produce a small number of boundary solutions. Of the solutions obtained from the combinations of constraints, that which provides the lowest sum of squares, having met all constraints, is then taken to be the global solution. The application of this approach uses a Microsoft Excel spreadsheet and macro, whereby data representing one of the 5000 Monte Carlo input combinations is copied into RAM wherein an algebraic matrix macro performs the necessary calculations simultaneously. The solution is then returned to the spreadsheet and the following row of data is copied as before. This process is automatically repeated until the solution for each section of the entire core has been calculated. The solution for each core section (i.e. the relative sediment contribution from each potential source) is directly output into a results table in conjunction with the associated relative mean error and the results are automatically represented in a pre-formatted plot, which then requires only the appropriate chronology (see above) to be applied. In this way the data for an entire core of between 40-70 sections can usually be reliably processed and the results displayed in a maximum of 20 minutes for composite fingerprints of up to 28 properties. Assistance with the coding of the refined mixing model was kindly supplied by The University of Exeter, College of Life and Environmental Sciences, Computing Development Office.

It is important to note that this novel algebraic approach to the application of the mixing model changes how the equations are solved, but does not change what is actually being solved. In addition, the processing time required is likely to become greater if large numbers of sources are being considered as the number of equations required increases exponentially with each additional source. This approach allows greatly enhanced flexibility in the exploration of additional refinements to the sediment fingerprinting process and thereby, of reliably achieving the optimum balance between robust source discrimination and an acceptable mixing model performance as assessed by goodness-of-fit.

3.9 Sediment source apportionment

The output from the mixing model applied to the individual floodplain sediment core sections, provided estimates of relative sediment source contributions over time. The error associated with the mixing model results was assessed using the Relative Mean Error (RME) statistic. The RME and associated goodness-of-fit were calculated for the apportionment result for each core section. The RME was derived by comparison of measured property concentrations with predicted property concentrations, based on the estimates for the percentage contributions from source groups (Collins *et al.*, 1997b, 2010a), viz.:

$$RME = \left[\frac{1}{n} \sum_{i=1}^{n} \left(\left(C_i - \left(\sum_{s=1}^{m} P_s S_{si} \right) \right) / C_i \right)^2 W_i \right] \tag{3.7}$$

Goodness-of-fit = 1 - RME

Walling and Collins (2000) suggest that a RME of <15% (i.e. an 85% goodness-of-fit) indicates that the mixing model has provided an acceptable prediction of the fingerprint property concentrations of a given sediment sample and consequently that the relative contributions of the potential sources estimated by the mixing model are therefore likely to be reliable for comparative purposes. However, it should be noted that whilst the test for goodness-of-fit confirms that the mixing model has the ability to provide an acceptable agreement between simulated and observed fingerprint property concentrations for a study catchment; this does not specifically validate the model output. Robust mixing model validation in the context of this floodplain sediment source fingerprinting study would require comparison with historic sediment source information, covering a period ca.100 years, provided by alternative techniques such as long-term sediment monitoring studies. Such information is seldom, if ever, available.

3.10 Historical catchment land use and agricultural management changes

Data on changes in land cover, crops and stock densities were extracted and collated following interrogation of the Agricultural Census Database (Agcensus) (EDINA, 2009). Data were obtained at 2 km x 2 km grid resolution from the area of the study catchments for the years 1969, 1972, 1976, 1979, 1981, 1988, 1993, 1996, 2000 and 2004. The compilation of data in the Agcensus database was derived from conversion of farm returns based on parish boundaries and was subject to certain limitations, illustrated in Figure 3.2. However, this method was considered to offer an acceptable procedure for establishing general land use trends. Existing studies and anecdotal evidence complemented the Agcensus data as sources of historical land use information (e.g. Stamp, 1940; Robinson and Armstrong, 1988; Robinson and Sutherland, 2002; Riley and Harvey, 2005; Short, 2007, Defra, 2010).

Land cover data were compiled for late-harvested crops often associated with high erosion risk and included crops such as, potatoes, sugar beet, beans, peas, turnips, swedes, mangolds and maize. Data were similarly combined for high erosion risk autumn-sown crops, including wheat, winter-barley and oilseed rape. Temporary grassland and permanent grassland data were also individually collated for comparative analysis.

Similarly, fluctuations in stocking patterns within study catchments were calculated from Agcensus livestock data. For comparative land use impact analysis, stocking densities (LU ha^{-1}) for cattle and sheep were calculated from headage per hectare data on the assumption that combined stock grazed the land area under permanent grassland for each associated year (Sullivan *et al*., 2004). The resolution of data for pig production did not discriminate between outdoor production systems or intensive indoor systems. Pigs were therefore excluded from the combined stocking density calculations on the assumption that their contribution could not be adequately defined.

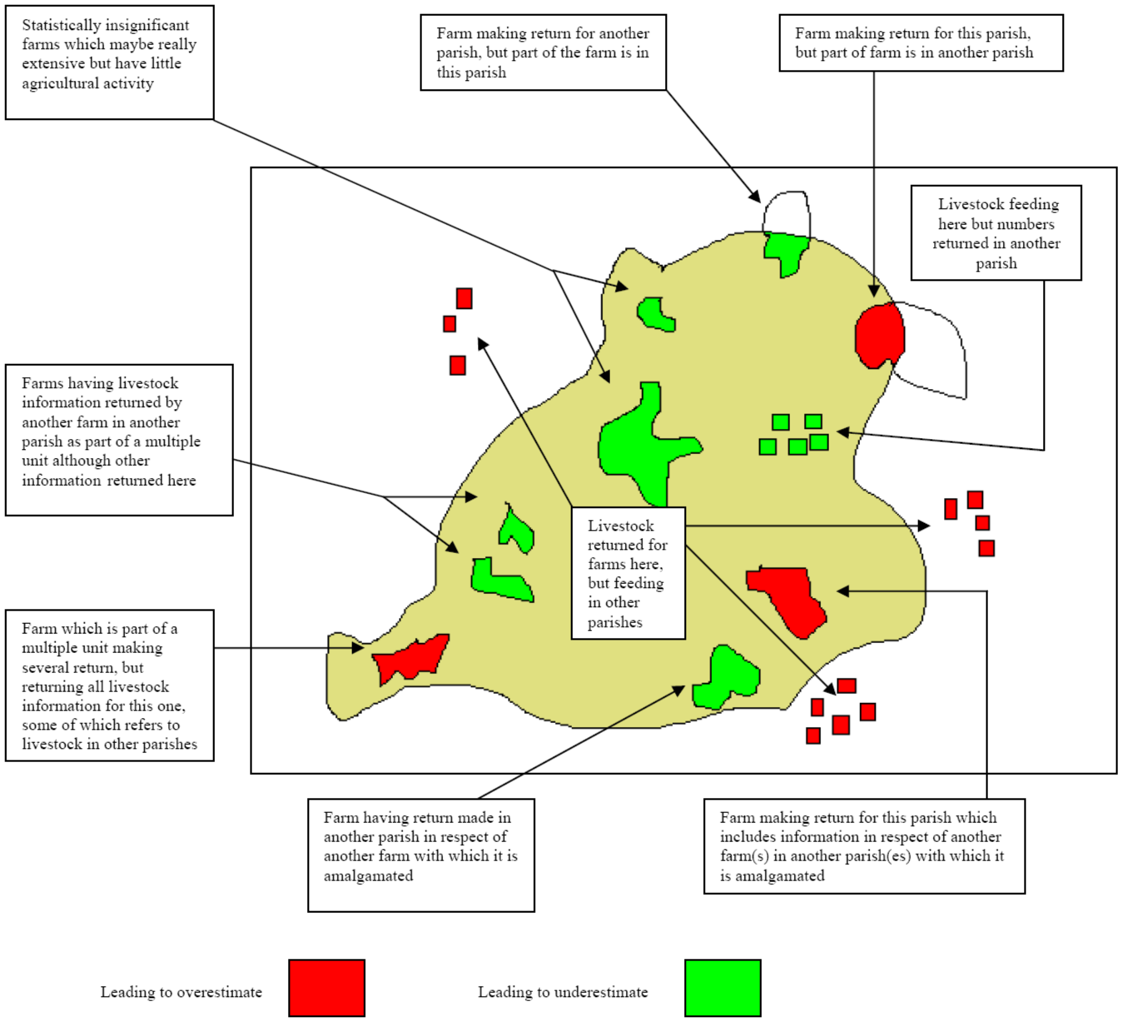

Figure 3.2 *Limitations of Agcensus data for 2km x 2 km grid squares based on parish scale farm returns (EDINA, 2009).*

Livestock units (LU), which are commonly used to assess the impact of grazing livestock on pasture by allowing comparison of live stock types, were calculated based broadly on Defra guidelines, as shown in Table 3.5 (Defra, 2006). The collation and presentation of the Agcensus cattle data in the available datasets were somewhat inconsistent across the time period, with the result that the precise age of cattle could not be adequately determined for certain years. Consequently, a representative average figure of 0.8 LU, as used by Sullivan *et al*. (2004), was applied to all cattle over 6 months for which data were available. Total LUs were divided across permanent grassland to provide estimates of stocking densities.

Table 3.6 Livestock Unit (LU) values (Defra 2006)

Animal	**Livestock Unit (LU)**
Dairy cow	1
Dry medium beef cow	0.7
Medium beef cow suckling	0.9
Calf under 6 months	0
Cow and unweaned calf	0.9
Heifer or steer under 1 year	0.6
Heifer or steer under 2 years	0.6
Heifer or steer over 2 years	0.7
Bull	0.9
Medium sheep	0.15

3.11 Summary

This chapter has detailed the various data processing methods applied during this study, including some proposed novel approaches designed to ensure the robust selection of suitable fingerprint geochemical properties and their reliable application within an adapted mass-balance mixing-model. The development of these refinements was facilitated by experimentation utilizing the data from the study catchments. The resulting sets of methodological steps were then applied in the manner represented by the sediment source fingerprinting decision tree to the individual study catchments and the results are reported over the following six chapters respectively. Each river catchment has unique characteristics and in order to account for this variation, the methodological application of the sediment source fingerprinting technique is required to be flexible, yet robust, and in this manner it may be described as a tool kit based on a generic decision tree.

CHAPTER 4 - THE RIVER TORRIDGE CATCHMENT: RESULTS AND INTERPRETATION

4.1 Introduction

This chapter is the first of six individual catchment case study chapters and presents the results and interpretation from the application of the sediment source fingerprinting technique to floodplain sediment cores from the River Torridge catchment, Devon, UK. The methodologies detailed in Chapters 2 and 3 have been applied with the aim of relating changes in the relative contributions from a number of potential source types to overbank sediment deposits in response to historical (ca. 100 years) land use change.

The River Torridge supports salmon, sea trout and brown trout. However, the salmonid population has decreased in recent years, prompting the Environment Agency (EA) to introduce a Salmon Action Plan for the catchment in 2008 (BBC, 2010a). In 2009 the river failed to reach its compliance conservation limits (CL) for spawning stocks and was designated ‘probably at risk’ (South West Observatory, 2010). Sediment associated problems related to declining salmonid fish populations in the River Torridge catchment have been highlighted in several previous studies (Nicholls, 2000; Walling *et al*., 2003; Walling, 2005). Sediment-related land use management changes that are of particular interest in this case study include the potential impacts of large-scale land drainage improvements and the effects of variations in stocking densities during the study period.

4.2 The River Torridge catchment description

The River Torridge catchment is a rural catchment situated in North Devon, England (Figure 4.1). The river rises on a low plateau at Baxworthy Cross, close to Clovely and the North Devon coast and then flows in a south easterly direction, past the villages of East and West Putford. It is joined by the River Waldon at a confluence close to the hamlet of Bradford, from where it flows in an easterly direction past the villages of Black Torrington and Sheepwash. The River Lew joins the River Torridge to the north of Hatherleigh, which then flows in a north easterly direction to be joined by the River Okement south of Meeth. Flowing north the river acquires the River Mere near Beaford, after which it flows in a north-westerly direction in large meander loops past the villages of Little Torrington, Great Torrington and Pillmouth acquiring the River

Yeo. The tidal limit of the River Torridge is at Weare Giffard becoming estuarine as it flows past the town of Bideford. The River Torridge joins the estuary of the River Taw between Appledore and Instow and then flows out into Bideford Bay. The sub-catchment identified for this study occupies a drainage basin area of approximately 250km^2 and incorporates the Upper River Torridge from its source near Baxworthy Cross and all major and minor tributaries down to a designated catchment outlet to the north of Hatherleigh, at Hele Barton.

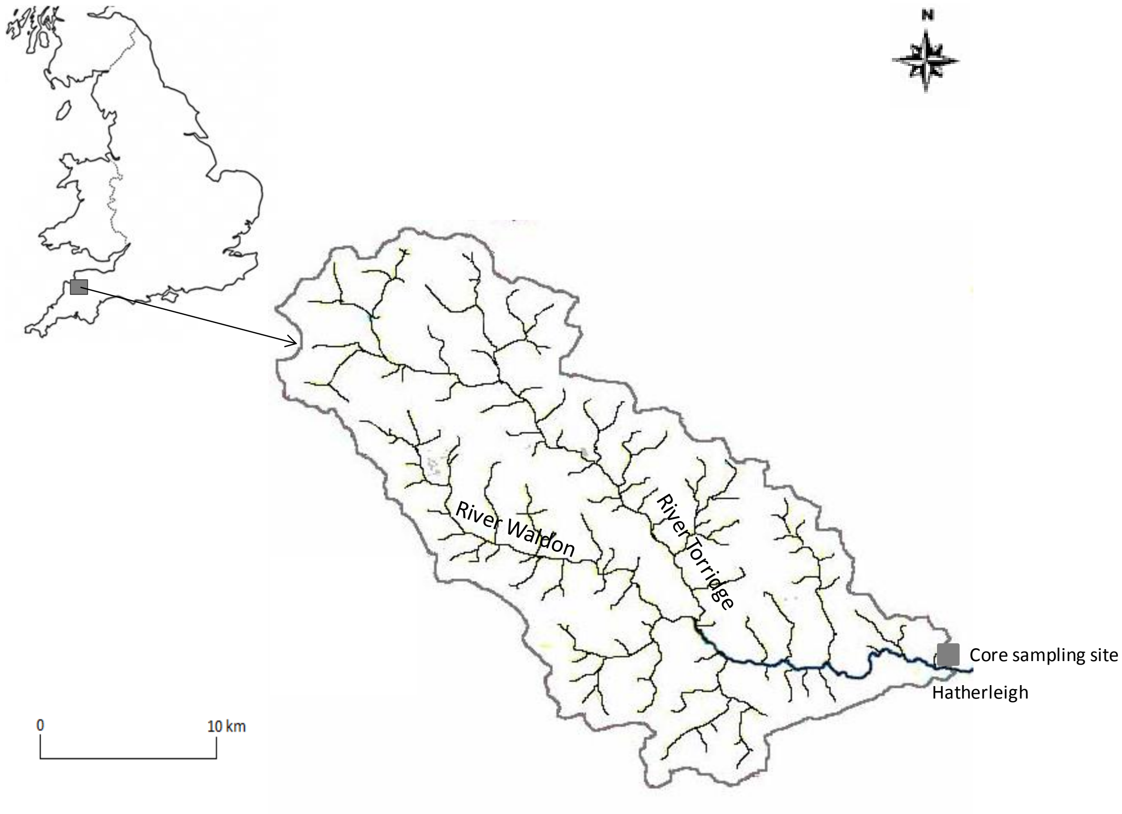

Figure 4.1 *The location and study area of the Upper River Torridge catchment, Devon, UK.*

The geology of the River Torridge catchment is impermeable granite below the southern tributaries which rise high on Dartmoor, the main area of the catchment is underlain by low permeability Devonian and Carboniferous rock which create a hydrology that responds relatively quickly to rainfall (Environment Agency, 2008). Rainfall in the catchment can be quite high, ranging from 800mm near the coast, up to 2,300mm on the upland areas of the moors (Environment Agency, 2009).

The soils of the River Torridge catchment are characterised in the headwaters and higher ground by predominantly slowly permeable, seasonally wet, acid loamy and clayey soils. Throughout the remainder of the catchment, there are large areas of freely draining slightly acid loamy soils. These areas are interspersed by areas of slightly acid clayey soils with impeded drainage (NSRI, 2010).

Land use in the catchment is dominated by dairy and livestock production. Grassland in the catchment includes some areas of rare Culm grassland, rough grazing occurs on the uplands, with some lowland areas of intensively managed temporary grass lays. There is a limited amount of arable cultivation in the River Torridge catchment, although this has been increasing over recent years in response to demand for livestock fodder crops (EDINA, 2009). The woodland in the catchment includes relatively small-scale mixed and coniferous plantations.

Figure 4.2 *The Upper River Torridge catchment, land use management practices that have created sediment-associated problems and risks. Clockwise from top left; livestock causing soil erosion and compaction; unfenced riparian zone leading to destruction of channel banks and excessive poaching by livestock, excessive in-channel sedimentation from field drains; fodder maize cultivation on hill slopes leaving soil exposed to mobilisation during winter months of high rainfall.*

The River Torridge forms a major part of the UNESCO North Devon Biosphere Reserve and incorporates three European Special Areas of Conservation (SACs) and 18

Sites of Special Scientific Interest (SSSIs) (Natural England, 2009; Environment Agency, 2008). The River Torridge, in conjunction with the River Taw, is synonymous in popular culture with otters, largely due to the two rivers being the setting for the Henry Williamson novel, "Tarka the Otter". The River Torridge catchment area is a popular destination for various tourist activities including canoeing, angling and bird-watching. Some of the sediment-associated problems and risks caused by land use management in the Upper Torridge catchment are shown in Figure 4.2.

4.3 Floodplain site selection

Potential floodplain sampling sites were identified for collection of overbank sediment cores through the use of topographic maps, satellite imagery, ground observation and anecdotal evidence. This process pinpointed sites which were regularly inundated by overbank flooding, with associated potential to receive and store sediment deposition. It was also important that such sites had not been cultivated within the recent past, in order to preserve the historical sediment record intact. This last requirement was particularly hard to substantiate and had to rely largely on anecdotal evidence from landowners. This was combined with an ecological appraisal of sward composition and biodiversity.

Two potential floodplain coring sites were identified within relatively close proximity to each other, one at Dippermill and the other at Hele Barton. Figure 4.3 shows the Upper River Torridge catchment and the location of the core sampling sites at Hele Barton. Areas on the floodplain with a slight depression were chosen, as these were deemed to be more likely to have retained overbank flood waters and thereby to represent depositional sinks. The possibility for the core sampling sites to represent sediment sinks was substantiated by the presence of fine sediment residue on vegetation and leaf litter. A reference core was also collected from a nearby undisturbed topographically level site above the floodplain, which had been subject to neither soil erosion nor sediment deposition. This site was assumed to represent a suitable control for quantifying the local reference ^{137}Cs fallout inventory during subsequent comparative ^{137}Cs inventory analysis.

Figure 4.3 *The Upper River Torridge catchment and location of the floodplain core and reference core sampling sites at Hele Barton, Devon, UK (Google Earth, 2010).*

In accordance with the paired core approach described in Chapter 2, two cores were collected from each of the floodplain sample sites at Hele Barton. The first floodplain core was collected for potential laboratory analysis and the second adjacent bulk core was collected for the purpose of estimating comparative sedimentation rates at the site. Following comparison of the ^{137}Cs inventories of the bulk floodplain cores with that of the reference site (1237Bq m^{-2}), shown in Figure 4.4, the floodplain core with the highest ^{137}Cs inventory (5431Bq m^{-2}), was identified as Core Site 1, at Hele Barton. This site was assumed to have received the greatest sediment deposition and the corresponding core collected for laboratory analysis was subsequently divided into 1cm sections, freeze dried, and homogenised in preparation for laboratory analysis.

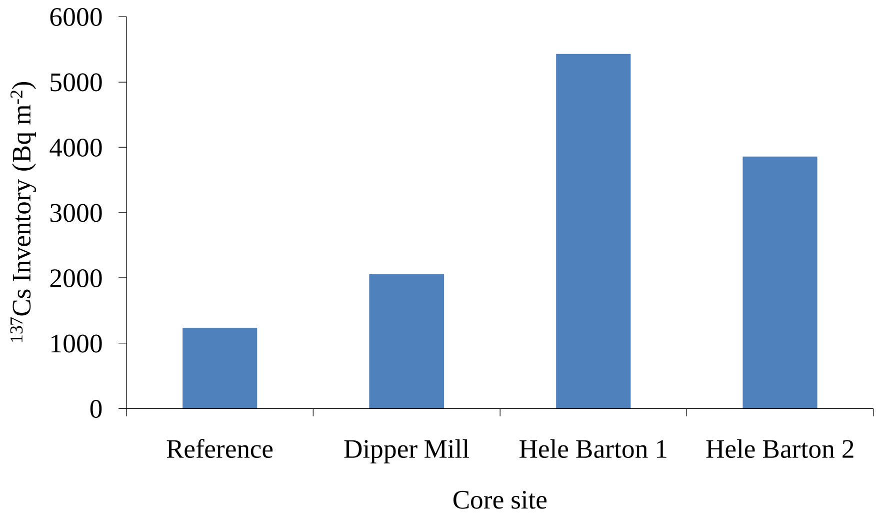

Figure 4.4 *^{137}Cs inventories for the local reference and floodplain bulk cores collected from the River Torridge catchment.*

4.4 ^{137}Cs radioisotope geochronology

^{137}Cs and $^{210}Pb_{ex}$ assay of individual core sections was undertaken to establish the chronology of the sediment core profile. The depth distribution profiles of ^{137}Cs and $^{210}Pb_{ex}$ activity concentration within the floodplain core are shown in Figures 4.5 and 4.6 respectively. The depth distribution of ^{137}Cs within the core was analysed and the horizon containing peak activity was identified at 11cm. It was assumed that the 11cm marker could be associated with the peak in bomb derived ^{137}Cs fallout attributed to 1963. Time-averaged sedimentation rates for the intervening 45 years to the date of core collection were then calculated at 0.24cm year^{-1} and extrapolated to provide an approximate chronology for the core sections. The appearance of ^{137}Cs at depths which the estimated chronology would suggest are before the release of ^{137}Cs into the atmosphere in the early 1950's (i.e. < 16cm), may possibly be due to bioturbation or leaching causing downward ^{137}Cs migration (Owens and Walling, 1996; Walling and He, 1997). Cambray *et al*., (1987) observed that the downward diffusion of ^{137}Cs will vary with soil type. Notwithstanding any apparent partial ^{137}Cs migration, the visual appearance of the profile indicated that sediment deposition had been continuous over time at a relatively constant rate and that the floodplain core site was likely to have been largely undisturbed during the recent past (ca.100 years).

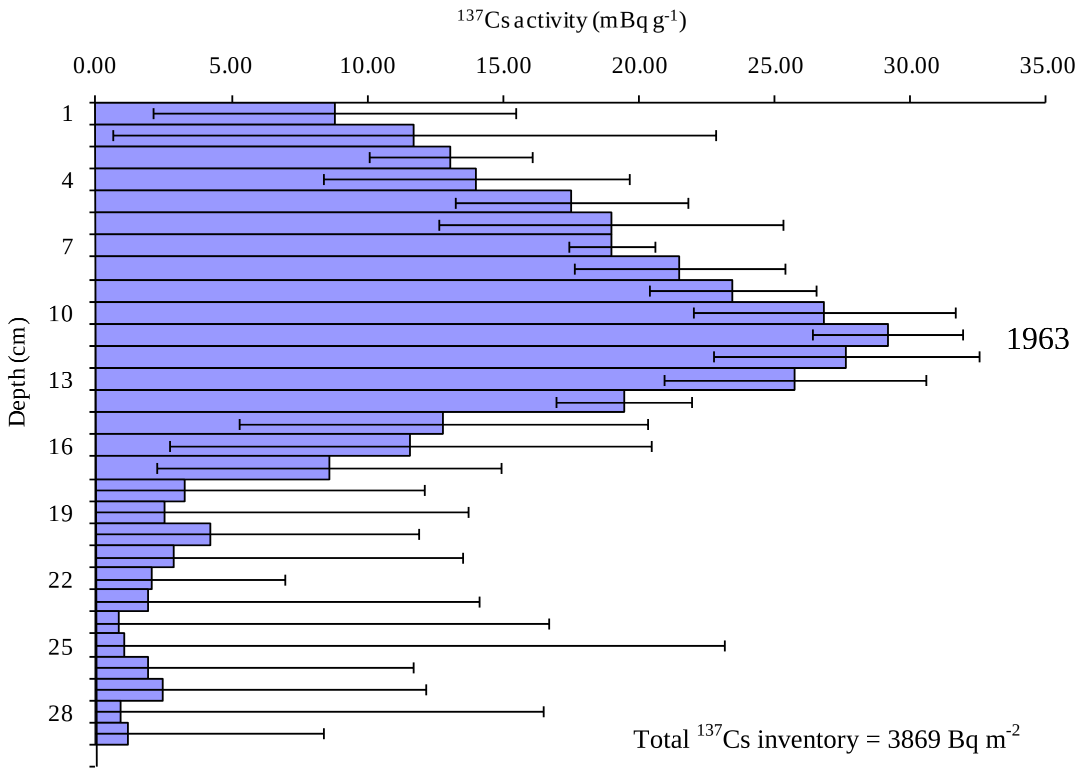

Figure 4.5 *The depth distribution profile of ^{137}Cs, and total ^{137}Cs inventory from the Hele Barton 1, River Torridge floodplain core.*

Analysis of the $^{210}Pb_{ex}$ vertical distribution profile also indicated that deposition over the previous 100 years had been largely uniform and continuous. Analytical uncertainty might account for some short term minor fluctuations in activity concentration. A chronology was estimated based on the Constant Flux: Constant Sedimentation (CF:CS) model (Robbins, 1978; Oldfield and Appleby, 1984), which assumed that the top 1cm layer of sediment in the core profile was deposited in the sampling year (2008), also that deposition over the previous 100 years had been largely uniform and quasi-continuous, as observed above. Based on the initial $^{210}Pb_{ex}$ activity concentration within the top 1cm layer and the decay half-life for ^{210}Pb of 22.3 years, an expected concentration for the year 1963 was estimated at 13.98 mBq g^{-1}, which was attributable to a depth of approximately 12cm. The $^{210}Pb_{ex}$ based estimate corresponded reasonably well with the ^{137}Cs based chronology estimate for 1963 of 11cm.

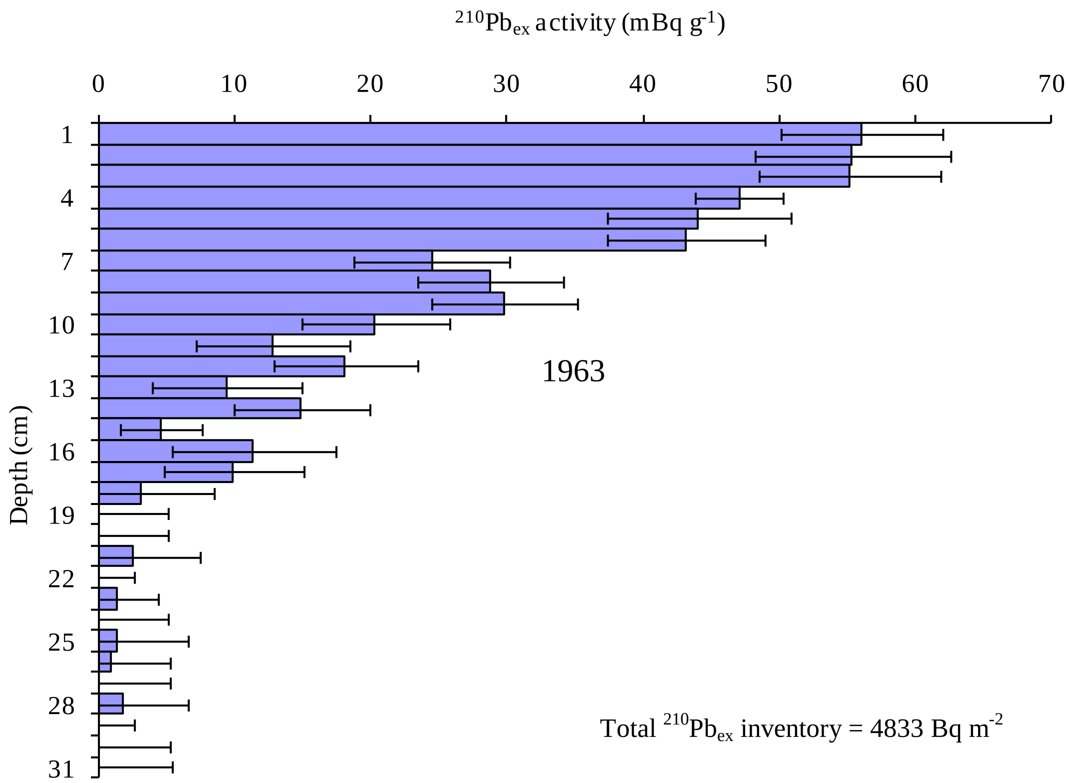

Figure 4.6 *The depth distribution profile of $^{210}Pb_{ex}$ and total $^{210}Pb_{ex}$ inventory from the Hele Barton 1, River Torridge floodplain core.*

4.5 The sediment source fingerprinting technique

4.5.1 Source samples

Surface scrapes (<2cm depth) were collected from three distinct potential sediment source groups, grassland topsoil, cultivated topsoil and eroding channel banks. The channel bank sources included open ditches and ephemeral channels which have incised into the subsoil. 30 samples were collected from each source group from 90 sites across the River Torridge study catchment. Laboratory analysis provided information on particle size distribution, specific surface area (SSA) and concentration values for a suite of 48 geochemical properties, from which to identify an appropriate composite fingerprint.

4.5.2 Particle size effects

Spearman's rho was used to test the correlation between sample SSA and geochemical property concentration within each of the three potential source groups (Table 4.1).

Table 4.1 *Spearman's rho correlation coefficients and significance for SSA versus property concentration from grassland, cultivated land and channel bank source groups.*

	Grassland		Cultivated land		Channel banks	
Property	Coefficient	Significance	Coefficient	Significance	Coefficient	Significance
Mg	0.194	0.304	0.014	0.94	-0.262	0.17
Al	.505(**)	0.004	.393(*)	0.029	-0.261	0.172
K	0.22	0.244	0.192	0.301	-0.346	0.066
Mn	-0.334	0.071	0.077	0.68	-0.057	0.77
Fe	-0.088	0.643	.435(*)	0.015	.459(*)	0.012
Li	0.231	0.218	0.16	0.389	-.413(*)	0.026
Na	-0.09	0.637	0.163	0.382	-.419(*)	0.024
Sc	-0.079	0.679	0.152	0.415	-0.155	0.423
Ti	0.235	0.21	0.169	0.364	-0.133	0.493
V	0.318	0.087	0.209	0.259	-0.35	0.063
Cr	0.334	0.071	0.335	0.065	-.392(*)	0.036
Co	-0.36	0.051	0.118	0.527	0.047	0.808
Ni	-0.235	0.212	0.301	0.1	-0.355	0.059
Cu	0.207	0.271	0.274	0.135	-.374(*)	0.045
Zn	0.048	0.803	0.074	0.694	-.489(**)	0.007
Ga	-0.015	0.937	.360(*)	0.046	-0.136	0.48
Ge	-0.173	0.361	0.227	0.218	0.094	0.629
As	0.097	0.608	0.353	0.051	.489(**)	0.007
Rb	0.234	0.214	0.29	0.114	-.473(**)	0.009
Sr	0.307	0.099	0.008	0.967	-0.189	0.326
Y	-0.055	0.774	.455(*)	0.01	0.064	0.743
Zr	-0.043	0.824	-0.029	0.876	-0.021	0.915
Mo	-0.103	0.586	0.22	0.235	0.33	0.08
Pd	-0.107	0.575	0.271	0.141	-0.131	0.498
Cd	-0.348	0.06	-0.034	0.855	-.563(**)	0.001
Sn	.615(**)	0	0.244	0.186	0.139	0.471
Sb	0.014	0.943	0.207	0.264	-.497(**)	0.006
Cs	-0.256	0.173	-0.19	0.305	0.292	0.125
Ba	0.015	0.938	0.315	0.084	-0.33	0.081
La	-.398(*)	0.029	0.296	0.105	0	1
Ce	0.34	0.066	.543(**)	0.002	0.291	0.125
Pr	0.139	0.465	.402(*)	0.025	0.256	0.181
Nd	0.102	0.592	.493(**)	0.005	0.283	0.137
Sm	0.022	0.908	.523(**)	0.003	0.242	0.206
Eu	-0.047	0.807	.392(*)	0.029	0.048	0.804
Gd	-0.098	0.608	.357(*)	0.049	0.013	0.947
Tb	-0.054	0.778	0.31	0.09	-0.064	0.743
Dy	-0.099	0.602	0.309	0.091	-0.107	0.581
Ho	-0.102	0.593	0.324	0.076	-0.121	0.531
Er	-0.088	0.644	0.353	0.051	-0.179	0.352
Yb	-0.106	0.578	.360(*)	0.047	-0.002	0.992
Hf	-0.169	0.372	0.321	0.078	-0.017	0.929
Tl	-0.073	0.7	0.032	0.865	-0.083	0.668
^{206}Pb	.449(*)	0.013	.365(*)	0.044	-0.052	0.79
^{207}Pb	0.235	0.212	0.245	0.184	-0.338	0.073
^{208}Pb	0.251	0.181	0.218	0.24	-0.318	0.092
Bi	0.243	0.195	0.22	0.235	-0.331	0.08
U	0.347	0.06	0.15	0.42	-0.106	0.585

* Correlation is significant at p = 0.05
** Correlation is significant at p = 0.01

Based on 144 grouped relationships, 10 (7%) showed significant correlation at $p = 0.01$ and 16 (11%) showed significant correlation at $p = 0.05$. Within the grassland, cultivated land and channel bank source groups, significant correlations ($p < 0.05$) were observed in 13%, 40% and 33% of cases, respectively. There were no instances where SSA correlated to property concentration values across all three source groups. Based on the above findings, it was considered inappropriate to apply particle size correction to the raw property concentration values in this case study (see Chapter 3).

4.5.3 Particle-size composition

Figure 4.7 compares the mean particle size distributions of the <63μm fraction of sediment retrieved from the River Torridge floodplain core and the three source groups. The particle size distribution of the floodplain sediment is clearly enriched in fines across the <63μm fraction range when compared the distributions of the respective source groups. This may reflect the selective mobilisation of the finer fractions from the source areas and the potential for finer particles to remain in suspension during transport.

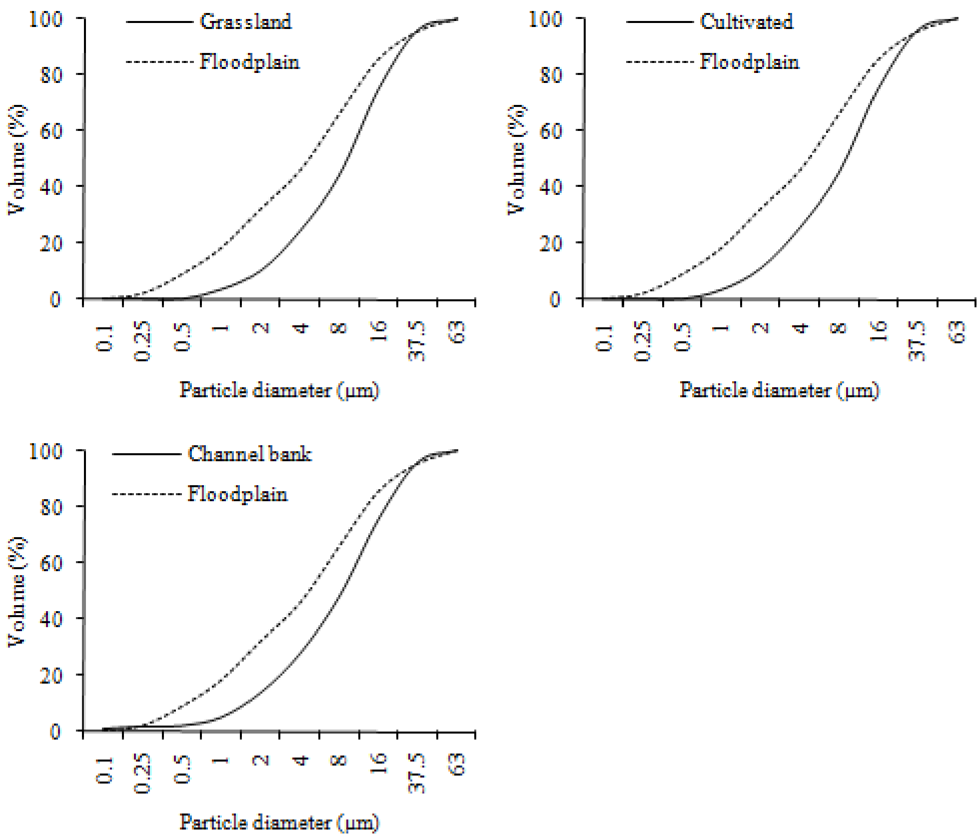

Figure 4.7 *Comparison of the mean cumulative particle size distribution of the <63μm fraction of samples from the grassland, cultivated land and channel bank source groups and sediment from the floodplain core sections.*

The particle size distribution of a sample is closely reflected by its SSA. Figure 4.8 shows the inter-sample group variability of mean and median SSA of the <63μm fraction of soil from the source groups and the floodplain core. This further emphasises the enrichment with finer fractions in the floodplain core. A greater heterogeneity of particle SSA within the source groups can also be observed by considering the variance between median and mean values.

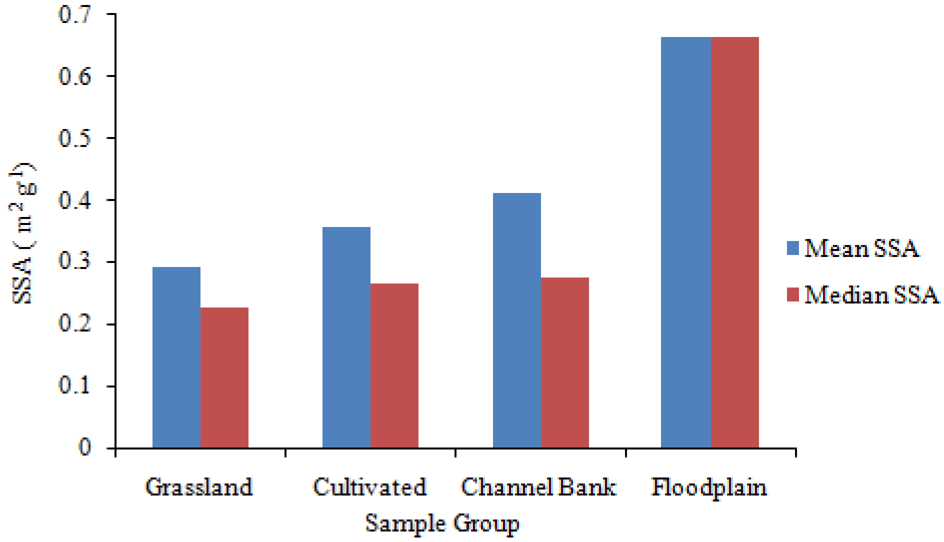

Figure 4.8 *Inter-sample group variability of mean and median SSA (m^2 g^{-1}) of the <63µm fraction of samples from the grassland, cultivated and channel bank source groups and sediment from the floodplain core sections.*

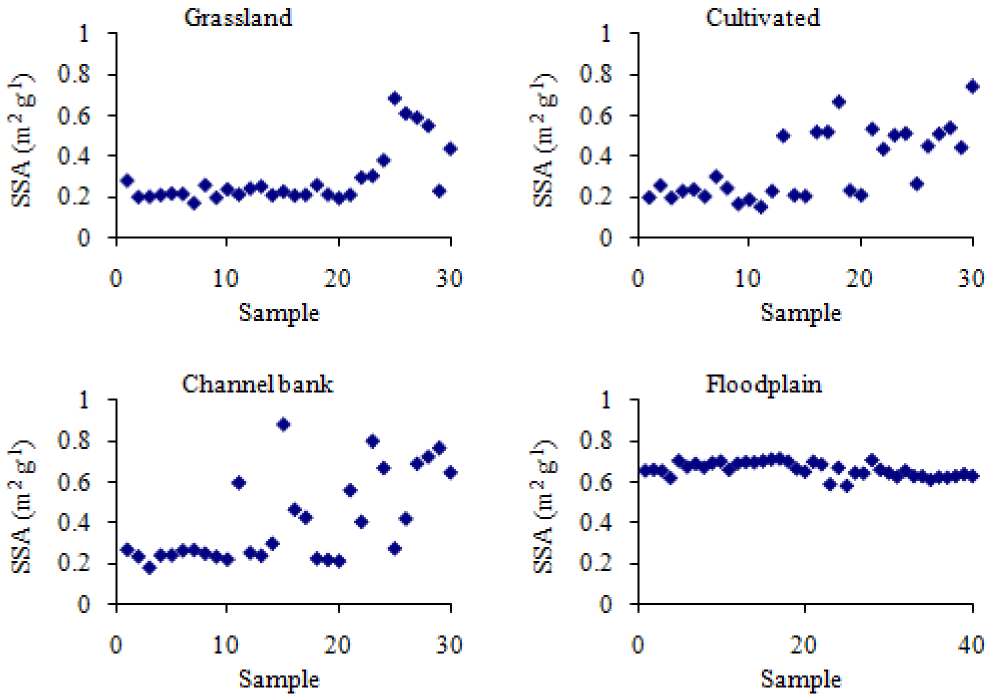

Figure 4.9 *The intra-group variability of SSA from the <63µm fraction of samples from the grassland, cultivated land and channel bank source groups and sediment from the floodplain core sections.*

Figure 4.9 shows the intra-group variability of SSA of the <63µm fraction of sediment associated with the three source groups and the floodplain core sections. This emphasises the heterogeneity of source sample SSA, particularly from cultivated topsoil sources, when compared to that of sediment from the floodplain core sections.

4.5.4 The property concentration range test

The next stage was to apply the data to a property concentration range test to assess the general conservative nature of sediment properties following the influence of soil erosion, sediment transport and post depositional processes on the floodplain such as, the effects of bioturbation, molecular diffusion in the porewaters and possible advection influence of groundwater flow. The range test allowed that any properties considered for subsequent inclusion within the fingerprint should offer a reasonable solution and optimum goodness of fit within the mixing model, in that, minimum and maximum property concentration values from the core horizons fell within the minimum and maximum range of source property values. The concentration range of the source groups was taken from the mean property concentration values plus or minus their respective standard deviation values to ensure continuity with mixing model input values used in the Monte Carlo framework (see Chapter 3). Table 4.2 displays the property concentration range test results for the River Torridge catchment.

Table 4.2 *The River Torridge catchment property concentration range test results*

Core range within source range	Core range overlaps source range min	Core range overlaps source range max	Core range above source range max	Source range within core range
Mg	Fe	Al	Ce	Na
Mn	Cu	K		V
Sc	As	Li		Cr
Ti	^{206}Pb	Ga		Rb
Co	^{207}Pb	Zr		Mo
Ni	^{208}Pb	Cd		Sn
Zn		La		Cs
Ge		Pr		Tl
Sr		Nd		
Y		Sm		
Pd		Gd		
Sb		Tb		
Ba		Ho		
Eu		Yb		
Dy		Hf		
Er		Bi		
		U		

Sixteen properties (Mg, Mn, Sc, Ti, Co, Ni, Zn, Ge, Sr, Y, Pd, Sb, Ba, Eu, Dy and Er) satisfied the range test requirements. Of the thirty-two properties which failed to satisfy the range test requirements, six properties (Fe, Cu, As, ^{206}Pb, ^{207}Pb, ^{208}Pb) had concentration ranges within the core which overlapped the source range minimum concentration value. Seventeen properties (Al, K, Li, Ga, Zr, Cd, La, Pr, Nd, Sm, Gd, Tb, Ho, Yb, Hf, Bi, U) had concentration ranges within the core which overlapped the source range maximum concentration value. One property (Ce) had a concentration range within the core which was above the source range maximum value. Eight properties (Na, V, Cr, Rb, Mo, Sn, Cs, Tl) had source concentration ranges which were within the sectioned core ranges.

4.5.5 Source discrimination: the Kruskal-Wallis H-test

The next stage in the selection of tracer properties to form the composite fingerprint was to test the ability of properties to differentiate between source types and was initially assessed using the Kruskal-Wallis *H*-test (Collins *et al*., 1997a). Greater *H* values are produced as the significance of inter-group contrasts increases. Table 4.3 presents the Kruskal-Wallis *H*-values and associated asymptotic significance.

Table 4.3 *H-values and asymptotic significance from the Kruskal-Wallis H-test for individual tracer properties to distinguish between the grassland, cultivated and channel bank source groups.*

Property	*H*-value	Significance
Mg	9.828	0.007
Mn	6.211	0.045
Sc	8.414	0.015
Ti	50.573	0.000
Co	37.271	0.000
Ni	32.141	0.000
Zn	20.454	0.000
Ge	12.105	0.002
Sr	24.844	0.000
Y	49.550	0.000
Pd	42.847	0.000
Sb	12.099	0.002
Ba	32.488	0.000
Eu	45.935	0.000
Er	47.455	0.000

Critical *H*-value = 5.99
p = 0.05

The test statistic was distributed as the Chi-Square with K-1 degrees of freedom (*df*) (where K = number of potential source groups i.e. 3). Thereafter, the critical value of 5.99 for 2 *df* of the Chi-Square distribution were used at p = 0.05. All the properties included in the test produced *H*-values above the critical value and were included in the next stage of ascertaining the optimum composite fingerprint.

4.5.6 Source discrimination: Multivariate Discriminant Function Analysis

A stepwise Multivariate Discriminant Function Analysis (MDFA), based on the minimization of Wilks' Lambda, was then applied to the properties passing the Kruskal-Wallis *H*-test (Collins *et al.*, 1997a). At each step, the property which minimised the overall Wilks' Lambda was entered. Maximum significance of F to enter a property was 0.05. Minimum significance of F to remove a property was 0.10. The MDFA tested the ability of the tracer properties to classify correctly the source samples into the appropriate source groups and also provided a quantification of the discriminatory power of the optimum composite fingerprint, as presented in Table 4.4.

Table 4.4 *Results from the stepwise MDFA for identifying the optimum composite fingerprint for discriminating grassland, cultivated and channel bank source groups, based on the minimisation of Wilks' Lambda*

Step	Property	Wilks' Lambda	Cumulative original grouped cases correctly classified (%)
1	Er	0.495	73.3
2	Ti	0.313	74.2
3	Ni	0.279	78.3
4	Pd	0.234	75.6

A composite fingerprint containing the four properties Ti, Ni, Pd and Er produced a Wilks' Lambda value of 0.234, which was the closest to zero that could be obtained following stepwise inclusion of all available properties. This fingerprint correctly classified 75.6% of the samples collected to represent the individual source types. Table 5.5 shows the predicted sample group against the actual group membership for the three source groups. It can be observed that grassland sources were by far the most poorly discriminated (54% of samples classified correctly). Ten of the misclassified grassland source samples were predicted to belong to the cultivated topsoil category and four grassland samples were predicted to belong to the channel bank source group. Cultivated topsoil samples were correctly discriminated in 84% of cases. The four misclassified cultivated topsoil samples were incorrectly predicted to be grassland samples. Channel bank samples were correctly discriminated in 90% of cases. Two channel bank samples were incorrectly predicted as grassland samples and one was incorrectly predicted as cultivated topsoil. The respective percentage of correct discrimination for the samples collected to represent the cultivated topsoil and channel bank source groups was 84%, and 90% respectively. Figure 4.10 illustrates the sample distribution around the three group centroids from the first two canonical discriminant functions following stepwise MDFA. The scatter plots illustrate the relatively poor discrimination offered between grassland and cultivated land by the stepwise derived fingerprint. Grassland samples were poorly grouped around the group centroid and displayed considerable overlap with samples from cultivated sources.

Table 4.5 *The comparison of predicted sample group membership against actual group membership for grassland, cultivated and channel bank source groups, with percentage of correctly classified cases within each group following stepwise MDFA.*

			Predicted Group Membership			Total
		Source group	Grassland	Cultivated	Channel Bank	
Original Group Membership	Count	Grassland	16	10	4	30
		Cultivated	4	26	0	30
		Channel Bank	2	1	27	30
	%	Grassland	54	33	13	100.0
		Cultivated	16	84	0	100.0
		Channel Bank	7	3	90	100.0

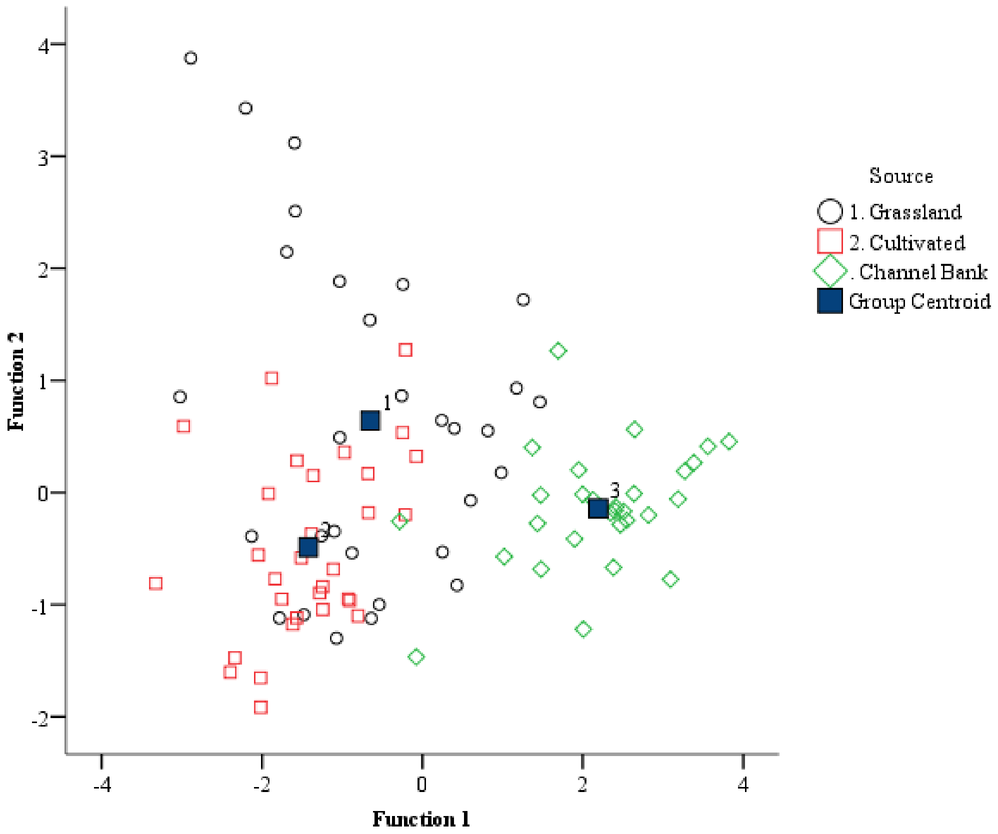

Figure 4.10 *Combined scatter plots showing sample distribution around group centroids from the two canonical discriminant functions applied to the grassland, cultivated and channel bank source groups following stepwise MDFA.*

The composite fingerprint selected using stepwise MDFA offered overall discrimination (75.6%) which could be considered sufficient to proceed to the sediment source ascription phase. However, in order to ascertain if improved discrimination could be obtained, simultaneous entry MDFA was applied to all properties which had passed the previous screening tests. The minimum tolerance level for entry was 0.01. Through the simultaneous inclusion of these properties it was possible to lower substantially the Wilks' Lambda to 0.151 (Table 4.6) and to improve discrimination to 85.6%. The optimum composite fingerprint obtained by simultaneous entry MDFA was comprised of sixteen properties (Mg, Mn, Sc, Ti, Co, Ni, Zn, Ge, Sr, Y, Pd, Sb, Ba, Eu, Dy and Er).

Table 4.6 *Wilks' Lambda Test of Functions for properties simultaneously entered into MDFA*

Test of Function(s)	Wilks' Lambda	Chi-square	Significance
1 through 2	0.151	150.2	000
2	0.645	34.8	003

Table 4.7 displays the discrimination results for the simultaneously entered sixteen property fingerprint. It was apparent that correct classification improved across all three source groups (grassland, cultivated land and channel banks) to 63%, 100%, and 93% respectively. Seven of the misclassified grassland samples were predicted to belong to the cultivated topsoil source group and four misclassified grassland samples were predicted as channel bank samples. All thirty samples from cultivated land were correctly classified. The two misclassified channel bank samples were predicted as members of the grassland topsoil group and cultivated topsoil group respectively. The difficulty of obtaining higher levels of discrimination for grassland may well reflect the influence of rotation in local farming systems. Some grassland samples may have been collected from sites which had been under arable cultivation in the recent past and may therefore still retain certain geochemical property characteristics of former land use. Alternatively, new grass leys, produced under intensive methods, may have been subjected to many similar inputs as land under arable production leading to similarities in geochemical signatures. Figure 4.11 illustrates the sample distribution around the three group centroids from the two canonical discriminant functions following simultaneous entry MDFA. The scatter plots help to illustrate the improved discrimination afforded to cultivated topsoil samples by the simultaneously entered fingerprint. Overall grouping of channel bank samples appears slightly more dispersed than that observed following stepwise MDFA, although the overlapping with samples

from the other source groups is reduced. Grassland samples remain relatively poorly grouped around the grassland group centroid and quite widely dispersed. Based on its greater discriminatory power, the sixteen property composite fingerprint was selected for use in the mixing model during the sediment source ascription phase.

Table 4.7 *Results from comparison of predicted sample group membership against actual group membership for source groups, with percentage of correctly classified cases within each group following simultaneous entry MDFA.*

			Predicted Group Membership			Total
		Source group	Grassland	Cultivated	Channel Bank	
Original Group Membership	Count	Grassland	19	7	4	30
		Cultivated	0	30	0	30
		Channel Bank	1	1	28	30
	%	Grassland	63	23	13	100.0
		Cultivated	.0	100	.0	100.0
		Channel Bank	3	3	93	100.0

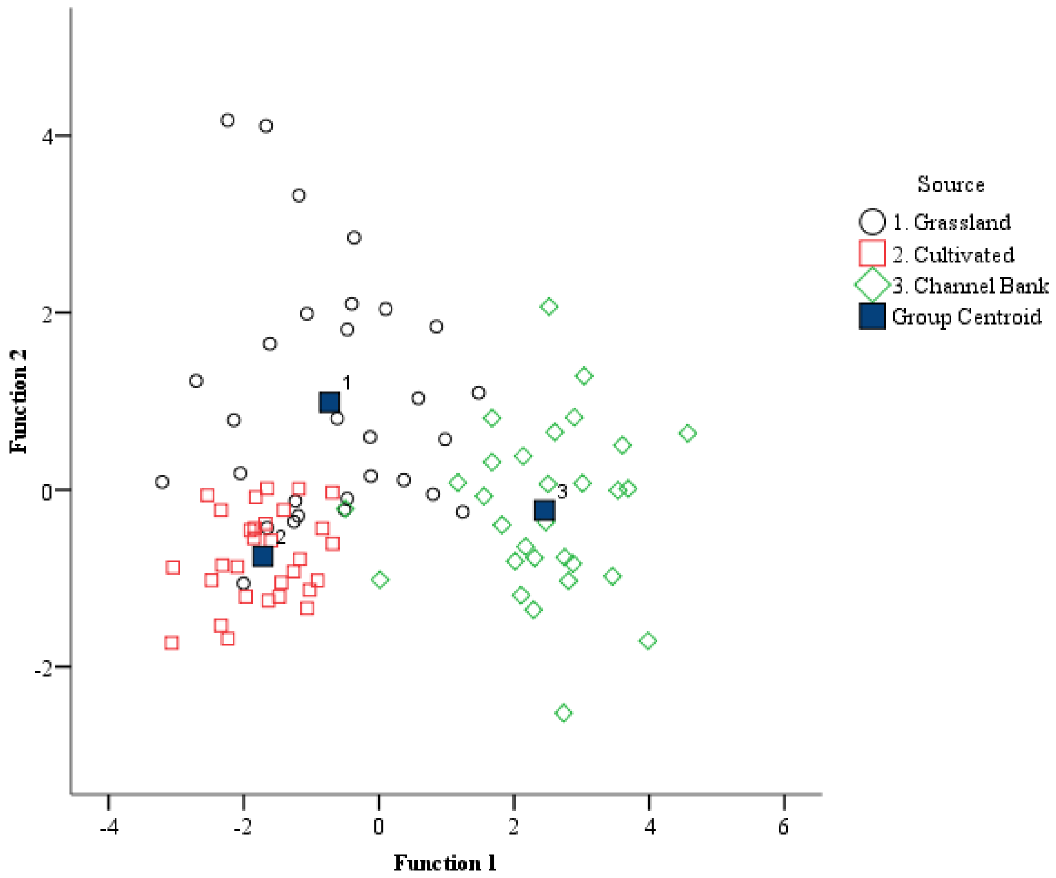

Figure 4.11 *Combined scatter plots showing sample distribution around group centroids from the two canonical discriminant functions applied to the grassland, cultivated and channel bank source groups following simultaneous entry MDFA.*

4.6 Application of the mixing model

A linear numerical mixing model, as described in Chapter 3, was utilized to provide an estimate of the relative contributions of the three potential source groups to the individual floodplain sediment core sections. The mixing model incorporated property-specific discrimination weightings derived from the entry of individual properties to MDFA (Table 4.8). A Monte-Carlo framework incorporated into the apportionment process provided explicit representation of the uncertainty associated with using relatively few samples to characterise the individual sediment source types.

Table 4.8 *Mixing model property-specific discrimination weightings.*

Property	Individual discrimination (%)	Weighting value
Mg	44.4	1.11
Mn	51.1	1.27
Sc	46.7	1.17
Ti	61.1	1.53
Co	58.9	1.47
Ni	52.2	1.30
Zn	50	1.25
Ge	51.1	1.28
Sr	54.4	1.36
Y	71.1	1.78
Pd	70	1.75
Sb	40	1
Ba	57.8	1.45
Eu	70	1.75
Dy	70	1.75
Er	73.3	1.83

4.7 Sediment source ascription and historical catchment land use changes

The output from the mixing model, applied to individual sediment sections from the floodplain core, provided percentage estimates of relative source contributions over time. The relative mean error (RME) (see Chapter 3) ranged from 10% to 20% with a mean for the combined sections of 13%, indicating a goodness-of-fit of 87%. Walling and Collins (2000) suggest that a RME of <15% indicates that the mixing model has provided an acceptable prediction of the measured fingerprint property concentrations of a given sediment sample. The source apportionment estimation and RME for individual core sections is shown in Table 4.9, with combined relative apportionment for the respective source groups over the study period illustrated in Figure 4.12. Based on the goodness-of-fit obtained, it was assumed that the relative contributions apportioned down the profile provided acceptable predictions of the fingerprint property concentrations.

Table 4.9 *Estimated sediment contributions (%) (± standard deviation) from grassland, cultivated land and channel bank sources in the Upper River Torridge catchment (1909-2008) with associated RME (%)*

		Estimated sediment contribution (%)			
Depth (cm)	Estimated date	Grassland	Cultivated	Channel Bank	RME (%)
1	2008	22 ±21	63±25	15±13	10
2	2004	31 ±21	50±26	19±14	11
3	1999	21 ±20	65±28	14±13	11
4	1995	30 ±24	48±26	22±18	11
5	1990	27 ±27	54±26	20±19	11
6	1986	35 ±31	38±24	27±25	13
7	1981	32 ±27	35±28	33±24	11
8	1977	31 ±27	42±26	27±23	11
9	1972	30 ±28	25±27	45±28	12
10	1968	32 ±26	41±21	28±21	13
11	1963	36 ±24	23±17	41±21	12
12	1959	31 ±23	24±19	45±20	12
13	1954	33 ±22	25±17	42±18	12
14	1950	29 ±20	31±18	40±17	13
15	1945	28±20	22±19	50±18	12
16	1941	33±21	25±18	42±17	14
17	1936	23±21	20±21	57±20	13
18	1932	28±18	27±14	44±15	12
19	1927	27±18	24±17	49±16	14
20	1923	23±21	17±19	61±20	13
21	1918	14±17	50±21	36±13	15
22	1914	24±17	34±19	42±16	20
23	1909	14±30	13±30	73±48	15

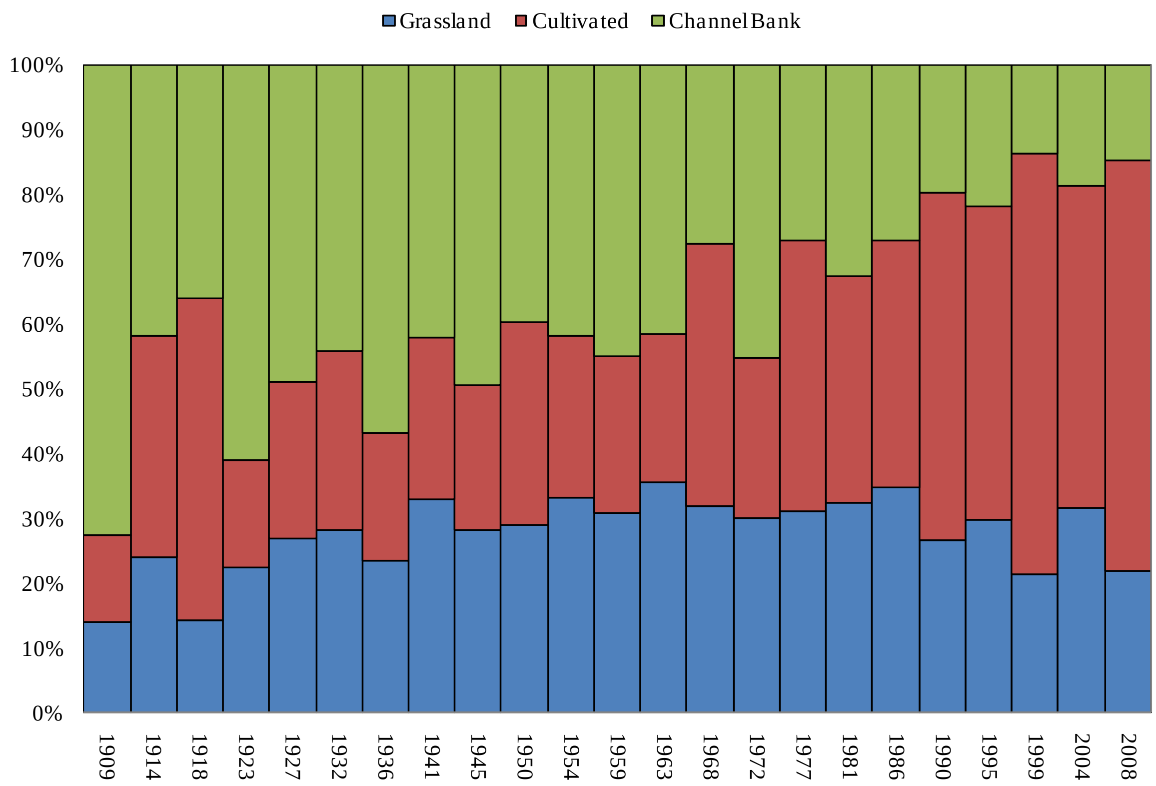

Figure 4.12 *Temporal changes in the relative contributions to floodplain sediment from grassland, cultivated land and channel bank source groups in the River Torridge catchment c.a. 1909 – 2008.*

The sediment source apportionment provided by the mixing model shows general fluctuations in relative contributions from sources over approximately the last 100 years. The greatest variation in relative source contributions occurred between cultivated land and channel bank sources. The results indicate that the largest mean contribution to overbank sediment in the Upper River Torridge catchment during the study period is from channel bank sources (38%). The high contribution from these sources partially reflects the large number of well developed, actively eroding channel banks on the main stem of the river and possibly the poaching and erosion caused throughout the catchment by livestock entering the water courses to drink. In addition, the River Torridge catchment has a relatively flashy discharge response and a high drainage density under wet conditions, with potentially significant contributions coming from the ditches and other agricultural drainage systems. The notable increase in contributions from channel bank sources in the early 1970s appears to coincide with a period of intensive drainage in the Torridge catchment in 1972-73 (Green, 1976). This drainage occurred largely on rough grazing land and unimproved grassland. One interpretation of the increase in contributions from channel bank sources at this time might suggest that the majority of sediment emanating from the newly created field drains was essentially subsurface material. In order to more fully assess the specific contributions coming from field drains a dedicated sampling strategy would be required to include field drains as a potential source (Russell *et al*., 2001; Foster *et al*., 2003). Maximum relative sediment contributions from channel bank sources of 72% were observed for the end of the first decade of the study period, whilst minimum relative contributions were observed at the end of the 1990s. The general trend over the study period indicated a relative declining sediment contribution from channel bank sources against increased contributions from cultivated topsoil sources, with the exception of the period at the beginning of the 1970s. The decrease in sediment contributions from channel bank sources between 1990 and 2004 may reflect increased land owner awareness of sediment related riparian issues and the uptake within the catchment of grant aided riparian protection. The types of environmentally related assistance available at the time included, funding for buffer strips under the Countryside Stewardship Scheme (CSS) and riparian fencing made available throughout the catchment by The West Country Rivers Trust under the EU funded CYCLEAU project (West Country Rivers Trust, 2010).

Contributions to overbank sediment derived from cultivated topsoil sources varied from a minimum contribution of 13% around 1909, to a maximum contribution of 65% in the late 1990s, with a mean contribution over the study period of 35%. Areas within the Upper River Torridge catchment under arable cultivation have changed in both size and crop type over the study period, which may have contributed to the changes in relative source contributions to overbank sediment; these changes are explicitly considered in greater detail below. Over the study period, contributions from grassland topsoil sources varied less than cultivated topsoil and channel bank sources, with a minimum contribution of 14% around 1909 and a maximum contribution of 36% occurring around the mid 1960s. The mean contribution from grassland topsoil sources to overbank sediment during the study period was 27%. The contribution to overbank sediments from grassland topsoil could be considered quite low in view of the dominance of grassland within the catchment. However, well established grassland areas are often more likely to evidence lower rates of topsoil loss due to water erosion compared to cultivated topsoil. This is due largely to the greater vegetation cover density of grassland, combined with a more dense root mass in the A horizon of the soil profile (Gysells, 2005). The general trend of increasing contributions from grassland topsoil from the beginning of the study period until the mid 1960s, may reflect increased stocking densities. Devon farmers took advantage of expanding demand for milk and improved transport links to increase herd sizes and thereby milk supply (Grigg, 1965). Overbank sediment contributions from grassland topsoil remained relatively stable from the mid 1960’s until the 1990s after which time relative contributions from grassland decreased as contributions from cultivated topsoil sources con-currently began to rise.

Overbank sediment contributions from cultivated land appear to increase considerably around the time of the First World War (1914-1918). On a national scale, the area of cultivated land increased from 3,468,000 ha in 1914 to 4,055,500 ha in 1919, as a result of the government led wartime ‘plough-up’ campaign (Sheail, 1973). The campaign led to large areas of permanent pasture land being ploughed up in an effort to increase arable production. The increase in arable cultivation was encouraged through the high prices achieved for arable crops through price protection for farmers, introduced by the War Cabinet in 1917 (Harvey and Riley, 2008; Sheail, 1976). The instigation of the plough-up campaign met with mixed results, as land that was poorly suited for arable production was often included in the effort. This land may have included some of the heavier clay soils in the Upper River Torridge catchment, where poor drainage could have led to increased erosion and runoff as impermeable soil was left exposed throughout the autumn and winter months to the high rates of Devon rainfall. The relative contribution of topsoil from cultivated sources appears to decline from the early 1920s this change coincides with the farming depression during the 1920s and 1930s which followed the Agriculture Act of 1921 (Grigg, 1965). The agricultural industry remained depressed throughout the mid to late 1930s. During those years farm incomes dropped considerably and labour costs made arable cultivation on unfavourable soils uneconomic. Similarly, throughout the 1920s and 1930s many ditches and channels were left unmanaged becoming overgrown and impeded by debris which may explain an observable general decline in channel bank sediment contributions throughout this period. The exceptions to this trend around the immediate pre and post-Second World War periods could possibly reflect renewed bank and ditch maintenance. With the outbreak of the Second World War in 1939, grassland was once again put under the plough. The area of land under tillage in Devon increased from ~12% in 1937 to ~24% by 1944 (Stamp, 1947). However, any influence of the Second World War plough-up in the catchment does not appear to have had a significant effect on observable sediment contributions from cultivated topsoil sources. This may have been due to increased selectivity of appropriate grasslands for conversion based on the experiences of the First World War. There was an observable increase in sediment contributions from grassland sources during the early Second World War period. This may be attributed to various developments in grassland management, such as the increased proportion of temporary leys, which were generally more productive than permanent grassland. The reduced area of land available for livestock increased stocking densities and would have increased the potential for both poaching and soil compaction. These changes were combined with increased connectivity between field and water courses through the clearing of ditches, the paving of roads and tracks and additional compaction of soils due to agricultural mechanisation.

In order to provide a more detailed analysis of land use change since the late 1960s, data on changes in land cover, crops and stocking densities for the Upper River Torridge catchment were extracted and collated from the Agcensus database (EDINA, 2009). Data were obtained at 2km x 2km grid resolution from the area of the catchment for years; 1969, 1972, 1976, 1979, 1981, 1988, 1993, 1995, 1997, 2000, 2003 and 2004.

Figure 4.13 shows livestock numbers for cattle and sheep in the catchment from 1969 to 2004. There was a steady increase in both cattle and sheep numbers from the late 1960s to the early 1990s from which time until 2004 livestock numbers generally declined, with numbers of sheep returning to 1960s levels and cattle numbers dropping by over 15%. The specific drop in livestock numbers in the early 2000s may be a direct reflection of the effects of foot and mouth disease, which hit many farms in Devon in 2001. There were a total of 173 foot-and-mouth cases confirmed in the county, which resulted in over 400,000 animals being slaughtered. A ‘contiguous cull' policy led to many animals from farms falling within close proximity of definite outbreaks being slaughtered as a precautionary measure (BBC, 2010b). A prime example of the devastating impact of the disease on a single farm in the Upper River Torridge catchment was the loss of 600 cattle and 1,500 sheep on Burdon Farm, Highampton (BBC, 2010b).

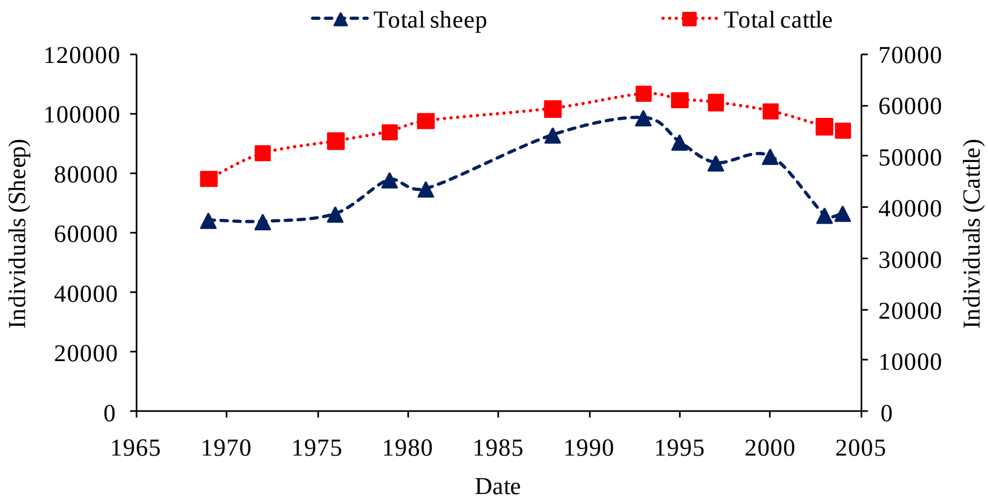

Figure 4.13 *Livestock numbers for cattle and sheep in the Upper River Torridge catchment from 1969 to 2004.*

In order to compare changes in stocking densities over the study period, individual livestock numbers were converted into livestock units as outlined in Chapter 3. Figure 4.14 shows the stocking density (LUs ha^{-1}) estimated from livestock units divided by available grassland, from 1969 to 2004. The peak in stocking density observed around 2000 and subsequent reduction thereafter serves to illustrate further the effects of foot and mouth on livestock numbers, which were perhaps also influenced by declining economic returns for dairy farmers over this period.

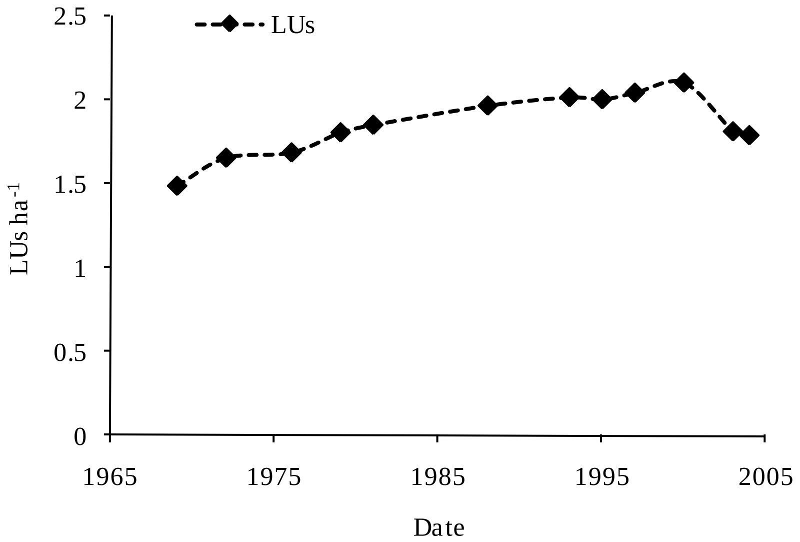

Figure 4.14 *Stocking density (LU ha^{-1}) in the River Torridge catchment 1969 – 2004.*

The general fluctuations in stocking density do not appear to have affected the relative sediment contributions from grassland sources. However, increases in the cultivation of fodder crops such as turnips, swedes and mangolds to feed the growing herd populations, could have contributed to significant concurrent increases in relative contributions from cultivated sources. This could thereby potentially have masked less significant increases in relative contributions from grassland sources.

Land cover data were compiled for late-harvested crops often associated with high erosion risk, including potatoes, sugar beet, beans, peas, turnips, swedes, mangolds, maize and linseed. The data were collated at catchment scale, between 1969 and 2004. Data were similarly combined for high erosion risk autumn-sown crops, including wheat, winter-barley and oilseed rape. Permanent grassland, temporary grassland and rough grazing data were also individually collated for comparative analysis. The combined plots are shown in Figure 4.15.

The historic dominance of permanent pasture as the major land use type in the Upper River Torridge catchment is clearly illustrated in Figure 4.14. The area under permanent grassland appears to have broadly increased in direct proportion to recorded decreases in rough grazing. This observed relationship is in accordance with land management practices for converting rough grazing into semi-improved permanent grassland through improved drainage and the application of nutrients. The area under temporary grazing has remained relatively stable throughout the study period.

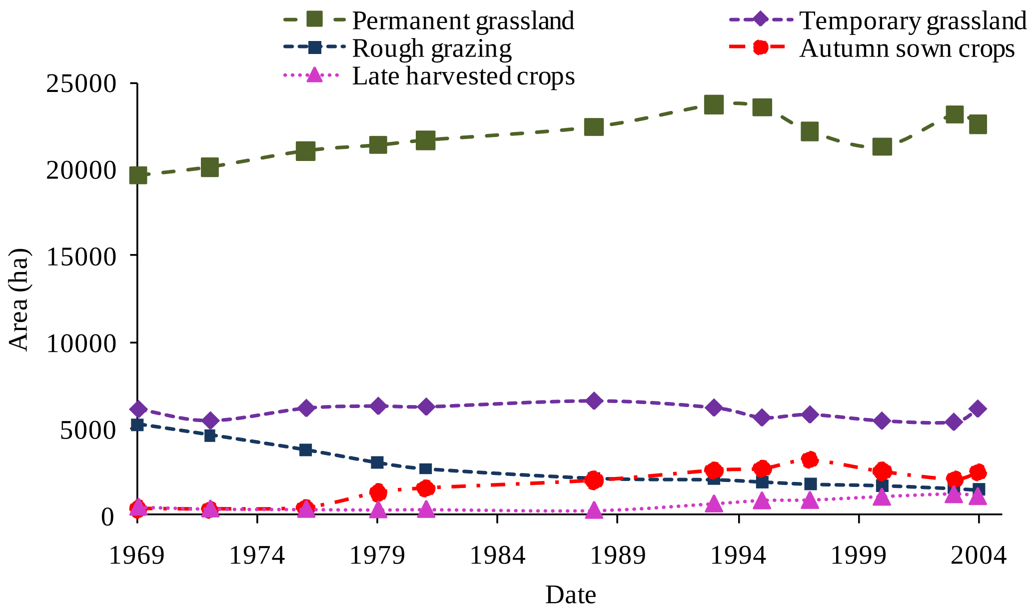

Figure 4.15 *Land cover areas for permanent grassland, temporary grassland, rough grazing, autumn sown crops and late harvested crops in the Upper River Torridge catchment 1969-2004.*

The changing land cover area under high erosion risk crop cultivation from 1969 – 2004 is shown in greater resolution in Figure 4.16.

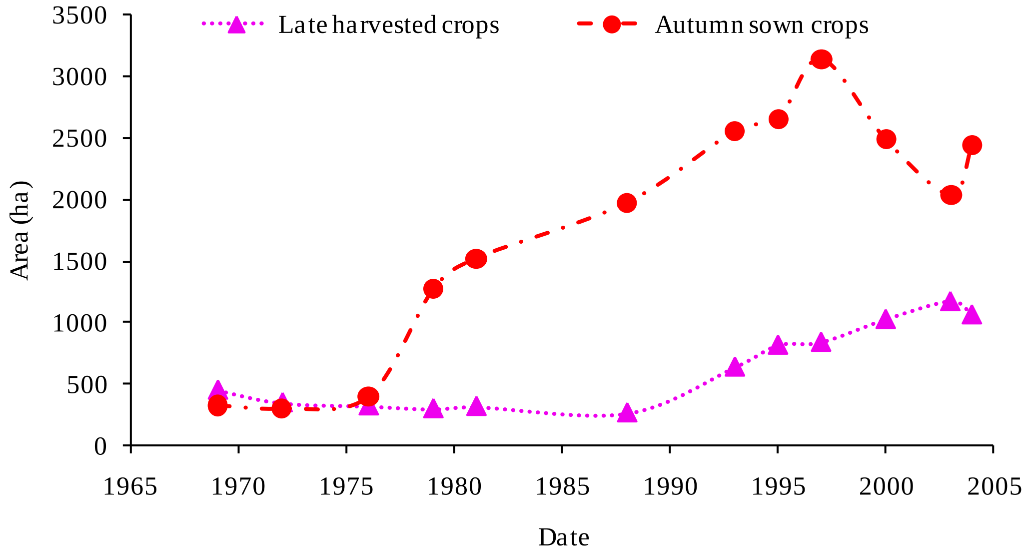

Figure 4.16 *Land cover areas for late harvested crops and autumn sown crops in the Upper River Torridge catchment 1969-2004*

From the mid 1970s until the end of the 1990s, there was a marked increase in the area under autumn sown crops. Late harvested crops also increased in land cover area from the late 1980s. Although the overall proportion of the total catchment area under these high erosion risk crops remained minimal compared to that under grassland, the period of expansion coincides with marked increases in relative sediment contributions from cultivated sources. Given the pollution problems associated specifically with sediment from cultivated sources, any increase in contribution, albeit relative to other sources, is likely to have had negative impacts on both water quality and riverine habitats.

4.8 Conclusion

The sediment source apportionment results from the application of the fingerprinting technique to floodplain overbank sediment of the Upper River Torridge catchment were reflective of general changes recorded in the historic land use data. The specific land use changes of initial interest in this case study (i.e. field drainage and stocking densities) have varying degrees of influence on sediment sources. Increased field drainage, which occurred particularly during the early 1970s, appeared to correspond with an observable increase in relative contributions from channel bank and sub-soil sources. However, this increase occurred over a limited period and additional targeted source sampling would be required to attribute robustly the proportion of sediment contributed strictly to field drain sources. Changes in stocking densities within the catchment since the 1960s do not appear to have had any observable effect on relative sediment contributions from grassland or channel bank sources. This may be due to a number of factors. The increased relative contributions from cultivated sources could have been sufficiently high that they reduced the significance of any increases from other sources. Alternatively, agri-environment schemes which encouraged improved livestock management and mitigation of impacts to water courses may have had a positive influence through the increased use of riparian fencing and buffer strips. The lack of catchment-scale sediment source changes in response to fluctuations in livestock numbers could also be indicative that the stocking densities have been within the carrying capacity of the land concerned, at least in terms of sediment-related environmental sustainability. Increased cultivation of high erosion risk crops has coincided with increased relative sediment contributions from cultivated sources. Although the expansion of autumn sown and late harvested crops has been on a relatively small area of the total catchment, the climate of the region is highly likely to compound the vulnerability to erosion caused to exposed soils. This is of particular concern given the increasing economic pressures for further expansion of such arable production and the higher intensity rainfall rates predicted in coming years due to climate change.

Future catchment management priorities will be required to anticipate these potential problems and appropriate mitigation measures will need to be established. Mitigation measures suitable for the Upper River Torridge catchment might include under sowing late harvested crops with a winter cover crop that can be used as livestock forage in the spring. In addition, farmers might be encouraged to restrict cultivation of high erosion risk crops to land with appropriate topography, combined with increased use of mitigating buffers to reduce connectivity between fields and water courses. However, sustainable soil management in conjunction with pressing water quality, river habitat and flood risk concerns may require a more long term view of the appropriateness of high erosion risk crop cultivation in areas subject to high rainfall rates.

The possibility of higher resolution interpretation of the case study results was somewhat restricted by the broad timescales covered by both the individual floodplain sediment core sections and the available land use data. Notwithstanding this observation, the technique was able to relate recent historical land use change to relative changes in the sources of floodplain overbank sedimentation with reasonable success and chronological accuracy.

CHAPTER 5 - THE RIVER AXE CATCHMENT:

RESULTS AND INTERPRETATION

5.1 Introduction

This chapter presents and interprets the results from the application of the sediment source fingerprinting technique to floodplain sediment cores from the River Axe catchment, South West England, UK, with the aim of relating relative changes in the source of floodplain overbank sediment to historical land use change in the recent past (ca. 50-100 years). The methodologies applied to this case study follow those detailed in Chapters 2 and 3.

Diffuse pollution problems associated with excessive fine sediment ingress from surrounding agricultural land have been cited as a major cause for concern in the River Axe catchment, leading to its listing as a Priority Catchment under the ECSFDI (Defra, 2009). In a report published by Natural England in August 2010, three riverine SSSIs within the catchment were considered to be in an ‘unfavourable recovering’ state, due to siltation problems. In the same report, land management conditions were described as ‘unfavourable’ due to widespread stock access causing bank erosion which could be exacerbated by high stocking rates (Natural England, 2010). The excessive sediment inputs have affected downstream riverine ecology and threatened internationally designated sites of high environmental conservation interest.

5.2 Study catchment description

The River Axe catchment is situated in South West England (Figure 5.1). The river rises in the Somerset hills near the village of Cheddington and flows west and south through the counties of Somerset, Dorset and Devon, before entering Lyme Bay at the coastal town of Seaton. The wider catchment has a total drainage area of approximately 420 km^2. Main tributaries in the upper catchment include the River Synderford and the Temple Brook. To the West and North West, the catchment is dominated by the Blackdown Hills and the tributaries, such as the River Yarty, the Umborne and Offwell Brooks and the River Coley. The sub-catchment identified for the purposes of this study incorporates the Upper River Axe catchment from its source near the village of

Cheddington, including all tributaries down to an identified catchment outlet at Chard Junction and encompasses a drainage basin area of approximately 85km^2 (Figure 5.1).

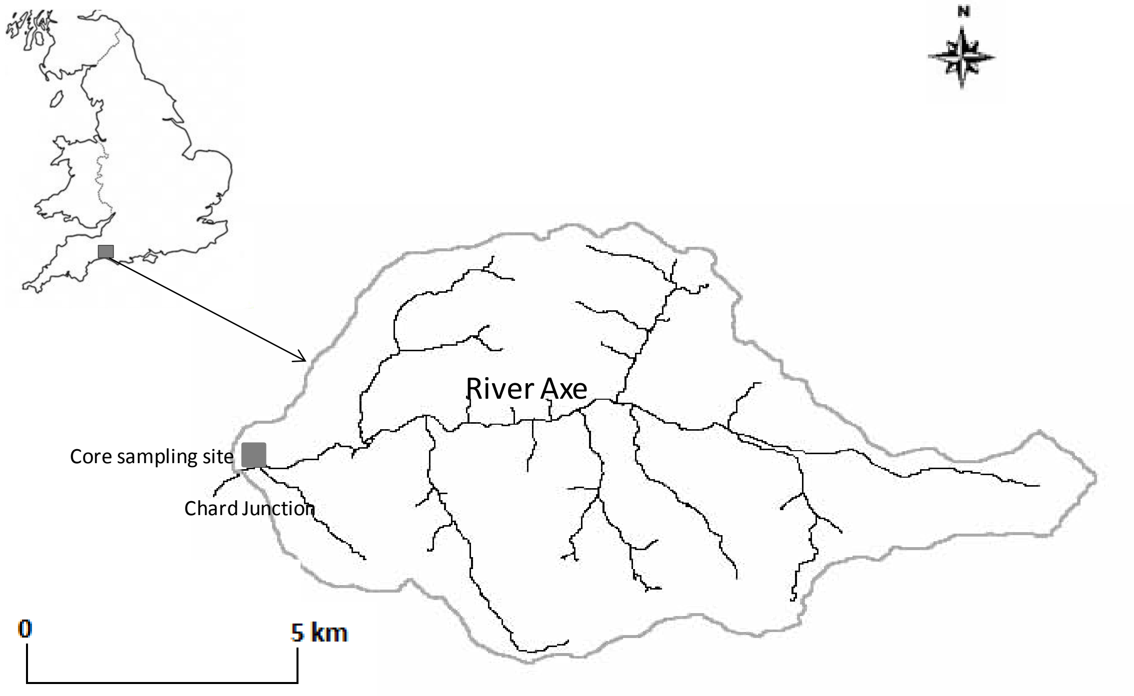

Figure 5.1 *The location and study area of the Upper River Axe catchment, Devon, UK.*

The geology of the River Axe catchment consists of Mesozoic (Triassic, Jurassic and Cretaceous) strata overlain by Tertiary (Eocene) deposits (Environment Agency, 2005). Relief in the catchment is predominantly moderate and the channel network drains from Greensand and Chalk headwaters. To the west, the River Axe catchment is underlain by Triassic Mercia mudstone. The upper catchment is underlain by the Blue Lias formation (Jurassic). These formations are overlain on the top of the Blackdown Hills in the east by chalk and elsewhere in the catchment by Upper Greensand (Cretaceous). Contiguous with the erosion of these various formations, in its lower reaches, the River Axe meanders through a well developed floodplain of muddy, sandy alluvium (Cycleau, 2004; EA, 2005; JNCC, 2006).

The soils of the upper catchment are characterised by slowly permeable seasonally-wet slightly acid, base rich soils of moderate fertility (NSRI, 2010). In the mid and lower catchment, the soils are dominated by heavier slightly acid loamy and clayey soils with impeded drainage, but with some areas of freely draining slightly acid loamy soils. The soils of the catchment upland plateaus are acid loams with a wet peaty surface (NSRI, 2010). The low permeability of the catchment produces a hydrological regime which is characterised by a fast response to rainfall, with rapid runoff (Cycleau, 2006).

The River Axe catchment contains five areas currently designated as Sites of Special Scientific Interest (SSSIs) due of the high levels of biodiversity present, including emergent macrophytes, insects, fishes and birds (Natural England, 2010). The river is also recognised as a Special Area of Conservation (SAC) due to its importance as a river supporting distinctive floating vegetation 'Ranunuculus communities' and three specific fish species of international importance; the Bullhead, Brook Lamprey and Sea Lamprey (Cycleau, 2006). The Blackdown Hills are designated as an Environmentally Sensitive Area (ESA). The coastline at the outflow of the River Axe, adjacent to the town of Seaton, is part of the UNESCO, Jurassic Coast World Heritage Site.

The land use changes of particular interest in this case study are the reported increase of fodder maize cultivation within the catchment over recent years, which has been associated with deleterious sediment associated impacts to fish spawning gravels and benthic habitats (CYLEAU, 2006; Defra, 2009a). In addition, increasingly intensive livestock and dairy production practises have also been a cause for concern, as stocking densities have increased over the last thirty years, particularly in the upper catchment (Figure 5.2) (Defra, 2009a).

Figure 5.2 *Sediment associated pressures and risks in the Upper River Axe catchment. Left to right, over-wintering of livestock on saturated riparian fields; excessive poaching around an unfenced spring-fed stream channel.*

5.3 Floodplain site selection

Potential floodplain sampling sites for the collection of overbank sediment cores were identified through the use of topographic maps, satellite imagery, ground observation and local anecdotal evidence. This process pinpointed sites which were regularly inundated by overbank flooding, with associated potential to receive and store sediment. Two suitable sites which met these criteria were identified immediately upstream of Broad Bridge, at Chard Junction, on land within the Forde Abby Estate (see Figure 5.3). In order to ensure that the historical sedimentation record was likely to be undisturbed at the sampling sites, it was necessary to establish that the locations had not been cultivated in the recent past. This was substantiated through discussion with the Forde Abby, Estate Manager, who had personal knowledge of the site for over 50 years. The anecdotal evidence was combined with a basic ecological appraisal of the sward composition and plant biodiversity at the sites. Plant species which are associated with less intensive agricultural land use such as Soft Rush (*Juncus effusus*) and Meadowsweet (*Filipendula ulmaria*) were observed. These species are also often associated with wet or damp uncultivated soils, such as those found on regularly inundated floodplains.

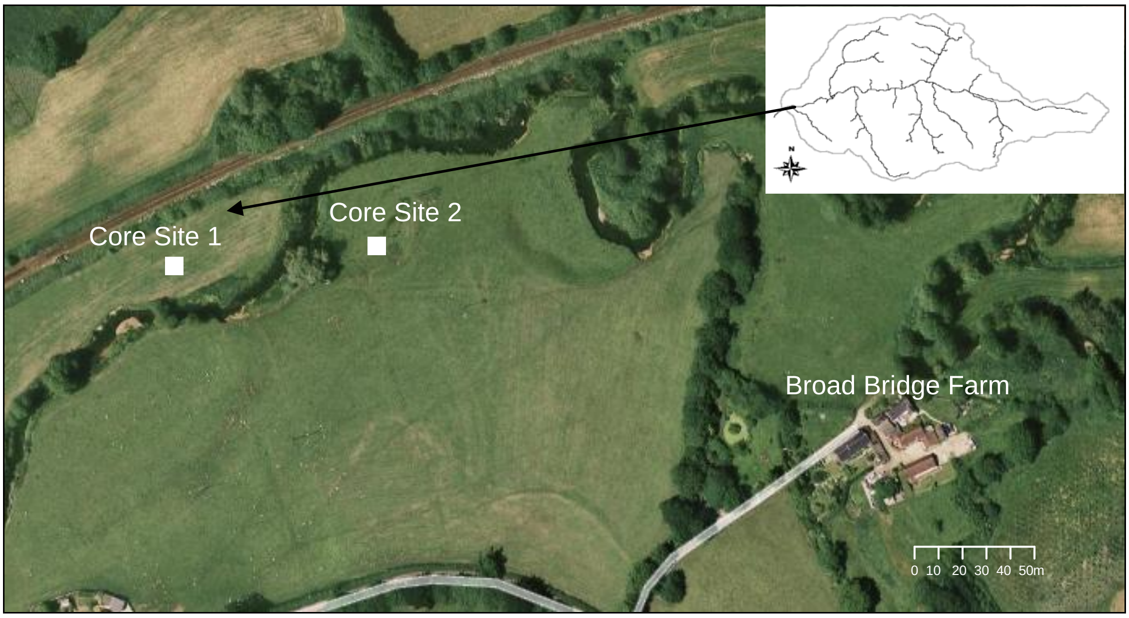

Figure 5.3 *Location of the Upper River Axe catchment floodplain core sampling sites at Broad Bridge, Chard Junction, Somerset, UK (Google Earth, 2009)*

The two key floodplain coring sites were identified within relatively close proximity to each other. Areas on the floodplain with a slight depression were chosen, as these were deemed more likely to have retained overbank flood waters and thereby to represent depositional sinks. The potential for the sites to represent sediment sinks was confirmed by the observation of recent flood trash lines slightly upslope of the coring sites and the presence of fine sediment coating the leaves of ground cover across the sample site areas. Cores were collected from the identified floodplain sites and the core from site 1 was sectioned into 1cm slices and prepared for laboratory analysis (see Chapter 2).

The Upper River Axe catchment was sampled early in this PhD study. At the time of floodplain coring, the use of control reference cores to provide local ^{137}Cs fallout inventories and bulk floodplain sediment cores to aid in estimating sites with the highest sedimentation rates, had not been incorporated into the sampling methodology. However, a previous study conducted by Walling and He (1992) reported a local fallout inventory of 2700 Bq m^{-2} estimated from soil samples collected from undisturbed non-eroding locations within the River Axe catchment. After decay correction to 2007, to correspond with the year of the floodplain core collection as part of this project, an inventory of 1900 Bq m^{-2} was estimated. This inventory represents an acceptable approximate contemporary control reference for atmospheric fallout ^{137}Cs within the catchment. A total ^{137}Cs inventory of 3380 Bq m^{-2} was obtained from the Broad Bridge floodplain core and was compared to the local fallout inventory presented in Table 5.1. The percentage exceedance of the local reference inventory by the floodplain core inventory was 178% and thereby established that the core sample site was likely to represent a depositional sink.

Table 5.1 *^{137}Cs inventories for the Upper River Axe floodplain sediment core and local fallout control reference.*

	^{137}Cs inventory (Bq m^{-2})
Floodplain core Chard Junction	3380
Local fallout control reference*	1900

* Estimated from soil samples collected from undisturbed non-eroding local sites (From: Walling and He, 1992)

5.4 ^{137}Cs radioisotope geochronology

^{137}Cs ($T_{1/2}$=30.17 yr) assay of individual 1cm core sections was undertaken by γ-ray spectrometry, in order to establish the chronology of the sediment core profile (see Chapter 2). The depth distribution profile of ^{137}Cs activity concentration within the

Upper River Axe floodplain core is shown in Figure 5.4. The depth distribution of ^{137}Cs within the core was analysed and the horizon containing peak activity was identified at 11cm. This horizon was assumed to correspond to the peak in ^{137}Cs fallout from atomic weapons testing which occurred in 1963. Time-averaged sedimentation rates for the intervening 45 years were then calculated at 0.24 cm year^{-1} and extrapolated over the depth of the core to provide an approximate chronology. The appearance of ^{137}Cs at depths which the chronology would suggest are before the release of ^{137}Cs into the atmosphere in the early 1950's (i.e. >16cm), may be due to bioturbation or leaching causing the downward migration of ^{137}Cs (Owens and Walling, 1996; Walling and He, 1997). The appearance of the profile suggested that deposition had been generally continuous over time and that the core site was largely undisturbed.

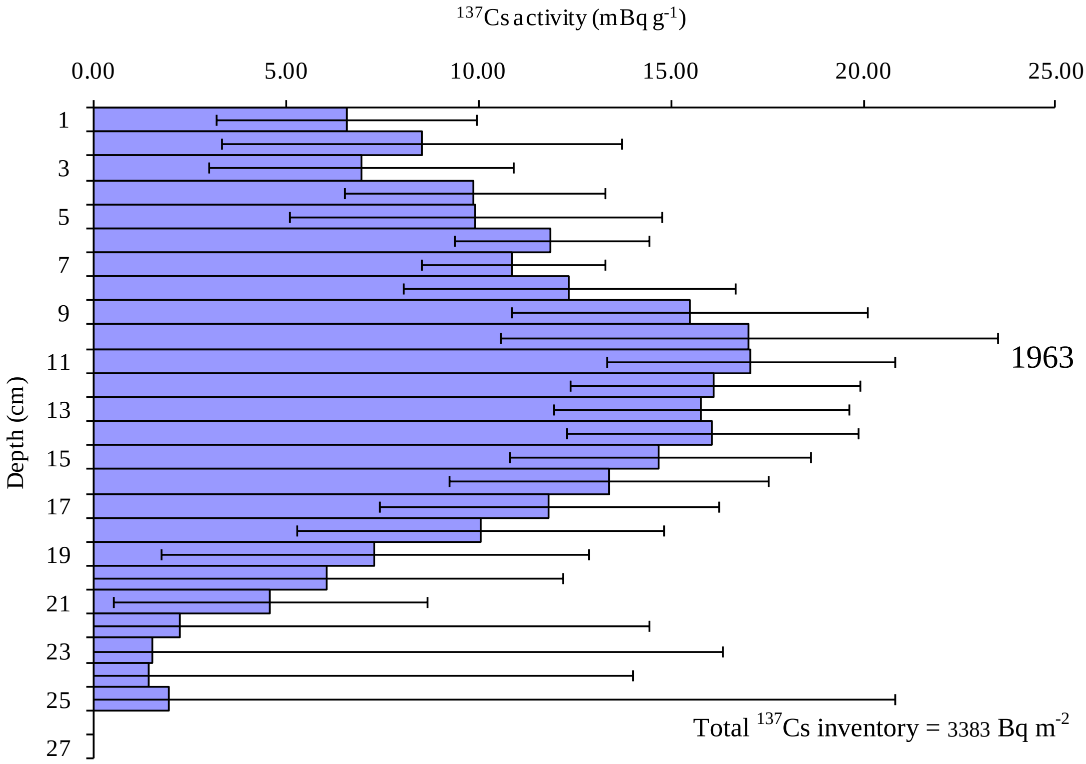

Figure 5.4 *The depth distribution profile of ^{137}Cs with associated total inventory for the Broad Bridge, Upper River Axe floodplain core*

5.5 The fingerprinting technique

5.5.1 Source samples

Surface scrapes representing material with the potential to erode (<2cm) were collected from 3 potential sediment source groups namely, grassland topsoil, cultivated topsoil and also eroding material from channel banks, which included subsurface material from field ditches and incising ephemeral channels. The source samples were collected from 90 sites throughout the River Axe catchment, providing 30 samples for each potential source group. The samples were prepared and analysed, as described in detail in Chapter 2. Analysis provided information on particle size distribution, SSA and concentration values for a potential suite of 48 geochemical properties from which to identify an appropriate composite fingerprint.

5.5.2 Particle size effects

In order to assess the importance of geochemical property concentration dependence on particle size, the available suite of 48 properties was tested for correlation between sample SSA and concentration within the three source groups using Spearman's rho (see Chapter 3). A summary of the results for correlation between sample SSA and property concentration is shown in Table 5.2.

Following statistical correlation analysis of a total of 4,320 geochemical property concentration values with SSA estimates for 90 individual samples within the three potential source groups, only 27% showed correlation with SSA at $p = 0.05$. Within the grassland, cultivated land and channel bank source groups, correlation was observed in 18%, 33% and 31% of cases, respectively. Only six properties (Cd, ^{206}Pb, ^{207}Pb, ^{208}Pb, Bi and U) produced significant correlation across all three source groups. More detailed investigation into the complex physico-chemical inter-dependencies between geochemical properties and the influence of particle size was considered outside of the remit and resources of this study. However, in view of the apparent lack of identifiable significant correlation between geochemical concentration values and SSA, it was considered that the application of correction factors to account for grain size dependencies would not be appropriate in this instance. It was therefore assumed that through disaggregating and sieving source and floodplain samples to <63μm during processing, sufficient account had already been taken of any nominal property concentration grain size dependencies and thereby an acceptable comparison of concentration values could be undertaken without the requirement of additional correction (see Chapter 3).

Table 5.2 *Spearman's rho correlation coefficients and significance for geochemical property concentrations versus SSA for the grassland topsoil, cultivated topsoil and eroding channel bank sediment source groups of the Upper River Axe catchment.*

	Grassland		Cultivated land		Channel banks	
Property	Coefficient	Significance	Coefficient	Significance	Coefficient	Significance
Mg	-0.138	0.234	0.058	0.381	-0.361(*)	0.023
Al	0.065	0.367	0.350(*)	0.029	0.061	0.373
K	0.245	0.096	0.433(*)	0.008	0.145	0.218
Mn	0.129	0.248	0.399(*)	0.014	0.047	0.401
Fe	0.162	0.196	0.16	0.2	0.161	0.194
Li	-0.231	0.11	0.023	0.452	-0.483(*)	0.003
Na	0.400(*)	0.014	0.181	0.169	0.360(*)	0.023
Sc	0.219	0.123	0.126	0.254	-0.011	0.476
Ti	0.262	0.081	0.313(*)	0.046	-0.005	0.488
V	-0.091	0.317	0.19	0.157	0.013	0.472
Cr	0.069	0.358	0.256	0.086	-0.137	0.231
Co	0.15	0.215	0.413(*)	0.012	-0.025	0.446
Ni	0.045	0.408	0.238	0.103	0.063	0.369
Cu	0.281	0.066	0.193	0.153	0.174	0.175
Zn	0.269	0.075	0.330(*)	0.038	0.016	0.466
Ga	0.099	0.301	0.229	0.112	0.095	0.305
Ge	0.197	0.149	0.472(*)	0.004	0.143	0.222
As	0.114	0.274	0.196	0.15	0.554(*)	0.001
Rb	0.046	0.404	0.398(*)	0.015	0.068	0.359
Sr	0.297	0.056	0.278	0.068	0.472(*)	0.004
Y	0.092	0.314	0.329(*)	0.038	0.16	0.195
Zr	0.406(*)	0.013	0.206	0.138	0.331(*)	0.034
Mo	-0.249	0.092	0.122	0.261	0.29	0.057
Pd	0.036	0.426	0.204	0.139	0.09	0.315
Cd	0.375(*)	0.02	0.396(*)	0.015	0.488(*)	0.003
In	0.224	0.118	0.146	0.22	0.489(*)	0.003
Sn	0.245	0.096	-0.063	0.371	0.609(*)	0
Sb	0.061	0.375	0.06	0.377	0.088	0.319
Cs	-0.096	0.307	0.016	0.467	-0.039	0.417
Ba	-0.026	0.446	0.185	0.164	0.263	0.076
La	0.12	0.263	0.18	0.17	0.001	0.499
Ce	0.026	0.447	0.171	0.183	-0.005	0.488
Pr	0.029	0.439	0.152	0.211	0.055	0.385
Nd	0.015	0.468	0.167	0.189	0.058	0.378
Sm	-0.007	0.486	0.171	0.183	0.105	0.287
Eu	0.05	0.397	0.206	0.137	0.095	0.305
Gd	0.026	0.445	0.198	0.147	0.041	0.413
Tb	0.068	0.36	0.257	0.085	0.095	0.306
Dy	0.048	0.401	0.288	0.062	0.047	0.401
Ho	0.063	0.371	0.265	0.078	0.049	0.396
Er	0.061	0.374	0.291	0.059	0.074	0.346
Yb	0.018	0.462	0.293	0.058	0.098	0.301
Hf	0.443(*)	0.007	0.236	0.105	0.334(*)	0.033
Tl	0.267	0.077	0.452(*)	0.006	0.047	0.402
^{206}Pb	0.346(*)	0.031	0.482(*)	0.003	0.341(*)	0.03
^{207}Pb	0.344(*)	0.031	0.497(*)	0.003	0.338(*)	0.032
^{208}Pb	0.355(*)	0.027	0.498(*)	0.003	0.350(*)	0.027
Bi	0.409(*)	0.012	0.331(*)	0.037	0.434(*)	0.007
U	0.439(*)	0.008	0.394(*)	0.016	0.484(*)	0.003

* Correlation is significant at p = 0.05

5.5.3 Particle size distribution

Figure 5.5 illustrates comparisons between the mean particle size distribution of the <63µm fraction of sediment from the Upper River Axe floodplain core and the three potential source groups. Although it was apparent that the floodplain samples were generally enriched in fines in comparison to those from each of the potential sediment source groups, this enrichment was limited to the <8µm fraction. The grassland source group particle size distribution was particularly close to that of the floodplain sediment samples, although it was comprised of a lesser volume of particles <4 µm.

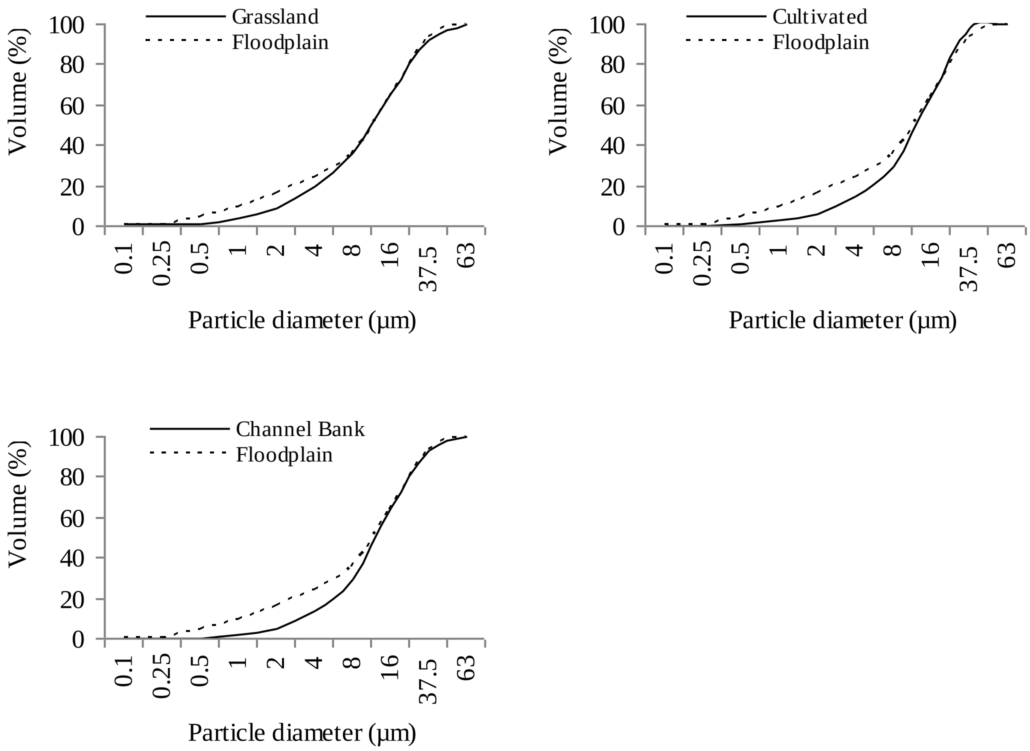

Figure 5.5 *A comparison of the mean cumulative particle size distribution (µm) of the <63µm fraction of sediment from the Upper River Axe floodplain core with corresponding information for the grassland, cultivated land and channel bank source groups*

Figure 5.6 shows the inter-sample group variability of median and mean SSA of the <63µm fraction of sediment from the floodplain core sections and the sample material from three potential source groups. The variation between mean and median SSA estimates of the individual source groups indicates that the values are not Normally distributed. Conversely, the SSA values of the floodplain sediment appear to be more normally distributed. The median and mean SSA estimates for the 3 source groups are all substantially lower than for those of the floodplain sediment sections. This is likely to be due to selective mobilisation of the finer fractions during water erosion and fluvial sorting processes during transport and floodplain deposition (Stone and Walling 1996; Walling *et al*., 1998; Walling and Amos, 1999).

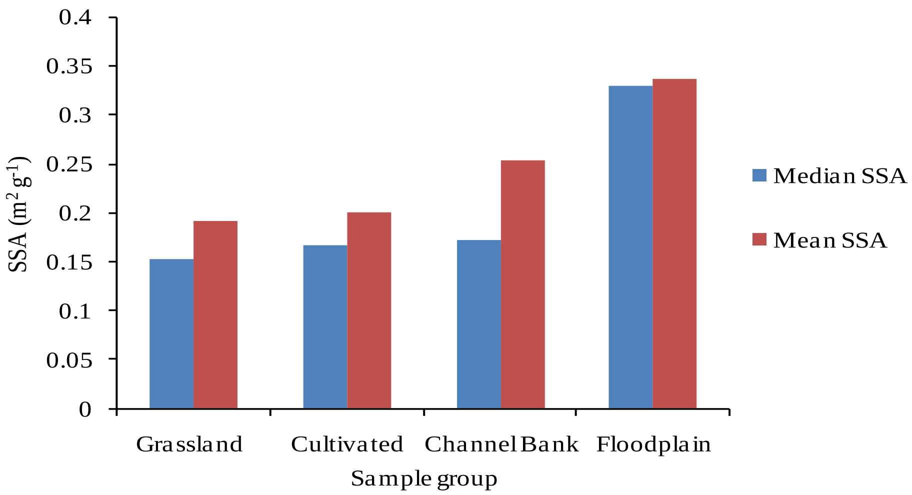

Figure 5.6 *Inter-sample group variability of mean and median SSA of the <63µm fraction of sediment from the Upper River Axe floodplain core and samples collected to represent the grassland, cultivated land and channel bank source groups*

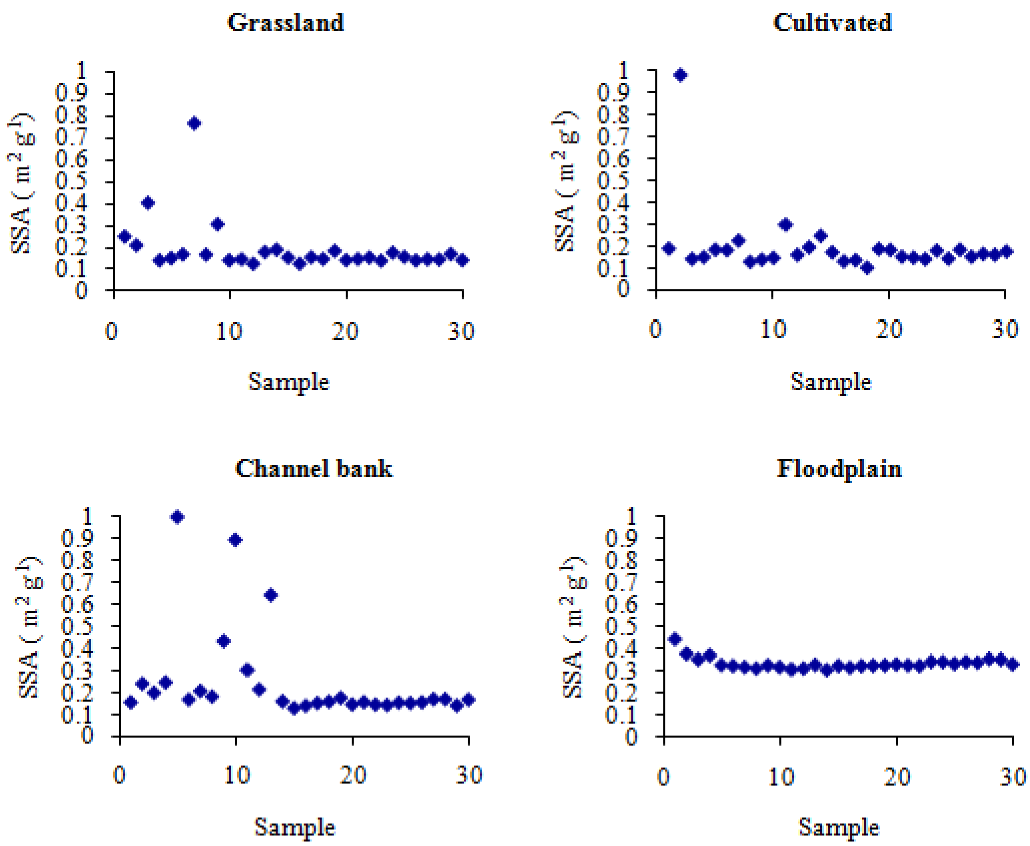

Figure 5.7 *Intra-group variability of SSA of the <63µm fraction of sediment from the River Axe floodplain core and samples collected to represent the grassland, cultivated land and channel bank source groups*

Figure 5.7 illustrates the intra-group variability of SSA of the <63µm fraction of the grassland, cultivated land and channel bank source groups and from the floodplain core sections, respectively. These plots show the effect which a relatively small number of potential outliers can have on SSA homogeneity between samples, as illustrated by the increased variance between mean and median SSA values indicated in Figure 5.4.

5.5.4 The fingerprint property concentration range test

The next stage in identifying properties suitable for inclusion in the composite fingerprint was to subject the data to a property concentration range test. Properties passing the test had ranges of concentration values in the floodplain sediment core sections which fell within the corresponding ranges of concentration values in the potential source material samples (see Chapter 3). Table 5.3 displays the property range test results for the Upper River Axe catchment. Of the 20 properties which failed to meet the range test requirement, 4 properties (Al, K, Fe and Rb) had concentration ranges within the core which were below the source range minimum concentration value, and 4 properties (Zr, Mo, Cd and Sb) had concentration ranges which overlapped the source range maximum value. A further 12 properties (Na, Sc, Ti, V Cr, Co, Ni, Cu, Tl, ^{206}Pb, ^{207}Pb and ^{208}Pb) had concentration ranges within the core which overlapped the source range minimum concentration value. Failing properties might possibly exhibit particularly labile behaviour and may be subject to transformation during mobilisation, suspension and transportation or following post-depositional pedogenic processes (De Vos *et al*., 2006; Gordev *et al*., 2004). However, it was slightly surprising to observe that the Al core range fell below the source range minimum as Al is generally considered to be a 'conservative' element and as such it has been used in previous studies for trace element normalisation purposes (Piper, 1973; Bruland, *et al*., 1974; Horowitz, 1991). Similarly Ti, which is also considered to be conservative and has been used in previous studies for normalisation purposes (Forstner and Wittman, 1981; Horowitz and Elrick, 1988; Horowitz, 1991), had property concentration core ranges overlapping the source range minimum. The 28 properties which met the range test were forwarded for further analysis.

Table 5.3 *The property range test results for the Upper River Axe catchment*

Core range within source range	**Core range overlaps source range min**	**Core range overlaps source range max**	**Core range below source range min**
Mg	Na	Zr	Al
Mn	Sc	Mo	K
Li	Ti	Cd	Fe
Zn	V	Sb	Rb
Ga	Cr		
Ge	Co		
As	Ni		
Sr	Cu		
Y	Tl		
Pd	^{206}Pb		
Sn	^{207}Pb		
Cs	^{208}Pb		
Ba			
La			
Ce			
Pr			
Nd			
Sm			
Eu			
Gd			
Tb			
Dy			
Ho			
Er			
Yb			
Hf			
Bi			
U			

Core range = Min to Max downcore property concentration values
Source range = Min Mean – Std Dev to Max Mean + Std Dev of mean source group property values

5.5.5 Source discrimination: the Kruskal-Wallis H-test

The next stage in the establishment of the optimum combination of tracer properties with which to form the composite fingerprint was to test which properties displayed significant differences between source types. These were initially established using the non-parametric Kruskal-Wallis *H*-test, applied to the source sample property value data (Collins *et al*., 1997a). A statistically significant output is indicative of source inter-group contrasts and greater *H*- values were produced as the significance of inter-group contrasts increased.

Table 5.4 presents the resultant *H*-values and asymptotic significance from the Kruskal-Wallis *H*-test applied to the property concentration values from the three potential source groups of the Upper River Axe catchment. The critical value of 5.99 for 2 *df* of the Chi-Square distribution was used at p = 0.05. Five properties (Mn, Zn, As, Ba and

Bi) produced *H*-values below the critical value and were removed from further consideration as viable fingerprint properties.

Table 5.4 *H-values and asymptotic significance from the Kruskal-Wallis H-test for the Upper River Axe catchment*

Property	*H*-value	Asymptotic significance
Mg	10.51	0.01
Mn	2.11	0.35*
Li	11.32	0.00
Zn	4.49	0.11*
Ga	5.35	0.07
Ge	9.98	0.01
As	2.75	0.25*
Sr	16.70	0.00
Y	28.26	0.00
Pd	30.72	0.00
Sn	0.37	0.83*
Cs	19.97	0.00
Ba	1.13	0.57*
La	40.39	0.00
Ce	47.69	0.00
Pr	44.90	0.00
Nd	44.42	0.00
Sm	44.24	0.00
Eu	38.83	0.00
Gd	44.40	0.00
Tb	39.77	0.00
Dy	36.45	0.00
Ho	35.01	0.00
Er	34.21	0.00
Yb	33.61	0.00
Hf	32.35	0.00
Bi	5.83	0.05*
U	7.10	0.03

Critical *H*-value = 5.99
* Not significant at p = 0.05

5.5.6 Source discrimination: Multivariate Discriminant Function Analysis

Multivariate Discriminant Function Analysis (MDFA), based on the minimization of Wilks' Lambda, was then conducted on the 19 properties which had passed the previous selection tests (Collins *et al*., 1997a). The initial MDFA was performed using a stepwise introduction of potential fingerprint properties to the analysis. At each step, the property which minimised the overall Wilks' Lambda was entered. Maximum significance of F to enter a property was 0.05 and minimum significance of F to remove a property was 0.10. The stepwise MDFA identified an optimum composite fingerprint comprising four properties (Ge, Cs, Ce and Hf), shown in Table 5.5. The composite fingerprint classified

74.7% of the original grouped cases correctly, with a Wilks' Lambda of 0.355. The inclusion of Ce during the second step reduced the percentage of correctly classified cases and the inclusion of Nd during the third step failed to improve further the number of cases correctly classified. However, inclusion of these properties concurrently reduced the Wilk's Lambda from 0.577 to 0.396. This serves to illustrate the importance of checking both the percentage of correctly classified cases as well as the Wilks' Lambda output results during the stepwise analyses to ensure that the ratio of error variance to total variance is minimized by the composite fingerprint selected.

Table 5.5 *Results from the stepwise MDFA for identifying the optimum composite fingerprint for discriminating grassland, cultivated land and channel bank source groups based on the minimisation of Wilks' Lambda*

Step	Property	Wilks' Lambda	Cumulative original grouped cases correctly classified (%)
1	Ge	0.577	64.8
2	Cs	0.461	63.7
3	Ce	0.396	63.7
4	Hf	0.355	74.7

The fingerprint produced by stepwise MDFA provided good overall discrimination for grassland with 80% of samples correctly classified, see Table 5.6. However, discrimination of cultivated sources was particularly poor, with only 53.33% of samples correctly classified. Of those cultivated samples incorrectly classified, 40% were predicted as belonging to the grassland source group. This might reflect the influence of the rotational cropping system in the catchment and the recent plough up of some grassland for the cultivation of maize (EDINA 2009; Defra, 2009). Fields under maize cultivation represented 48% of the cultivated source sample sites.

Table 5.6 *The comparison of predicted sample group membership against actual group membership for grassland, cultivated and channel bank source groups, with percentage of correctly classified cases within each group following stepwise MDFA.*

<table>
<tr><td colspan="3" rowspan="2">Source Group</td><td colspan="3">Predicted Group Membership</td><td rowspan="2">Total</td></tr>
<tr><td>Grassland</td><td>Cultivated</td><td>Channel Banks</td></tr>
<tr><td rowspan="6">Original Group Membership</td><td rowspan="3">Count</td><td>Grassland</td><td>24</td><td>4</td><td>2</td><td>30</td></tr>
<tr><td>Cultivated</td><td>12</td><td>16</td><td>2</td><td>30</td></tr>
<tr><td>Channel Banks</td><td>2</td><td>1</td><td>28</td><td>31</td></tr>
<tr><td rowspan="3">%</td><td>Grassland</td><td>80.00</td><td>13.33</td><td>6.67</td><td>100.00</td></tr>
<tr><td>Cultivated</td><td>40.00</td><td>53.33</td><td>6.67</td><td>100.00</td></tr>
<tr><td>Channel Banks</td><td>6.45</td><td>3.23</td><td>90.32</td><td>100.00</td></tr>
</table>

Figure 5.8 illustrates the sample distribution around the three group centroids from the first two canonical discriminant functions following stepwise MDFA. The considerable scatter highlights the particularly poor discrimination of cultivated sources, which overlap substantially with grassland sources.

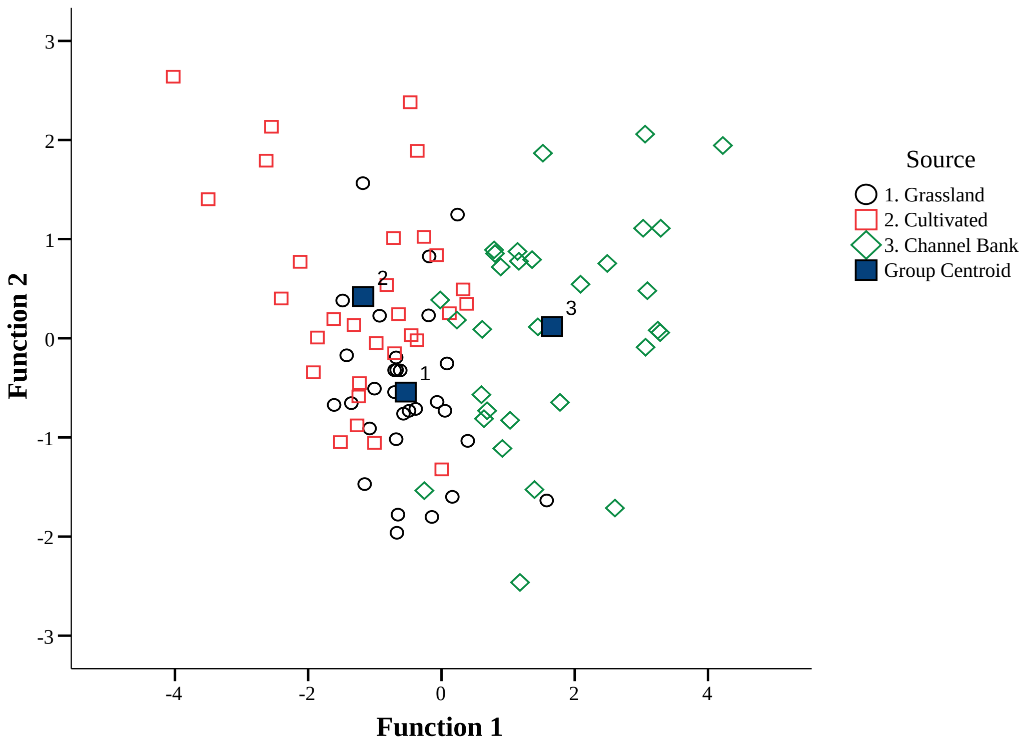

Figure 5.8 *Combined scatter plots showing sample distribution around group centroids from the two canonical discriminant functions applied to the grassland, cultivated land and channel bank source groups from the River Axe catchment following stepwise MDFA*

Generally, the source discrimination achieved by stepwise MDFA was below that reported in several previous studies conducted in the UK (Collins *et al*., 1997a; Collins *et al*., 1997b; Owens *et al*., 1999; Gruszowski *et al*., 2003; Chapman *et al*., 2005; Collins and Walling, 2007). Consequently, simultaneous entry MDFA was applied and an improved level of discrimination (85.6%) was achieved with a Wilks Lambda of 0.18 (Table 5.7). The composite fingerprint identified by simultaneous entry MDFA was comprised of 17 properties (Mg, Li, Zn, Ga, Ge, Sr, Y, Pd, Cs, La, Ce, Pr, Nd, Sm, Tb, Dy and Yb). The improved discrimination of the grassland, cultivated land and channel bank sources groups is shown in Table 5.8 and is further clearly illustrated in the more compact combined scatter plots shown in Figure 5.9 This composite fingerprint provided sufficient discrimination to enter the component properties into the mixing model.

Table 5.7 *Wilks' Lambda Test of Functions for fingerprint properties simultaneously entered into MDFA*

Test of Function(s)	Wilks' Lambda	Chi-square	df	Sig.
1 through 2	0.18	131.75	42.00	0.00
2	0.66	32.46	20.00	0.04

Table 5.8 *The comparison of predicted sample group membership against actual group membership for grassland, cultivated and channel bank source groups, with percentage of correctly classified cases within each group following simultaneous entry MDFA.*

		Source Group	Predicted Group Membership			Total
			Grassland	Cultivated	Channel Banks	
Original Group Membership	Count	Grassland	27	3	0	30
		Cultivated	5	24	1	30
		Channel Banks	3	1	26	30
	%	Grassland	90.0	10.0	.0	100.0
		Cultivated	16.7	80.0	3.3	100.0
		Channel Banks	10.0	3.3	86.7	100.0

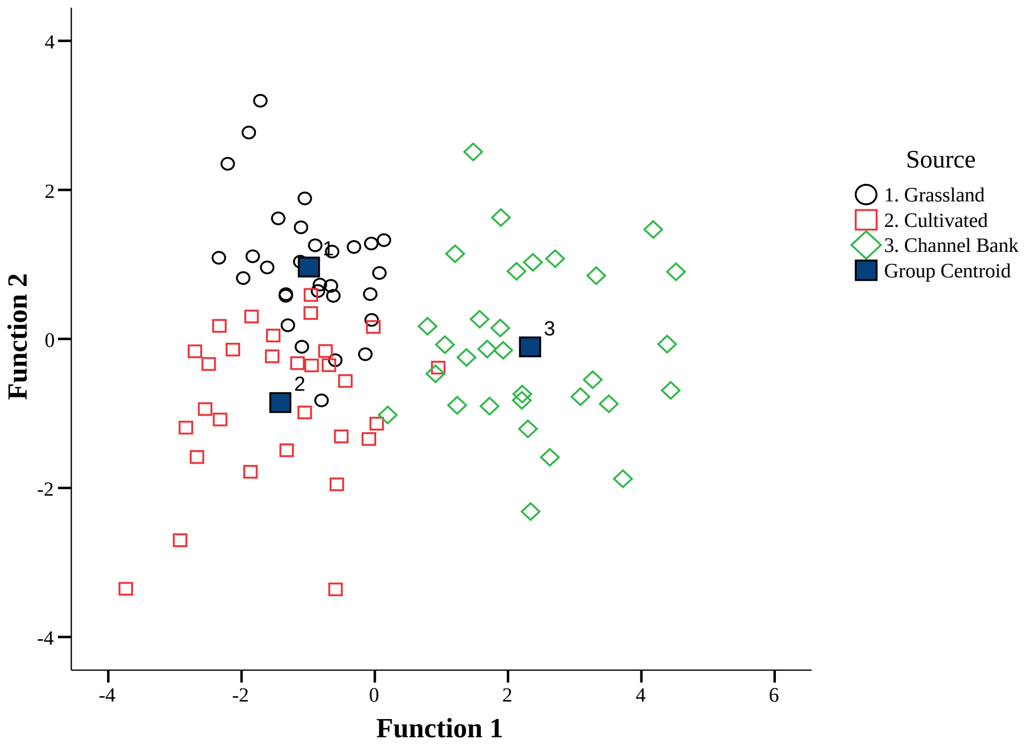

Figure 5.9 *Combined scatter plots showing sample distribution around group centroids from the two canonical discriminant functions applied to the grassland, cultivated land and channel bank source groups from the River Axe catchment following simultaneous entry MDFA*

5.6 Application of the Mixing Model

Application of a linear numerical mass-balance mixing model provides an estimate of the relative contributions from the three potential sediment source groups to the individual floodplain core sections (described in Chapter 3). The mixing model incorporated property-specific discrimination weightings derived from the entry of individual properties to MDFA (Table 5.9). A Monte-Carlo framework incorporated into the apportionment process provides explicit representation of the uncertainty associated with using relatively few samples to characterise the individual sediment source types, as represented by their mean fingerprint property concentrations.

Table 5.9 *Mixing model property-specific discrimination weightings.*

Property	Individual discrimination (%)	Weighting value
Mg	78.9	1.11
Li	56.7	1.27
Ga	42.2	1.17
Ge	63.3	1.53
Sr	41.1	1.47
Y	38.9	1.30
Pd	56.7	1.25
Cs	55.6	1.28
La	58.2	1.36
Ce	68.3	1.78
Pr	61.1	1.75
Nd	61.1	1
Tb	69.3	1.45
Dy	62.2	1.75
Yb	64.9	1.75

5.7 Sediment source apportionment and historical catchment land use changes

The sediment source apportionment and associated Relative Mean Error (RME) for each of the floodplain sediment core sections is presented in Table 5.11. The RME for the combined sediment core section relative source contribution estimates was 6.2%, giving a mean goodness-of-fit of 93.8%. The high level of goodness-of -fit confirmed that the mixing model was capable of simulating meaningful floodplain sediment mixtures and the RME values compared very favourably with those reported in other recent fingerprinting studies (Walling *et al*., 1999; Collins *et al*., 2010a, b). The apportionment estimates of relative source sediment contributions from ca. 1908 to 2007 are illustrated in Figure 5.10. Relative sediment contributions from channel bank sources displayed the greatest variation over the period, with a maximum contribution of 34% between 1913 and 1917 and a minimum contribution of 2% in the late 1970s. The relative contributions from grassland sources ranged from a maximum of 81% in the late 1970s, to a minimum of 41% between 2003 and 2007. Cultivated land generally provided the least variation in relative contributions over the study period, with a maximum contribution of 33% between 2003 and 2007 and a minimum contribution of 12% at the beginning of the 20th century. The time-averaged relative sediment contributions from grassland topsoil, cultivated topsoil and channel bank sources were 65%, 15% and 20% respectively.

Table 5.10 *Estimated sediment contributions (%) (± standard deviation) from grassland, cultivated land and channel bank sources in the Upper River Axe catchment (1908-2007) with associated RME (%)*

		Estimated sediment contribution (%)			
Depth (cm)	Estimated chronology	Grassland	Cultivated	Channel Bank	RME (%)
1	2007	41±16	33±14	26±8	7
2	2003	72±29	16±7	12±7	4
3	1998	56±28	14±8	29±13	4
4	1994	60±27	14±9	25±11	3
5	1989	72±29	15±8	13±5	4
6	1985	75±30	16±6	9±4	6
7	1981	79±32	16±7	4±3	8
8	1976	81±31	17±11	2±3	8
9	1972	80±33	17±8	3±6	9
10	1967	73±32	15±9	12±7	6
11	1963	78±33	16±7	5±6	9
12	1959	75±32	15±6	10±4	7
13	1955	69±31	14±6	17±5	7
14	1950	65±30	14±5	21±15	6
15	1946	68±31	14±5	18±13	6
16	1942	58±29	13±6	29±14	5
17	1938	65±31	14±9	21±16	6
18	1934	64±31	14±6	23±16	7
19	1929	69±32	14±8	16±7	7
20	1925	62±30	13±6	25±11	6
21	1921	66±32	14±7	20±10	8
22	1917	64±31	14±5	22±10	7
23	1913	54±29	12±5	34±13	6
24	1908	57±29	13±6	30±12	6

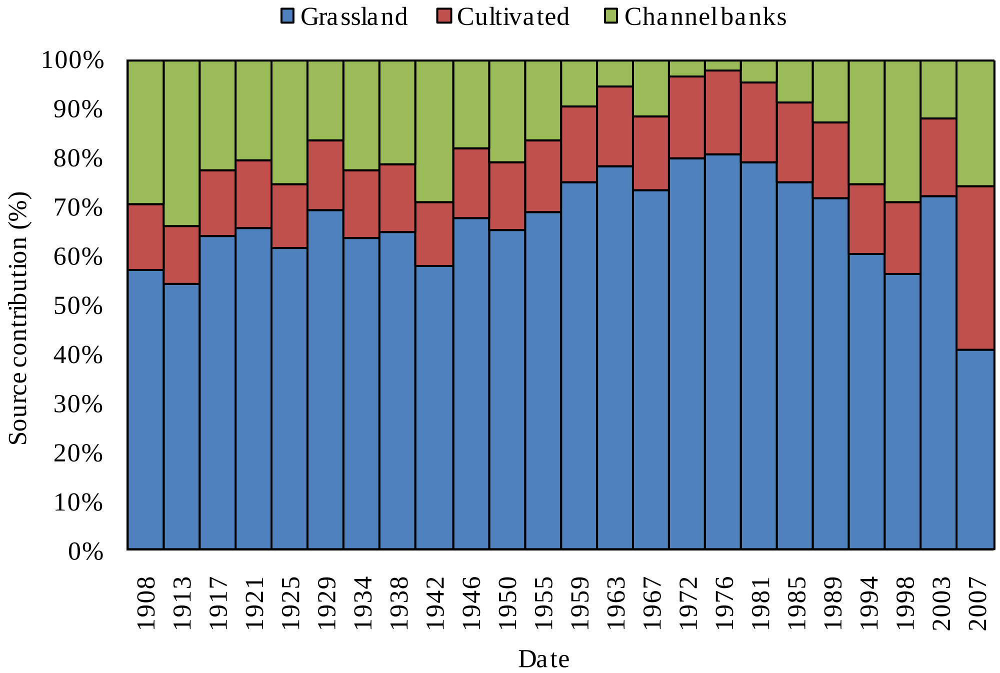

Figure 5.10 *Temporal changes in the relative contributions to floodplain sediment from grassland, cultivated land and channel bank source groups in the Upper River Axe catchment ca. 1908 – 2007*

In general, the relative sediment contributions from cultivated sources showed very little fluctuation over time. In the period from the early 1900s up to the beginning of the Second World War, contributions from cultivated sources remained fairly stable at around 13% on average. Throughout the duration of the Second World War (1939-1946), the source contributions from cultivated land showed little significant fluctuation, although the amount of land within the county which was converted to arable production during this period increased by up to 30% (Murray, 1955). The increase in cultivated land use was probably due in part to the WARAGS plough-up subsidy which peaked in 1942 at £2.00 per acre and the additional acreage payments for potatoes which peaked in 1945 (Murray, 1955). Records for this area were not of sufficient resolution to ascertain whether fields in the Upper River Axe catchment were ploughed up at this time. However, given the size and characteristics of the entire catchment, it seems likely that at least part of the drainage basin would have been affected. It is possible that any wartime plough up which did occur in the River Axe catchment was largely confined to areas below the extent of this study and therefore an increase in sediment from this source would not necessarily be obvious on the floodplains of the upper reaches. There is an apparent decrease in relative sediment contributions from grassland sources in the early 1940s and this may reflect a reduction in the areas under grassland following plough up. The landscape of the River Axe catchment is divided by many traditional earth banks and well established hedges. As observed in Chapter 4, these field boundaries can limit the connectivity between any ploughed land and the river channel. Furthermore, any additional cultivation would not necessarily have been in the riparian fields or other areas with high connectivity to water courses and as such land would have been prone to flood inundation. If connectivity between fields and the river is low, the potential impact of land use change in those fields on downstream sediment sources will be greatly reduced.

During the 1970s, relative sediment contributions from cultivated sources show a small increase from 15% to 17.5%. There followed, a gradual decline in relative contributions from cultivated sources through the 1980s and 1990s down to 14%. The largest relative contribution from cultivated sources (33%) occurred within the four years up to and including 2007. This might be of some concern as the catchment was under considerable scrutiny over this time and farmers have been particularly encouraged to take advantage of Entry Level Stewardship (ELS) in conjunction with the ECSFDI and other agri-environment schemes such as Farm Advice Training and Information (FATI).

From the beginning of the 1900s up to the mid 1930s contributions from channel banks display a gradual decline. During this period of depression there was a decline in agricultural production. Although dairy and livestock were relatively resilient, many livestock herds were reduced as agricultural labourers left the countryside (Winter and Lobley, 2009). A reduction of livestock numbers at this time may have eased poaching pressure on eroding channel banks. Relative contributions from grassland sources increase at this time which might suggest an increased impact from livestock. The increased relative contribution from grassland sources may have occurred as a consequence of limited land drainage maintenance leading to greater field saturation and increased poaching, rather than effects of increased stocking densities. Similarly, channel bank relative sediment contributions may have decreased in response to lack of bank maintenance, leading to the scrubbing up of riparian zones and the clogging of tributary channels slowing flows and thereby reducing bank erosion. During the years of the Second World War there is an apparent increase in channel bank contributions. Throughout the duration of the war ditches and channels were cleared to improve drainage and increase production (Murray, 1955) which could have influenced the increased relative contribution from channel bank sources.

Data on changes in land cover, crops and stock densities were extracted and collated from the Agricultural Census Database (Agcensus) (Defra/EDINA, 2009). Data were obtained at 2km x 2km grid resolution from the area of the catchment for years; 1969, 1972, 1976, 1979, 1981, 1988, 1993, 1996, 2000 and 2004. Existing studies complemented the Agcensus data as a source of information.

The advent and spread of maize cultivation is a major concern in relation to increased down-stream sediment problems within the Axe catchment (Cycleau, 2006; Defra, 2009). Land cover data of maize cultivation and other late-harvested crops, which are associated with high erosion risk (Quinton and Catt, 2004; Evans, 2005; Austerwald, 2006; Feiner and Austerwald, 2007), including potatoes and sugar beet were collated at catchment scale between 1969 and 2004. Data were similarly combined for high erosion risk autumn-sown crops, including wheat, winter-barley and oilseed rape. Land cover data for permanent pasture and temporary grassland were also collated and compared with those above for comparative analysis (Figure 5.11). The historic dominance of permanent grassland, mainly used for dairy and sheep production, as the major land use type in the catchment is clearly illustrated. Temporary grassland has generally been the second largest land use type and this would have been largely used to provide winter feed for the dairy herds, whilst also acting as a break crop in arable rotation patterns. The trend of the area under grassland since 1969 bears a close relationship to the trend in relative sediment contributions from this source presented in Figure 5.10. As grassland is by far the largest land use in the catchment it might be expected that any major changes in grassland cover would have dominant effect on relative apportionment of sediment source contributions. The rise of maize cultivation since the mid 1970s, illustrated in Figure 5.12, is reflected in the increase of late-harvested crops, of which maize dominates. The increase of autumn sown crops appears to have occupied land previously under permanent and temporary grassland. The area under late harvested crops has increased since the late 1980s, as the yield from these cultivars has benefitted from the development of hardier varieties, intensive production techniques and warmer winters.

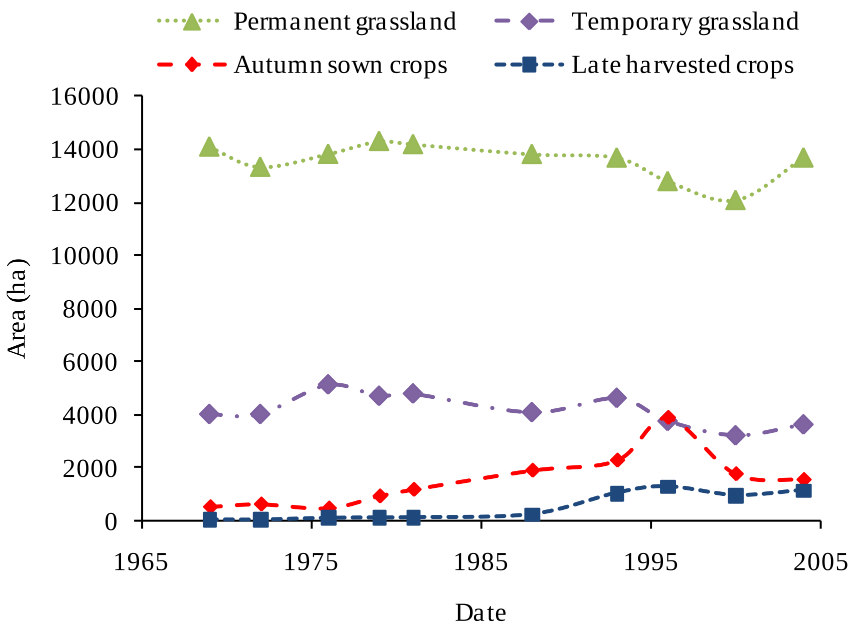

Figure 5.11 *Land cover area (ha) for permanent grassland, temporary grassland, autumn sown crops and late harvested crops in the Upper River Axe catchment 1969-2004*

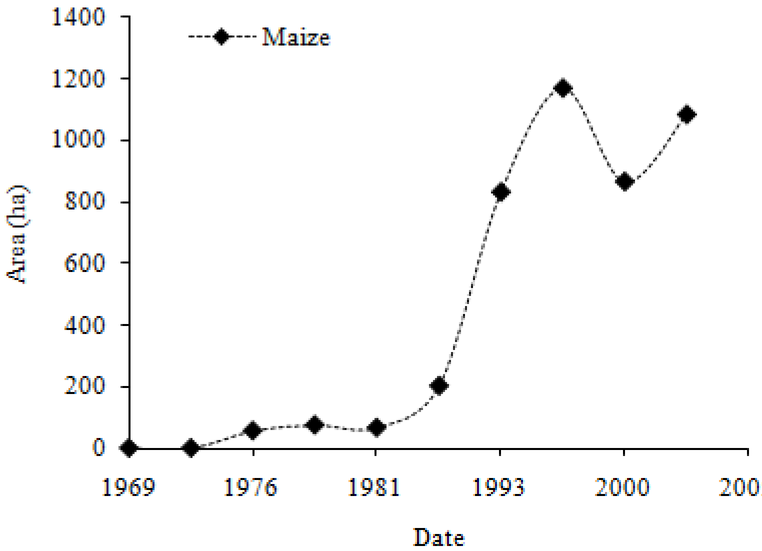

Figure 5.12 *Land cover area for maize cultivation in the Upper River Axe catchment 1969-2004*

It is perhaps surprising that there was so little apparent change in the relative contributions to floodplain sediment coming from cultivated sources over the last 30-40 years. The absence of a definitive relationship between changes in land area under cultivation and the variations in relative cultivated source contributions is interesting, particularly when the increases in high erosion-risk crops over the period are considered. However, despite the total area of the study catchment under all types of cultivation ranging from 2128 ha in 1969 to a peak of 5912 ha in 1996, largely due to increases in fodder maize cultivation, the proportion of total agricultural land area affected only ranged from 9% to an uncharacteristic peak of 25% over the same period (Figure 5.13). The mean average land cover area under arable cultivation as a proportion of the total land area between 1969 and 2005 was just 12%. It may be that effects of short term sediment source variations at this scale are difficult to detect due the limitations of temporal and spatial data available in this study. Conversely, it may be that the influence of the land cover changes on the sources of overbank sediment deposited on the study floodplain, during the study period, was essentially minimal.

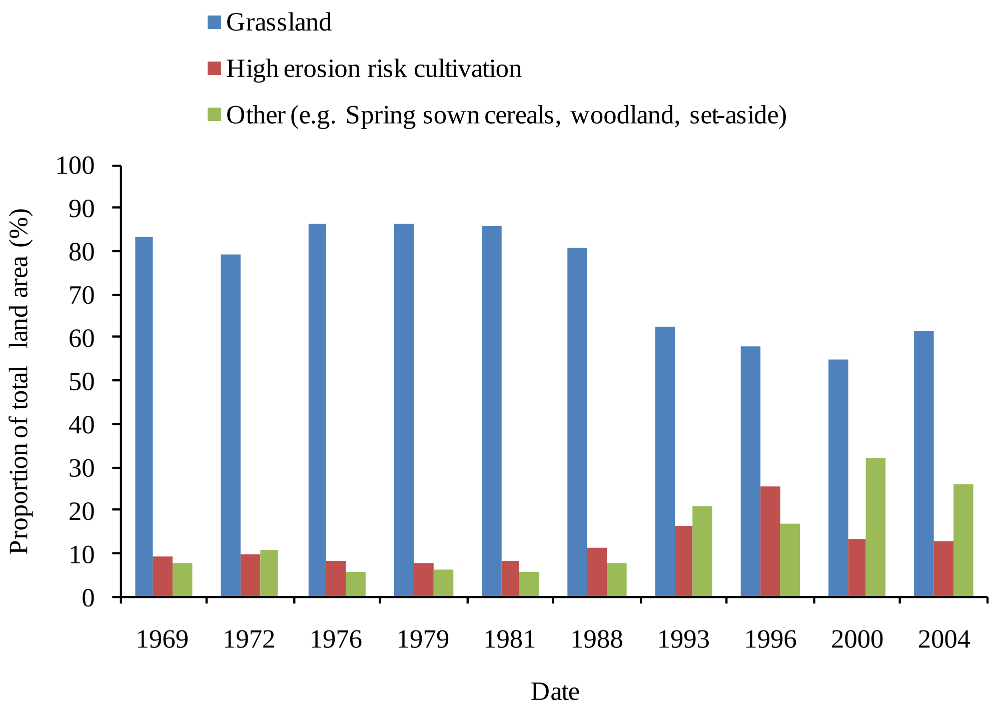

Figure 5.13 *A comparison of the relative proportions of total land area occupied by grassland, high erosion risk cultivation and other agricultural uses including spring sown cereals, set-aside and woodland in the Upper River Axe catchment (1969-2004)*

Fluctuations in stocking patterns for cattle and sheep within the catchment can be observed in Figure 5.14. Total numbers of cattle and calves over 6 months increased steadily from 32,562 in 1969 to a peak in 1979 of 39,897, from which year total numbers slowly declined to just 30,000 by 2004. Total sheep numbers increased sharply from 13,290 in 1972 to over 41,000 by the beginning of the 1990s. From 1993 numbers declined through the early mid 1990s but grew significantly again from 1996 to a peak of 44,500 by 2004. The total number of pigs grew rapidly from 11,879 head in 1969 to a peak of 34,611 by 1993. Since 1993 pig numbers declined sharply to just 4,412 in 2004. This severe decline reflects both the decreasing margins in UK pig production (Lewis, 2006) and possibly also the impacts of welfare and environmentally orientated controls on pig production since the mid 1990s (FAWC, 2009). However, the Agcensus data for pig production did not discriminate between outdoor production systems and intensive indoor systems, which have been prolific in the catchment. Consequently, on the basis that their outdoor numbers could not be reliably defined, Pigs were excluded from the combined stocking density calculations below. This introduces a certain limitation into the estimation of stocking densities as high rates of soil erosion and runoff have been directly associated with fields occupied by pigs (Evans, 2004).

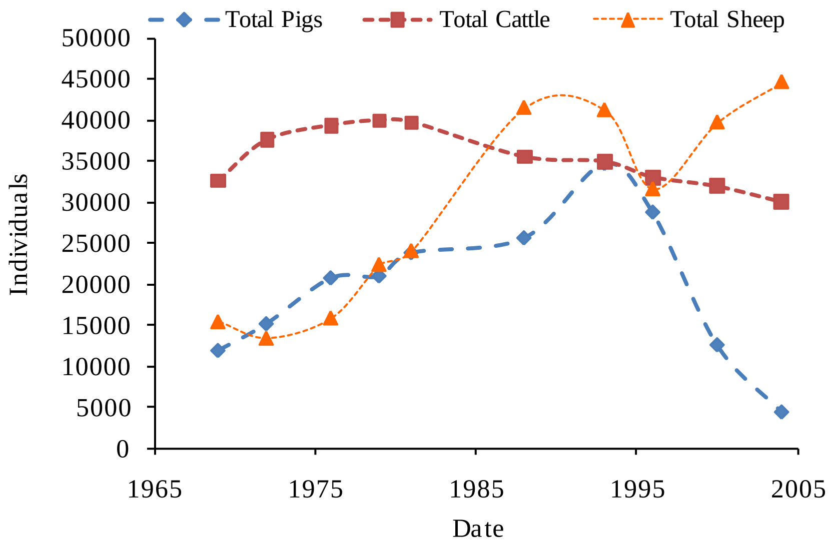

Figure 5.14 *Livestock numbers for pigs, cattle and sheep in the Upper River Axe catchment from 1969 to 2004*

For comparative land use impact analysis, Livestock Unit (LU) stocking densities were calculated from cattle and sheep data on the assumption that combined stock grazed the land area under permanent grassland and rough grazing for each associated year (see Chapter 3). The variations in stocking densities (LU ha^{-1}) in the Upper River Axe catchment 1969-2004 can be seen in Figure 5.15.

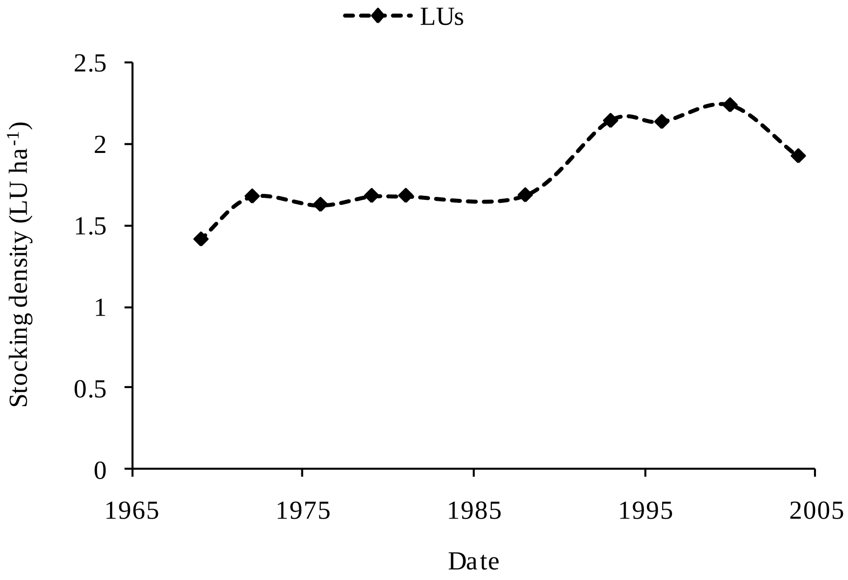

Figure 5.15 *Stocking density in the Upper River Axe catchment 1969-2004 (LU ha^{-1})*

Following comparison of changes in stocking densities with source apportionment estimates, relative sediment contributions from channel banks appear to bear some correlation with stocking density variations observed after 1969. This suggests that an increased level of bank erosion has occurred during periods of higher stocking densities. In this instance it may be that bank erosion is a more dominant consequence of higher stocking densities than factors such as compaction and field poaching which might have led to increased contributions directly from grassland top soils. However, when stocking densities peaked towards the end of the 1990s and the beginning of the 2000s, an increased contribution from permanent grassland is observed. This could be an indication that threshold livestock carrying capacities were exceeded at this time, leading to a sharp increase in sediment mobilisation and run-off as areas of over-stocked pasture degraded.

5.8 Conclusion

The Upper River Axe catchment is dominated by permanent grassland under intensive dairy production and although the area under arable production supports a large percentage of high erosion risk crops, the overall land cover occupied by arable production is relatively small. These basic relationships have been reflected by the sediment apportionment results following application of the source fingerprinting technique. The interpretation drawn here cannot be extrapolated to the wider River Axe catchment without further research and in no way precludes the potential for maize cultivation in the mid and lower areas of the catchment to influence localised or downstream sedimentation problems.

Relative sediment contributions from channel banks appeared to increase during recorded periods of higher stocking densities. This would echo the unfavourable land management described in the recent Natural England report, which suggested that widespread stock access to stream channels was causing bank erosion, exacerbated by high stocking rates (Natural England, 2010). This is a particularly good example of the utility of the fingerprinting technique applied in a retrospective manner to inform and confirm the basis for current management priorities. Appropriate mitigation would include the fencing of channel banks to restrict livestock access and the construction of appropriately designed livestock drinking access points.

Although the general relative proportions of source contributions predicted by the mixing model are not dissimilar to the general proportions of land use type, there is a lack of resolution, particularly in response to fluctuations in high erosion risk crops, such as maize. Limitations which may have influenced the lack of resolution include various possibilities. The extent and type of field boundaries in the catchment, combined with the distance of cultivated fields to the river channel could be buffering the sediment associated effects of increases in areas of land under arable cultivation. It is also important to be aware that a comparison between source group samples and floodplain sediment horizons only allows an investigation of changes in the source of sediment deposited during flood events which result in overbank deposition, as opposed to changes in the source of the sediment load transported by all other flows which do not overbank. Without further specific analysis, it is difficult to estimate the proportion and representative qualities of the total sediment load being represented by overbank sediment stored on the study sub-catchment floodplain. The floodplain at Broad Bridge is less developed than the downstream floodplains which occur as the River Axe valley widens and levels out towards the estuarine reaches. The riparian fields forming the flood plain at this location are bordered on one side by a railway embankment and on the other by a road embankment. This topographic detail could influence the nature of the flow and sedimentation patterns during high magnitude flood events, particularly as the flow backs up against the bridge structure.

Notwithstanding the points above, these results served to confirm the observations from previous studies of the potential for intensively managed grassland to influence the sediment source contributions in a catchment considerably (Foster and Walling, 1994; Collins *et al*., 1997; Russell *et al*., 2001; Walling *et al*., 2003; Owens *et al*., 2005; Bilotta *et al*., 2007).

CHAPTER 6 - THE RIVER ARROW CATCHMENT:

RESULTS AND INTERPRETATION

6.1 Introduction

In this third case study chapter, the results and interpretation from the application of the sediment source fingerprinting technique to floodplain sediment core sections within the River Arrow Catchment, Herefordshire, UK, are presented. The main aim of this study was to relate relative changes in the sources of floodplain overbank sediment to contemporaneous land use change in the recent past (ca.30-50 years).

Sediment associated environmental and ecological problems have been reported in the River Arrow catchment and also downstream on the River Lugg and River Wye catchments of which the River Arrow is an important tributary. Particular concerns have been raised in relation to the effects of excessive sedimentation on the breeding habitats of Salmonid species (The Wye and Usk Foundation, 2006). These concerns have led to the designation of the River Wye and the River Lugg, incorporating its main tributary, the River Arrow, as Priority Catchments within the ECSFDI (Environment Agency, 2008; Defra, 2010a). The primary land use change of concern in this case study is the recent expansion of intensive potato cultivation within the catchment. Fine tills are prepared in lateral rows on hill slopes, in conjunction with potentially high connectivity to watercourses.

6.2 River Arrow catchment description

The River Arrow rises near the English/Welsh border in Powys, and then flows in an easterly direction through Newchurch and Michaelchurch-on-Arrow into Herefordshire (Figure 6.1). The River Arrow continues east through Herefordshire, via Kington, Lyonshall, Staunton-on-Arrow, Pembridge, Eardisland, Arrow Green, Monkland and Ivington. The River Arrow has a confluence with the River Lugg south of Leominster, which in turn has a confluence with the River Wye at Mordiford, 14 km downstream of Hereford. The rivers and associated floodplains of Herefordshire are of substantial conservation interest and as such the county includes the longest length of river designated for its conservation value of any county in England (Herefordshire Nature Trust, 2009).

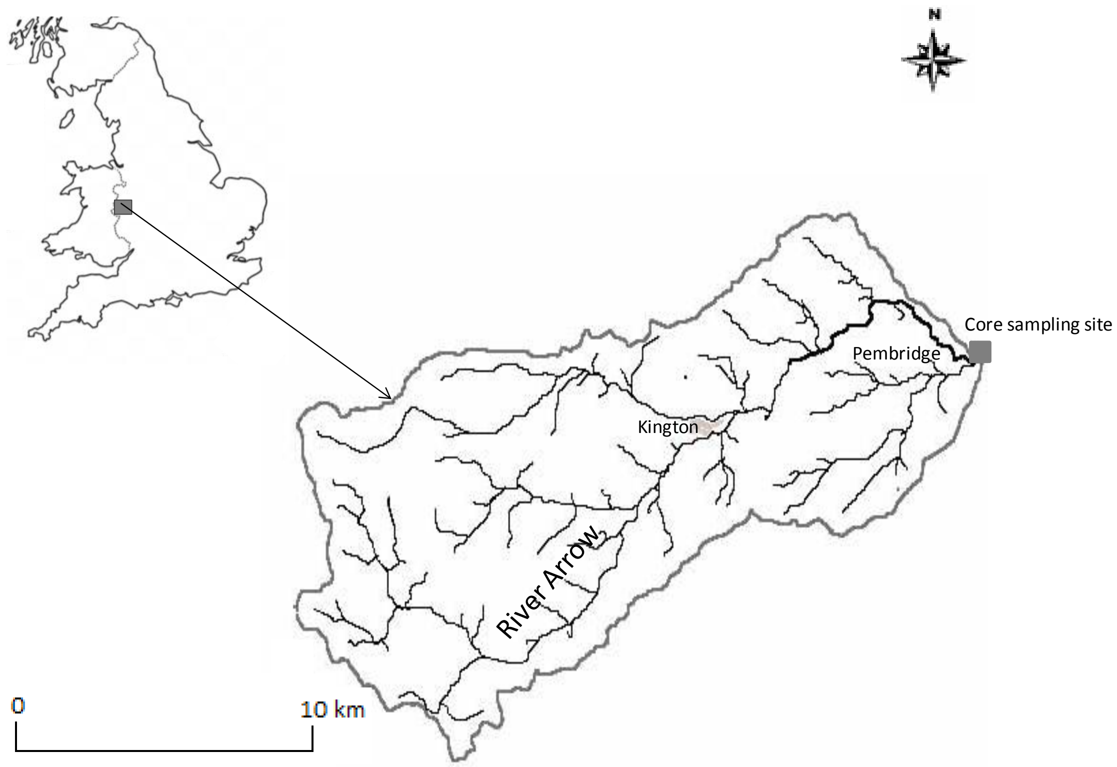

__Figure 6.1__ The location and study area of the River Arrow catchment, Herefordshire, UK.

The geology in the west of the River Arrow catchment features bedrock of Silurian Wenlock limestone with some Igneous intrusions (Crown copyright, 1934; Crown copyright, 2009). This gives way towards the East to Raglan Mudstone and Old Red Sandstone. These are overlain by various Glaciofluvial Deposits with significant Alluviam occurring in the downstream floodplain area, particularly between Staunton-on-Arrow and the confluence with the River Lugg below Leominster. The River Arrow catchment incorporates a number of Regionally Important Geological and Geomorphological Sites (RIGS), such as Barton Farm at Kington, which has Quaternary, Pleistocene, Late Devonian, Hereford Formation and Glacial Moraine (Herefordshire and Worcestershire Earth Heritage Trust, 2009)

The soils of the River Arrow catchment are characterised in the headwaters of the upland west by predominantly freely draining, acid, loamy soils, over rock. The mid and lower catchment incorporates more free draining lime-rich loamy soils, combined with smaller areas of slowly permeable, seasonally wet, acid, loamy and clayey soils (NSRI, 2007). The upland land cover is dominated by rough grazing and permanent semi-improved pasture and is largely under sheep production at this time, (illustrated in Figure 6.2).

Figure 6.2 *Upland sheep production in the Upper River Arrow catchment*

Land use in the mid and lower catchment combines arable production with dairy and livestock production on improved grassland (NSRI, 2007). The free draining fertile soils of the mid-catchment valley bottom support a variety of arable production, including maize, oilseed rape and a significantly recently increased area under potato cultivation. Since the late 1990s advances in sub-soiling techniques have facilitated greater opportunities for potato cultivation on the areas of heavier soils. A continued strong market for potatoes ensures that local land owners receive good rents from large scale producers (Collins, 2009. pers. comm.). Potato producers are often keen to use land which has not been previously used, as this ensures a crop less affected by common potato diseases, leading to reduced spraying applications and thereby lower production costs (Collins, 2009. pers. comm.). The area also encompasses a small number of farms engaged in field-vegetable and fruit cultivation which is mainly apple production. The large-scale use of polytunnels, which have become a ubiquitous feature further east in the county, were not in evidence in the catchment during the study. Woodland areas in the catchment include several relatively small-scale conifer plantations various areas in the upland west incorporate oak and ash, whilst further down the catchment some pockets of lime rich ancient semi-natural woodlands survive (Herefordshire Nature Trust, 2009). The sub-catchment identified for this study incorporates the River Arrow and all major and minor tributaries down to a catchment outlet with a suitable floodplain for taking core samples situated between Pembridge and Erdisland. The key land use change under consideration within the River Arrow catchment is the growth of intensive potato cultivation, illustrated in Figure 6.3. Intensive production practises, including vertical downslope fine-till preparation, often coupled with high connectivity to water courses and a lack of mitigation measures, were deemed to provide ample cause for concern and justification for investigation.

Figure 6.3 *Fields directly adjacent to water courses prepared for intensive potato cultivation in the River Arrow catchment*

6.3 Floodplain site selection

Potential floodplain sampling sites were identified for collection of overbank sediment cores through the use of topographic maps, satellite imagery, ground observation and anecdotal evidence. This process pinpointed sites which were regularly inundated by overbank flooding, with associated potential to receive and store sediment. Three key potential floodplain coring sites were identified within relatively close proximity to each other. Figure 6.4 shows the location of the core sampling sites at Twyford Farm, Pembridge and at Folly Farm, Eardisland. It was important that the sites had not been cultivated within the recent past, in order to preserve the historical sediment record intact. This requirement was substantiated through discussion with the Twyford Farm owner, who had personal knowledge of the site going back 40 years and the family of the Folly Farm owner, who had knowledge of the site for over 55 years. The potential for these sites to represent sediment sinks was confirmed following discussions with the land owners about the nature and extent of regular overbank flood inundations.

The anecdotal evidence was combined with a basic ecological appraisal of the sward composition and plant biodiversity at the sites. The species Soft Rush (*Juncus effusus*), often associated with wet or damp uncultivated soils, was observed at both floodplain locations. Marsh Marigold (*Calitha palustris*) and Yellow Flag Iris (*Iris pseudacorus)* were also observed in the wetter spots at the Folly Farm site. These species could be considered to be positive indicators of poorly drained, unploughed and regularly inundated floodplains. The sward at both sites appeared to contain a diverse combination of grasses including fescus and meadow grasses, further indicating a general lack of cultivation.

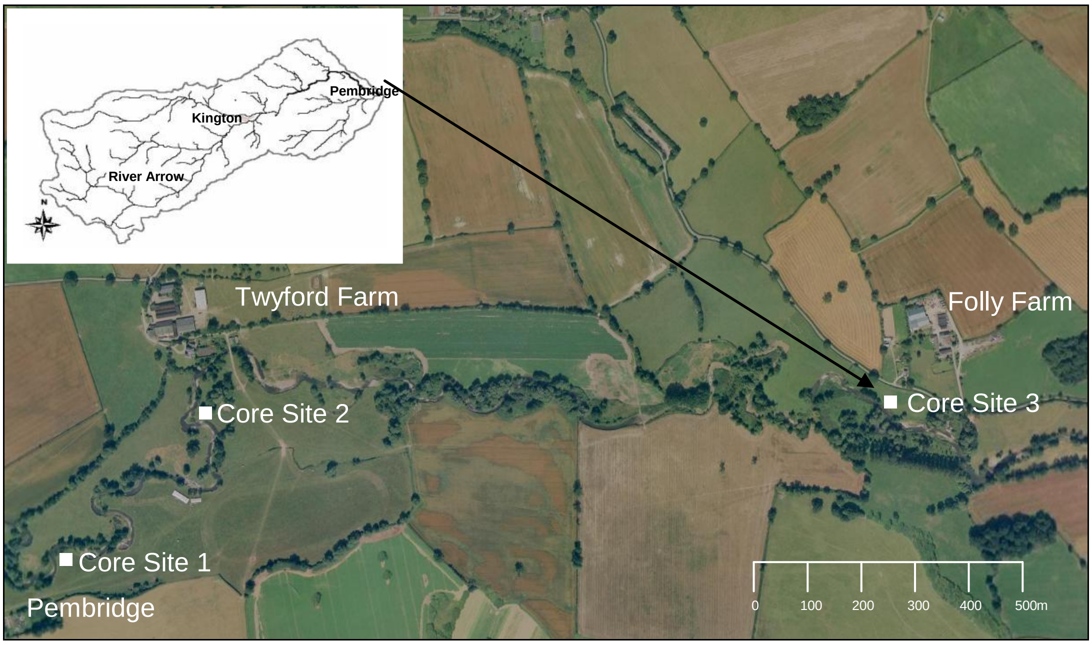

Figure 6.4 *The River Arrow catchment floodplain core sampling sites at Twyford Farm, Pembridge and Folly Farm, Earlisand, Herefordshire, U.K (Google Earth, 2009).*

A total of six cores with potential for use in subsequent sectioned analysis were collected from the identified sites. Two reference cores were also collected from nearby undisturbed topographically level sites overlooking the floodplain. The reference sites were considered unlikely to have been subject to either soil erosion or sediment deposition and could therefore be considered as representing a ^{137}Cs atmospheric fallout control reference for the immediate area during subsequent radioisotope inventory analysis. For each core with potential for use in subsequent sectioned analysis, an adjacent core was extracted for the purpose of estimating the ^{137}Cs bulk inventory for the associated site. The bulk cores were dried, then sieved to <2mm and analysed for ^{137}Cs using a gamma spectrometer as outlined in Chapter 3. The bulk inventories were compared with those of the reference sites. Following comparison of the floodplain core bulk inventories to that of the reference site, illustrated in Figure 6.5, the floodplain site estimated to have received the greatest sediment deposition was identified as Site 2, at Twyford Farm. The corresponding core 2 from Site 2 was accordingly sectioned into 1cm horizons, dried, disaggregated, sieved and prepared for laboratory analysis.

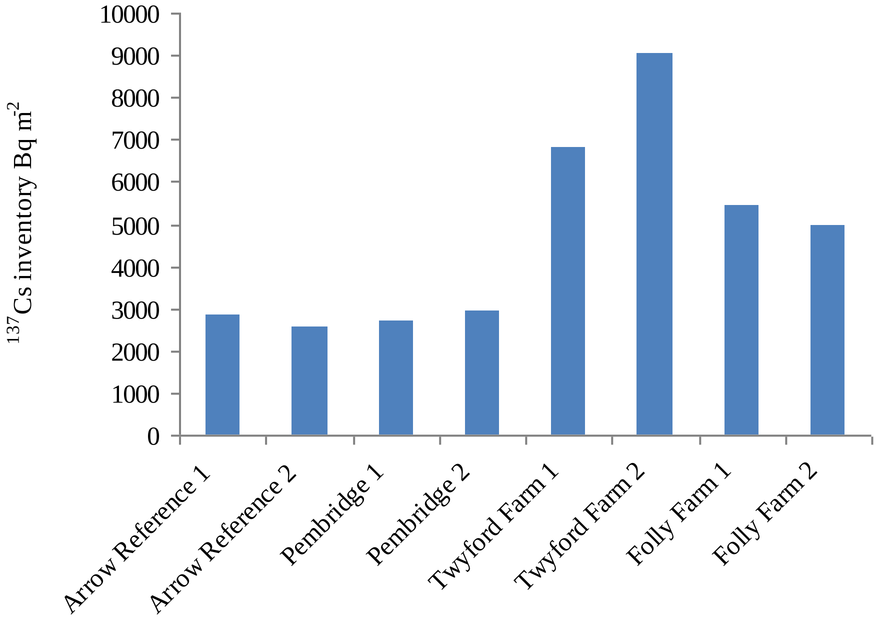

Figure 6.5 *^{137}Cs inventories for the floodplain and local reference cores collected from the River Arrow catchment*

6.4 ^{137}Cs Radioisotope Geochronology

The depth distribution profile of ^{137}Cs activity concentration within the River Arrow floodplain core was determined, shown in Figure 6.6. The depth distribution of ^{137}Cs within the core was analysed and the horizon containing peak activity was identified at 55cm. ^{137}Cs activity was detected in the deepest section of the core which prompted further investigation in order to establish whether the observered peak was from either bomb derived sources which peaked in 1963 or possibly a later peak from the Chernobyl disaster in 1986. The appearance of the peak suggested the latter, in that the peak was sharp with no gradual build-up over time as might be expected if the preceding years were representing the increase of bomb testing from the early 1950s. Further, investigation of historic maps indicated that the river channel actually appeared to flow through the area of the core site in the 1960s, which would fairly conclusively exclude the possibility of the peak being formed in 1963. The 55cm horizon was therefore taken to correspond to the ^{137}Cs fallout from the Chernobyl disaster which occurred in 1986. A time-averaged deposition rate for the intervening 22 years was then calculated at 2.5cm year^{-1} and this was extrapolated over the depth of sediment within the core to provide an approximate chronology.

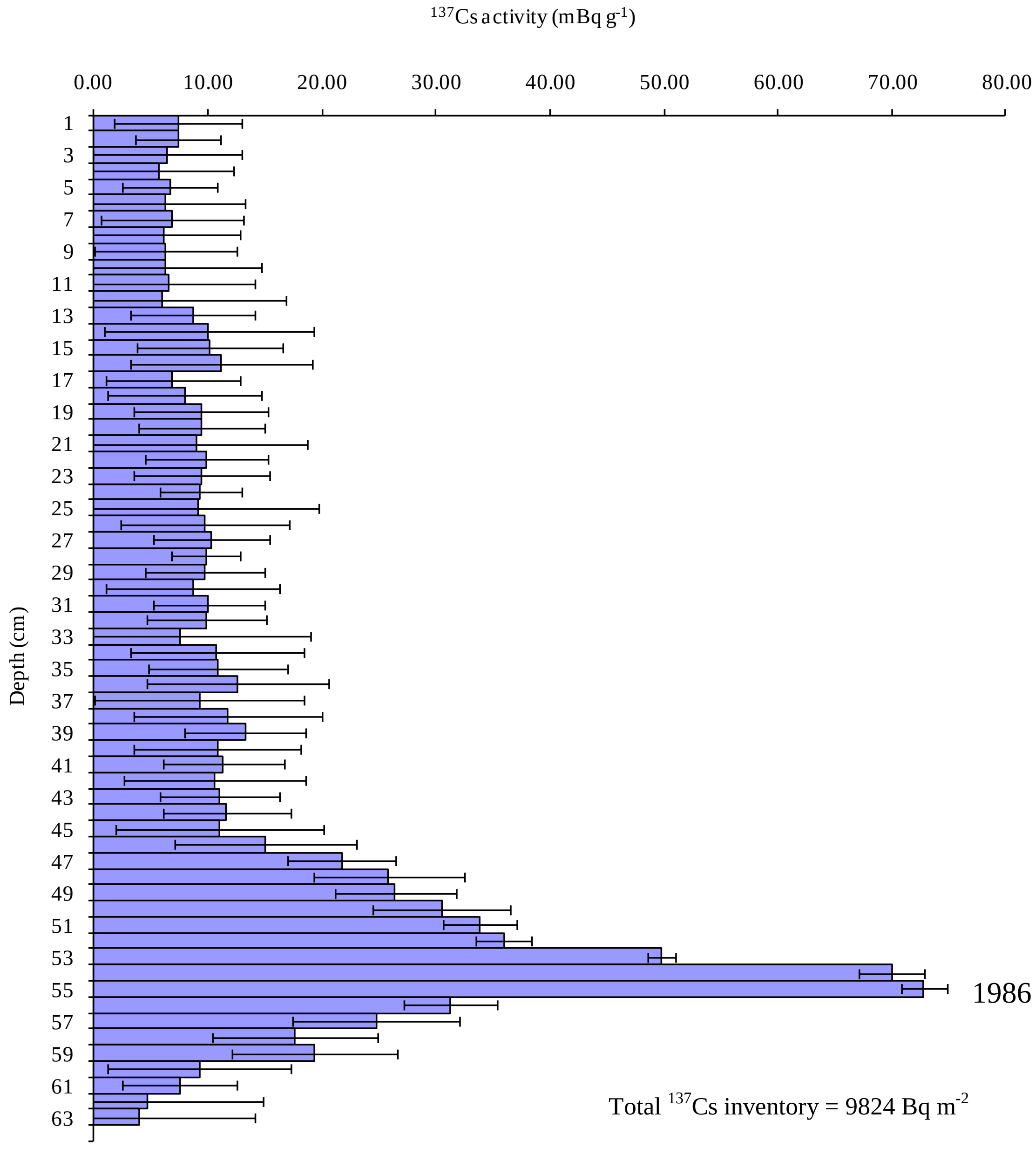

Figure 6.6 *The depth distribution profile of ^{137}Cs with associated total inventory from the Twyford Farm, River Arrow floodplain core*

6.4 The Fingerprinting Technique

6.4.1 Source samples

Surface scrapes (<2cm depth) from 4 distinct potential sediment source groups namely, topsoil of grassland, topsoil of cultivated land, topsoil of woodland and eroding material from channel banks and sub-surface sources, were retrieved from 119 sites throughout the River Arrow catchment, providing 30, 30, 29 and 30 samples for each source group respectively. To improve representation each source sample comprised between 5-10 sub-samples collected from an immediate 0.5 km^2 area. The samples were prepared and analysed, as described in detail in Chapter 3. Analysis provided information on particle size distribution, specific surface area (SSA) and concentration values for a suite of 48 geochemical properties, including heavy metals, trace metals, lanthanides and actinides, from which to identify an appropriate composite fingerprint.

6.4.2 Particle size effects

Following the methodology detailed in Chapter 3 the basic relationship between SSA and property concentration values was analysed before committing to the application of particle size correction factors. The available suite of 48 properties was tested for correlation between sample SSA and property concentration within the four source groups using Spearman's rho. A summary of results for correlation between sample SSA and property concentration is presented in Table 6.1.

Based on 196 grouped relationships, only 9 (4.6%) showed significant correlation at $p = 0.01$ and just a further 15 (9.4%) showed significant correlation at $p = 0.05$. Within grassland, cultivated land, woodland and channel bank source groups, significant correlation, $p < 0.05$, can be observed in 8%, 10%, 2% and 29% of cases respectively. No single property concentration exhibited significant correlation with SSA across all four source groups. Channel bank material exhibited the highest incidence of correlation with SSA. This material may have been more exposed to kinetic processes than surface source samples and been subjected to increased particle size-related sorption activity.

In view of the correlation results, it was not considered necessary to apply particle size correction in this instance on the basis that it could over-simplify the relationship between SSA and property concentration, potentially leading to over-correction of certain properties and unrepresentative corrected data values. It was assumed that by disaggregating and sieving source and floodplain samples to <63μm during processing, sufficient account had already been taken of any nominal grain size dependencies and thereby an acceptable comparison of concentration values could be undertaken without additional correction.

Table 6.1 *Spearman's rho correlation coefficients and significance for SSA and fingerprint property concentrations from grassland, cultivated land, woodland and channel bank source groups*

Property	Grassland Coefficient	Significance	Cultivated Coefficient	Significance	Woodland Coefficient	Significance	Channel Banks Coefficient	Significance
Mg	-0.187	0.305	-0.212	0.229	0.145	0.454	0.201	0.27
Al	0.141	0.442	0.104	0.558	0.2	0.299	0.337	0.059
K	-0.362(*)	0.042	-0.079	0.658	0.234	0.222	0.319	0.076
Mn	-0.15	0.413	-0.076	0.669	0.285	0.134	0.283	0.116
Fe	-0.089	0.628	-0.001	0.994	0.188	0.328	0.527(**)	0.002
Li	0.224	0.217	-0.271	0.121	0.176	0.361	0.256	0.157
Na	-0.426(*)	0.015	-0.362(*)	0.036	0.351	0.062	0.176	0.336
Sc	-0.205	0.261	-0.21	0.234	0.298	0.117	0.168	0.358
Ti	-0.19	0.297	-0.291	0.095	-0.249	0.192	-0.287	0.112
V	0.047	0.796	0.133	0.454	0.21	0.275	0.405(*)	0.022
Cr	0.065	0.723	0	0.998	0.201	0.295	0.304	0.091
Co	-0.102	0.577	-0.339(*)	0.05	0.28	0.142	0.464(**)	0.008
Ni	-0.058	0.752	-0.226	0.198	0.261	0.171	0.398(*)	0.024
Cu	-0.146	0.426	-0.09	0.612	-0.141	0.464	0.18	0.324
Zn	-0.390(*)	0.027	-0.139	0.432	0.091	0.64	0.308	0.087
Ga	-0.038	0.837	-0.145	0.415	0.1	0.608	0.218	0.231
Ge	-0.173	0.343	-0.133	0.454	0.157	0.417	0.572(**)	0.001
As	0.307	0.087	0.187	0.29	0.085	0.66	0.488(**)	0.005
Rb	0.478(**)	0.006	0.202	0.252	0.405(*)	0.029	0.408(*)	0.02
Sr	-0.308	0.086	-0.16	0.366	-0.06	0.757	0.262	0.147
Y	-0.039	0.83	-0.315	0.07	-0.223	0.246	-0.317	0.077
Zr	-0.188	0.302	-0.179	0.312	0.258	0.176	-0.146	0.425
Mo	-0.054	0.767	-0.306	0.079	0.048	0.804	-0.019	0.917
Pd	-0.253	0.163	-0.094	0.597	-0.121	0.533	0.477(**)	0.006
Cd	-0.015	0.936	0.052	0.769	0.126	0.514	0.434(*)	0.013
Sn	0.074	0.687	-0.322	0.063	0.132	0.495	-0.045	0.806
Sb	-0.138	0.453	-0.201	0.255	0.14	0.468	-0.17	0.353
Cs	0.037	0.841	0.035	0.845	0.223	0.246	0.274	0.13
Ba	-0.113	0.538	-0.159	0.37	-0.088	0.649	0.244	0.179
La	0	1	-0.340(*)	0.049	-0.252	0.187	-0.489(**)	0.005
Ce	0.055	0.766	-0.294	0.092	-0.096	0.622	-0.440(*)	0.012
Pr	-0.006	0.972	-0.331	0.056	-0.169	0.381	-0.347	0.052
Nd	-0.019	0.92	-0.372(*)	0.03	-0.169	0.38	-0.333	0.063
Sm	-0.137	0.454	-0.294	0.092	-0.151	0.434	-0.205	0.261
Eu	-0.12	0.511	-0.318	0.067	-0.172	0.371	-0.093	0.611
Gd	-0.166	0.364	-0.343(*)	0.047	-0.19	0.324	0.011	0.954
Tb	-0.127	0.488	-0.318	0.067	-0.141	0.464	-0.205	0.26
Dy	-0.158	0.389	-0.32	0.065	-0.121	0.531	-0.073	0.691
Ho	-0.164	0.37	-0.331	0.056	-0.143	0.46	-0.067	0.714
Er	-0.18	0.324	-0.32	0.065	-0.144	0.457	-0.063	0.73
Yb	-0.2	0.272	-0.303	0.082	-0.148	0.444	-0.042	0.821
Hf	-0.225	0.215	-0.157	0.375	0.331	0.079	-0.023	0.902
Tl	0.175	0.339	0.118	0.506	0.222	0.248	0.486(**)	0.005
Pb	-0.025	0.891	-0.025	0.887	0.15	0.438	0.226	0.213
^{207}Pb	-0.051	0.783	-0.094	0.598	0.111	0.567	0.205	0.261
^{208}Pb	-0.019	0.917	-0.021	0.905	0.162	0.402	0.211	0.247
Bi	0.16	0.383	-0.033	0.854	0.198	0.303	0.392(*)	0.026
U	0.036	0.846	-0.279	0.111	0.002	0.99	0.213	0.242

* Correlation is significant at p = 0.05
** Correlation is significant at p = 0.01

6.4.3 Particle-size distribution

Figure 6.7 illustrates comparison between the mean particle size distribution of the <63µm fraction of sediment from the River Arrow floodplain core and the four source groups. In this instance the source group samples were slightly more enriched in fines in comparison to those from the floodplain, this comparative enrichment was relatively modest and the source group distributions were generally similar to those from the floodplain. The area of the sample floodplain was relatively high in the overall drainage basin and as such it may be that finer material stayed in suspension at this point, where overbank flow rates may be quite high. The woodland particle size distribution was the most enriched in fines and this may reflect reduced erosion of fine soil particles due to the mitigating effects of canopy cover and leaf litter.

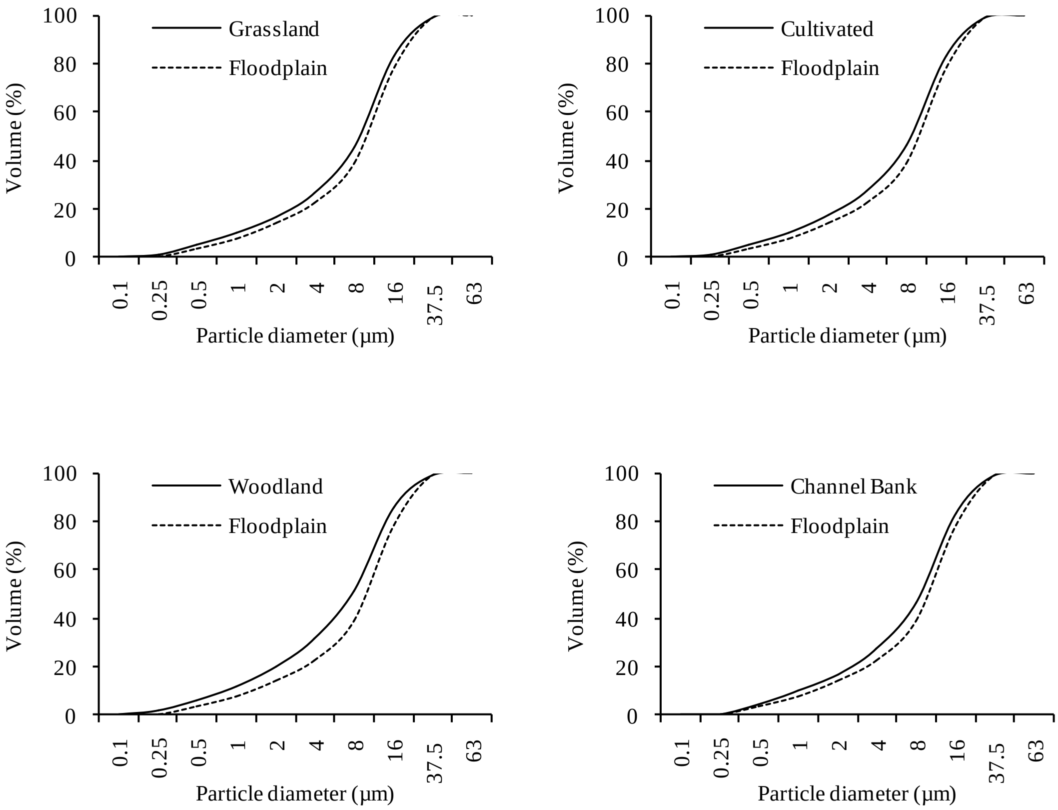

Figure 6.7 *A comparison of the mean particle size distribution (µm) of the <63µm fraction of sediment from the River Arrow floodplain core and source sample material from the grassland, cultivated land, woodland and channel bank source groups.*

Particle size distribution can be closely associated with specific surface area (SSA). Figure 6.8 shows the inter-sample group variability of mean and median SSA of the <63µm fraction of sediment from the floodplain core and the four source groups.

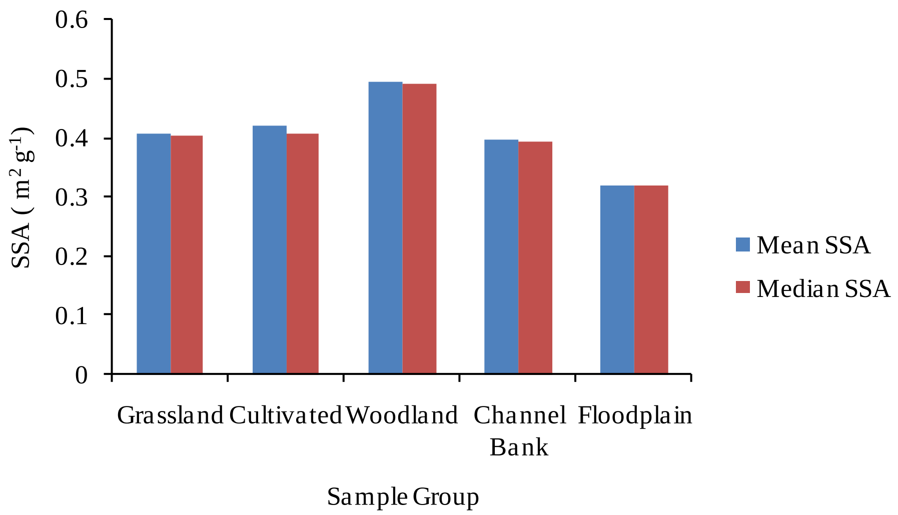

Figure 6.8 *Inter-sample group variability of mean and median SSA (m^2 g^{-1}) of the <63µm fraction of sediment from the River Arrow floodplain core and source sample material from the grassland, cultivated land, woodland and channel bank source groups*

The similarity between the mean and median SSA values indicates that the data were likely to be normally distributed and thereby were not unduly affected by the effect of outliers in this instance. It is also apparent that the mean and median SSA estimates for grassland, cultivated land and channel bank are very similar and did not differ greatly from those of the floodplain samples. Figure 6.9 shows the intra-group variability of SSA of the <63µm fraction of sediment retrieved from the four source groups and the floodplain sediment core sections, which further illustrates the relatively homogenous nature of SSA within each group.

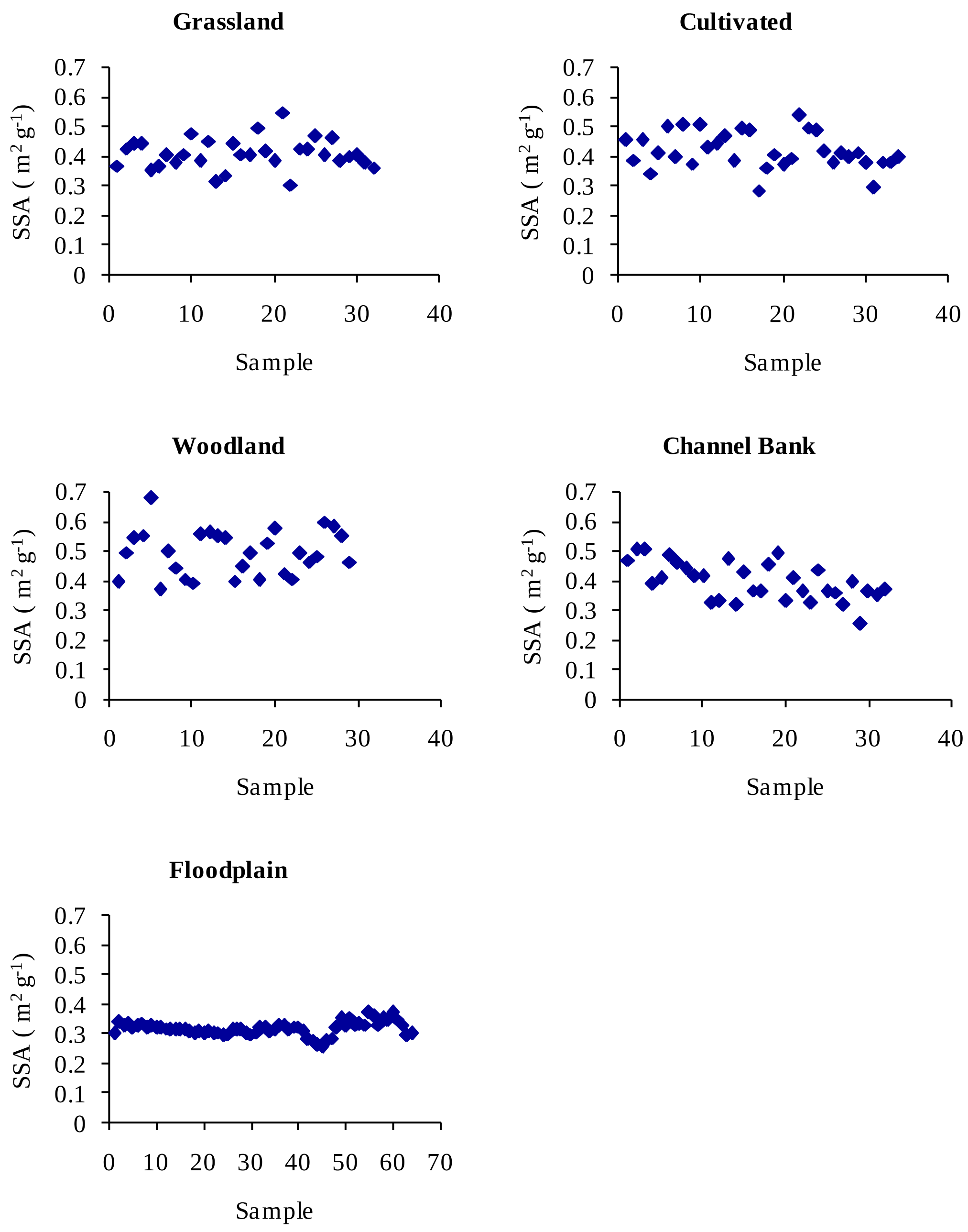

Figure 6.9 *The intra-group variability of SSA of the <63µm fraction of sediment from the River Arrow floodplain core and source sample material from the grassland, cultivated land, woodland and channel bank source groups.*

6.4.4 The fingerprint property concentration range test

The next stage was to apply the data to a property concentration range test to assess the general conservative nature of sediment properties following the influence of soil erosion, sediment transport and post depositional processes on the floodplain such as, the effects of bioturbation, molecular diffusion in the porewaters and possible advection influence of groundwater flow. The range test allowed that any properties considered for subsequent inclusion within the fingerprint should offer a reasonable solution and optimum goodness of fit within the mixing model, in that, minimum and maximum property concentration values from the core horizons fell within the minimum and maximum range of source property values. Table 6.2 presents the property range test results for the River Arrow catchment.

Table 6.2 *Results from the fingerprint property concentration range test.*

Core range within source range	**Core range overlaps source range min**	**Core range overlaps source range max**	**Source range within core range**
Mg	Al	Zr	Cs
K	Sc	Mo	
Mn	V	Cd	
Li	Ge	Sn	
Na	Rb	Sb	
Ti	Tl	^{206}Pb	
Cr	Fe	^{207}Pb	
Co		^{208}Pb	
Ni		Bi	
Cu		U	
Zn			
Ga			
As			
Sr			
Y			
Pd			
Ba			
La			
Ce			
Pr			
Nd			
Sm			
Eu			
Gd			
Tb			
Dy			
Ho			
Er			
Yb			
Hf			

Core range = Min to Max core property concentration values
Source range = Min Mean – Std Dev to Max Mean + Std Dev of mean source group property concentration values

Of the eighteen properties which failed to meet the range test requirement, six properties Al, Fe, Sc, V, Ge, Rb and Tl had concentration ranges within the core which overlapped the source range minimum concentration value, ten properties Zr, Mo, Cd, Sn, Sb, ^{206}Pb, ^{207}Pb, ^{208}Pb, Bi, and U had concentration ranges which overlapped the source range maximum value. 1 property, Cs had source concentration ranges which were within the core range. The Al and Fe core ranges overlapped the source range minimum. As observed above Al is generally considered to be a conservative element and has been used in previous studies for trace element normalisation purposes (Piper, 1973; Bruland, *et al*., 1974; Horowitz, 1991), both Al and Fe may be subject to release from sediment resulting from the formation of Al-phosphate and Fe-phosphate complexes or precipitants following the field application of phosphate based fertilizers (Chiang *et al*, 2008). Conversely, it is well known that trace metals can be taken up and concentrated by sediments and suspended particulate matter in aquatic systems. Heavy metal properties, such as Pb and Cd, which had core ranges that overlapped the source range maximums, may possibly have become concentrated following introduction of contaminants to the river corridor via road runoff pathways and from the urban centre of Kington.

6.4.5 Source discrimination: the Kruskal-Wallis H-test

The next stage in the establishment of the optimum combination of tracer properties with which to form the composite fingerprint was to test the ability of properties to differentiate between source types. This was initially assessed using the Kruskal-Wallis *H*-test (Collins *et al*., 1997a), wherein greater *H* values are produced as the significance of inter-group contrasts increases. Table 6.3 presents the resultant *H*-values and asymptotic significance from the Kruskal-Wallis *H*-test applied to ascertain the ability of individual tracer properties to distinguish between the four potential source groups. The test statistic was distributed as the Chi-Square with K-1 degrees of freedom (*df*) (where K = number of potential source groups i.e. 4). Thereafter, the critical value of 7.81 for 3 *df* of the Chi-Square distribution were used at $p < 0.05$. Two properties (Na and Cu) with *H*-values <7.81 were consequently removed from consideration as viable fingerprint properties at this stage.

Table 6.3 *H-values and asymptotic significance from the Kruskal-Wallis H-test utilised to ascertain the ability of individual tracer properties to distinguish between the grassland, cultivated land, woodland and channel bank source groups.*

Property	*H*-value	Asymptotic Significance
Mg	37.81	0.00
K	22.80	0.00
Mn	10.40	0.02
Li	38.35	0.00
Na	0.84	0.84*
Ti	18.20	0.00
Cr	40.94	0.00
Co	11.32	0.01
Ni	13.64	0.00
Cu	0.43	0.93*
Zn	10.40	0.02
Ga	20.66	0.00
As	21.91	0.00
Sr	17.55	0.00
Y	16.61	0.00
Pd	14.92	0.00
Ba	21.27	0.00
La	22.21	0.00
Ce	18.65	0.00
Pr	20.04	0.00
Nd	24.73	0.00
Sm	23.86	0.00
Eu	24.18	0.00
Gd	28.23	0.00
Tb	20.68	0.00
Dy	21.39	0.00
Ho	21.11	0.00
Er	21.59	0.00
Yb	20.81	0.00
Hf	34.44	0.00

Critical value = 7.81
* Not significant at $p = 0.05$

6.4.6 Source discrimination: Multivariate Discriminant Function Analysis

Multivariate Discriminant Function Analysis (MDFA), using the minimization of Wilks' Lambda, was then applied to those properties which had passed the Kruskal Wallis *H*-test. The MDFA tested the ability of the tracer properties to correctly classify the source samples into the appropriate source groups and also provided a quantification of the discriminatory power of the optimum composite fingerprint. The MDFA was initially performed using the stepwise procedure (Collins *et al*., 1997a), where maximum significance of F to enter a property was 0.05 and minimum significance of F to remove a property was 0.10. The results of the stepwise MFDA are presented in Table 6.4.

Table 6.4 *Results from the stepwise MDFA based on the minimisation of Wilks' Lambda in identifying the optimum composite fingerprint for discriminating between grassland, cultivated land, woodland and channel bank source groups in the River Arrow catchment.*

Step	Property	Wilks' Lambda	Cumulative original grouped cases correctly classified (%)
1	Mg	0.67	41.7
2	Cr	0.43	55.1
3	K	0.33	60.6
4	As	0.28	66.9
5	Ni	0.24	66.1
6	Hf	0.21	64.6
7	Zn	0.19	69.3

A composite fingerprint containing the seven properties Mg, Cr, K, As, Ni Hf and Zn produced a Wilks' Lambda value of 0.19, which was the closest to zero that could be obtained following stepwise inclusion of all available properties. However, this fingerprint classified only 69.3% of the original grouped cases correctly. Table 6.5 shows the predicted sample group against the actual group membership for the four source groups, where it can be observed that grassland in particular was poorly discriminated at only 53.33% of correctly classified cases.

Table 6.5 *Results from comparison of predicted sample group membership against actual group membership for the grassland, cultivated land, woodland and channel bank source groups, with percentage of correctly classified cases within each group following stepwise MDFA*

			Predicted Group Membership				Total
		Source Group	Grassland	Cultivated	Woodland	Channel Banks	
Original Group Membership	Count	Grassland	16.00	5.00	7.00	2.00	30.00
		Cultivated	7.00	21.00	0.00	2.00	30.00
		Woodland	6.00	1.00	22.00	0.00	29.00
		Channel Banks	4.00	1.00	1.00	24.00	30.00
	%	Grassland	53.33	16.67	23.33	6.67	100.00
		Cultivated	23.33	70.00	0.00	6.67	100.00
		Woodland	20.69	3.45	75.86	0.00	100.00
		Channel Banks	13.33	3.33	3.33	80.00	100.00

Figure 6.10 illustrates the sample distribution around the four group centroids from the first two canonical discriminant functions following stepwise MDFA. The scatter plots further illustrate the relatively poor discrimination offered by the stepwise derived fingerprint. The group centroids appear to be very close to each other and there is considerable overlap between samples from all source groups. It was considered that

this fingerprint offered insufficient discrimination to proceed with confidence to the ascription phase.

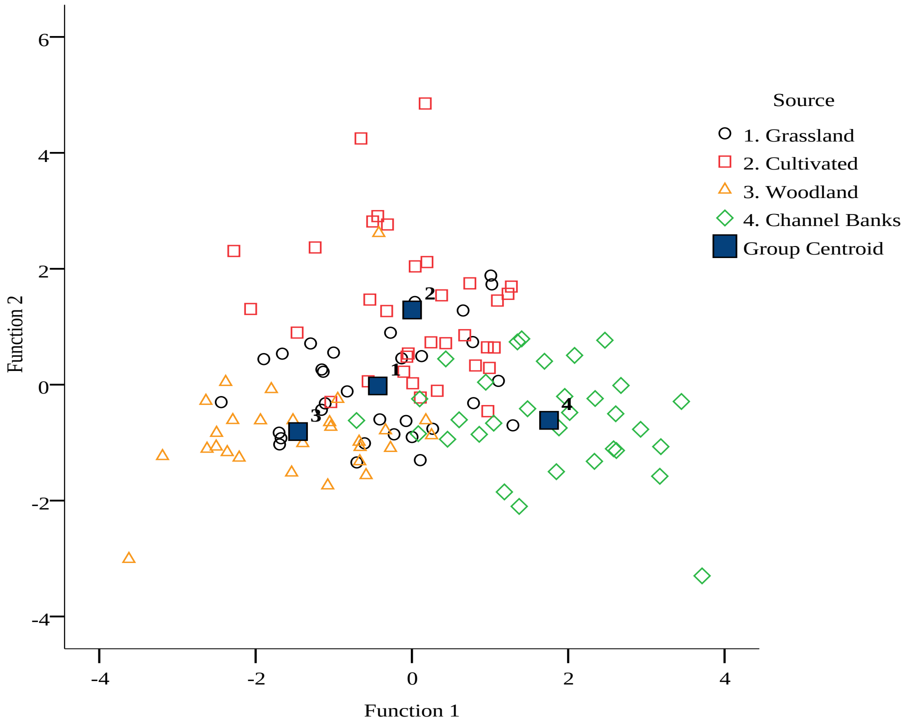

Figure 6.10 *Combined scatter plots showing sample distribution around group centroids from the first two canonical discriminant functions applied to the grassland, cultivated land, woodland and channel bank source groups in the River Arrow catchment following stepwise MDFA.*

Following the relatively poor discrimination achieved by the stepwise entry MDFA, a comparative method using simultaneous entry MDFA was then performed on those properties which had passed the Kruskal Wallis *H*-test. The simultaneous entry MDFA produced a reduced Wilks' Lambda of 0.06, as shown in Table 6.6, and to improved overall discrimination to 87.4% of original grouped cases correctly classified. This fingerprint was derived from an increased number of 26 properties Mg, Hf, Li, Fe, Gd, Nd, Eu, K, Ce, La, Sm, Ni, Sr, Er, Pd, Co, Cr, T,i, Ga, Y, Mn, Pr, As, Zn, Ba and Tb.

Table 6.6 *Wilks' Lambda Test of Functions for properties simultaneously entered into MDFA*

Test of Function(s)	Wilks' Lambda	Chi-square	Significance
1 through 3	0.06	283.54	0.00
2 through 3	0.26	137.03	0.00
3	0.63	47.84	0.00

Table 6.7 presents the discrimination results for the simultaneously entered 26 property fingerprint. It is immediately apparent that discrimination has improved across all source groups, with grassland in particular being improved substantially from 53.33% produced by stepwise MDFA to 76.67% from simultaneous entry. The cultivated land, woodland and channel bank source groups were discriminated at 96.67%, 82.76% and 93.33% respectively.

Table 6.7 *Results from comparison of predicted sample group membership against actual group membership for the grassland, cultivated land, woodland and channel bank source groups, with percentage of correctly classified cases within each group following simultaneous entry MDFA*

			Predicted Group Membership				Total
		Source Group	Grassland	Cultivated	Woodland	Channel Banks	
Original Group Membership	Count	Grassland	23.00	2.00	4.00	1.00	30.00
		Cultivated	1.00	29.00	0.00	0.00	30.00
		Woodland	4.00	1.00	24.00	0.00	29.00
		Channel Banks	0.00	1.00	1.00	28.00	30.00
	%	Grassland	76.67	6.67	13.33	3.33	100.00
		Cultivated	3.33	96.67	0.00	0.00	100.00
		Woodland	13.79	3.45	82.76	0.00	100.00
		Channel Banks	0.00	3.33	3.33	93.33	100.00

Figure 6.11 illustrates the sample distribution around the four group centroids from the first two canonical discriminant functions following simultaneous entry MFDA. The scatter plots illustrate the improved discrimination afforded by the simultaneously entered fingerprint. The group centroids appear more disperate and greater separation can be generally observed between samples from respective source groups, although some overlapping is still evident. It was considered that this composite fingerprint offered acceptable discrimination to proceed reliably to the apportionment phase.

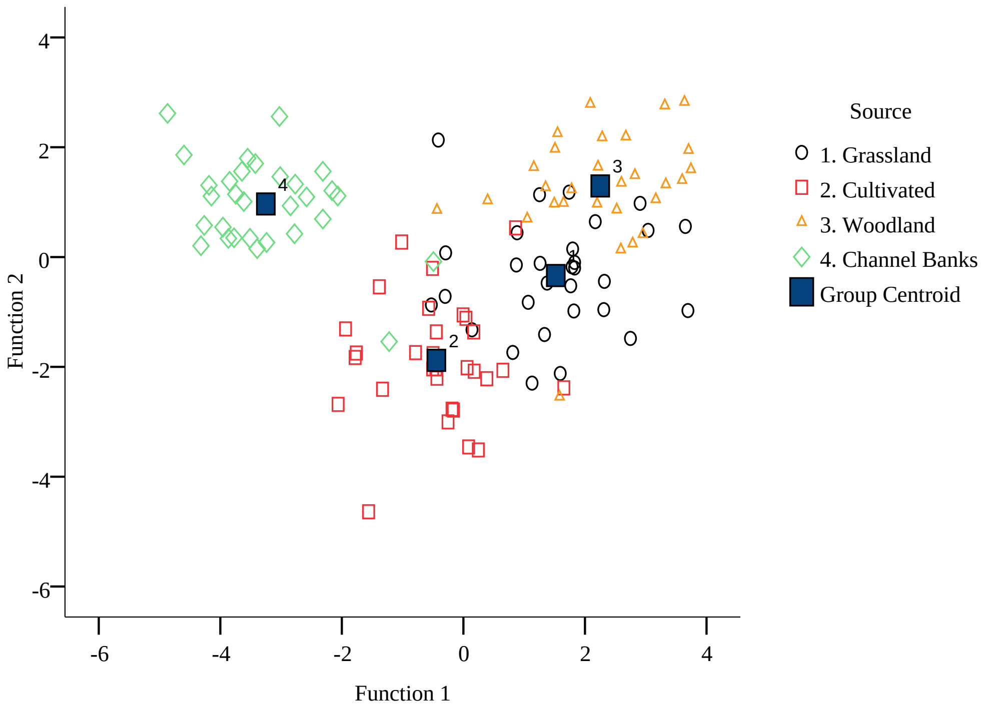

Figure 6.11 *Combined scatter plots showing sample distribution around group centroids from the first two canonical discriminant functions applied to the grassland, cultivated land, woodland and channel bank source groups from the River Arrow catchment following simultaneous entry MDFA.*

6.8 Application of the Mixing Model

A linear numerical mixing model, as described in Chapter 3, was subsequently employed to provide an estimate of the relative contribution of the four potential sediment sources to the individual downcore floodplain sections. The mixing model utilized property-specific weightings, presented in table 6.8. The weightings were based on the discriminatory power of individual fingerprint properties established by individual entry into MDFA and accounted for the variable contributions made by different properties to overall fingerprint discrimination. Uncertainty associated with using a relatively small number of source samples to estimate property mean concentration values was recognised explicitly by the incorporation of a Monte Carlo sampling framework (Collins and Walling, 2007) (see Chapter 3).

Table 6.8 *Mixing model property-specific discrimination weightings*

Property	Individual discrimination	Weighting
Cr	49.60	1.555
Sm	47.90	1.502
Ga	46.20	1.448
Pd	45.40	1.423
Mg	43.70	1.370
Gd	42.90	1.345
Li	42.00	1.317
Eu	42.00	1.317
Er	41.20	1.292
Tb	40.30	1.263
Sr	39.50	1.238
Fe	38.70	1.213
La	38.70	1.213
Hf	38.70	1.213
K	37.80	1.185
Ba	37.80	1.185
As	37.00	1.160
Mn	36.10	1.132
Y	36.10	1.132
Pr	36.10	1.132
Ti	34.50	1.082
Ce	34.50	1.082
Co	32.80	1.028
Ni	32.80	1.028
Nd	32.80	1.028
Zn	31.90	1.000

6.9 Sediment source ascription and historical catchment land use changes

The output from the mixing model applied to sediment from the floodplain core sections, provided estimates of relative source group contributions over time (ca. 1956-2008). The Relative Mean Error (RME) for the combined estimates was 6.6%, which indicated a mean goodness-of-fit of 93.4%. The goodness-of-fit was derived by comparison of measured property concentrations with predicted property concentrations, based on the estimates for the percentage contributions from source groups (see Chapter 3 for details). The apportionment of relative source group contributions over time and RME for each respective sediment core section is presented in Table 6.9. Sediment source apportionment estimates from the respective source groups over the study period are collectively presented in Figure 6.12.

Table 6.9 *Estimated sediment contributions (%) (± standard deviation) from grassland, cultivated land, woodland and channel bank sources in the River Arrow catchment (ca.1955-2008) with associated relative mean error (RME) (%)*

		Estimated sediment contribution (%)				
Depth (cm)	Estimated chronology	Grassland	Cultivated	Woodland	Channel Bank	RME
1	2008	46±19	22±15	15±16	17±11	7
2	2007	35±17	24±15	8±12	33±12	5
3	2007	30±15	25±15	6±9	40±12	4
4	2007	28±15	25±15	3±7	43±12	5
5	2006	30±15	26±14	4±7	40±11	4
6	2006	35±17	24±16	6±11	35±13	5
7	2005	32±15	26±14	4±8	38±11	4
8	2005	28±14	25±14	3±6	43±11	4
9	2004	36±17	24±15	7±11	33±12	6
10	2004	21±13	26±14	1±4	51±12	4
11	2004	26±14	23±14	3±6	48±12	4
12	2003	29±15	23±15	3±7	45±13	4
13	2003	23±13	26±14	2±4	49±12	4
14	2002	25±13	26±14	2±5	48±11	4
15	2002	25±13	26±14	2±5	47±11	3
16	2002	26±13	26±14	3±6	45±11	4
17	2001	33±15	26±14	4±8	36±11	5
18	2001	31±16	26±16	4±8	39±12	5
19	2000	17±13	27±15	1±3	55±12	4
20	2000	14±12	30±14	0±2	56±12	4
21	2000	21±13	28±14	1±3	49±11	4
22	1999	25±14	28±15	2±5	46±12	4
23	1999	27±15	26±16	3±6	44±13	5
24	1998	28±15	27±15	3±7	42±12	4
25	1998	27±15	23±15	4±8	45±13	4
26	1997	28±14	29±15	2±5	41±12	4
27	1997	24±14	29±15	1±4	45±12	4
28	1997	36±17	27±16	6±11	31±13	5
29	1996	33±17	26±16	5±9	36±13	5
30	1996	31±15	25±14	4±8	40±12	4
31	1995	31±16	25±16	4±8	40±13	4
32	1995	29±15	27±16	2±6	42±13	5
33	1995	38±20	33±19	9±14	20±14	7
34	1994	41±23	32±20	11±16	16±14	9
35	1994	39±24	30±21	12±17	19±16	9
36	1993	35±21	35±20	7±13	23±17	7
37	1993	37±23	35±21	8±14	21±17	8
38	1993	21±18	37±21	1±5	41±19	6
39	1992	35±23	33±22	7±13	24±18	8
40	1992	39±24	34±22	9±15	17±17	8
41	1991	38±23	33±21	10±16	18±16	8
42	1991	35±24	29±22	11±16	26±19	9
43	1991	36±26	25±22	13±19	25±20	12
44	1990	38±27	27±24	13±20	22±19	13
45	1990	39±28	26±22	17±23	18±18	15
46	1989	37±27	31±24	13±19	20±19	12
47	1989	37±26	29±23	13±19	21±19	10
48	1988	37±25	34±21	13±17	16±16	8
49	1988	36±23	38±21	8±13	19±17	7
50	1988	30±20	41±20	4±9	25±17	6
51	1987	33±22	33±21	8±13	27±18	7
52	1987	31±22	34±21	7±12	28±19	8
53	1986	31±23	33±22	8±13	27±19	7
54	1986	32±24	36±23	9±14	24±19	8
55	1986	23±19	43±21	3±7	31±19	6
56	1985	23±21	42±22	3±7	32±21	6
57	1985	26±22	41±22	4±10	29±21	6
58	1984	23±20	43±21	3±7	31±20	5
59	1984	34±23	40±21	9±13	17±16	8
60	1984	24±20	43±21	3±7	30±19	7
61	1983	35±25	39±22	10±15	17±17	8
62	1983	39±27	33±23	15±20	13±16	11
63	1982	42±32	25±24	22±26	11±16	18
64	1982	36±27	36±20	13±24	14±13	9

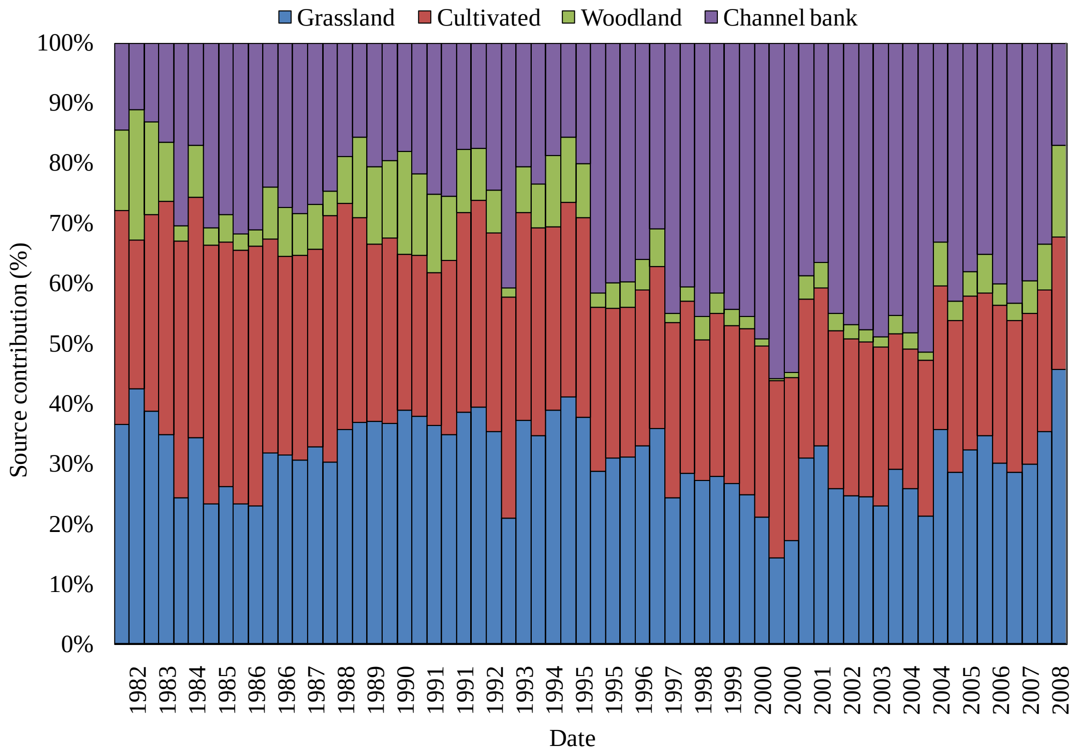

Figure 6.12 *Temporal changes in the relative contributions to floodplain sediment from grassland, cultivated land, woodland and channel bank source groups in the River Arrow catchment ca. 1982–2008.*

The source apportionment showed general fluctuations in the relative sediment contributions from the source groups over approximately 26 years, 1982-2008. Channel bank sources showed the widest range of relative contributions from a low of 14% around 1982 to a peak contribution of 55% in 2000. The channel bank relative contributions remained fairly high until around 2004, from which point they generally declined to a contribution in 2008 of 17%. Mean relative sediment contributions from channel banks for the study period were 32%. Grassland sources contributed around 42% in 1982 and declined to 23% in the mid 1980's, from which point relative contributions grew steadily throughout the early to mid 1990's. There was a decline in relative contributions from grassland sources throughout the mid to late 1990s, followed by a more general increase from around 2000 to 2008. Mean relative sediment contributions from grassland sources over the study period was 31%. Cultivated source relative contributions appear to have remained fairly consistent over the time period, with a peak contribution around 1986 of 42% decreasing steadily to the lowest apparent relative contribution of 22% around 2008. Cultivated source mean relative contributions over the study period were 29%. The relative sediment contributions from woodland sources varied quite considerably, from a peak of 20% in 1982 to a minimum contribution of 0.4% in 2000. Woodland related contributions appear to have grown from the mid 1980s to 17% around 1970. Throughout the 1970s woodland contribution rates slowly declined and remained low throughout the 1980s, 1990s and early 2000s. The top section of the core representing 2007/2008 contained an uncharacteristic relative contribution from woodland sources of 15%. Mean relative contributions from woodland topsoil sources over the study period were 6%.

Data from the Agcensus Database (EDINA, 2009) representing changes in land cover, cropping patterns and livestock numbers throughout the area of the catchment were collated for the years; 1969, 1972, 1976, 1981, 1988, 1993, 1996, 2000 and 2004. Existing published information and personal communication complemented the Agcensus data as sources of reference for land use changes in the recent past. It should be borne in mind that the trend lines between the Agcensus data points are included here for illustrative purposes and therefore values which are represented for the intervening years are not quantified.

The potential sediment problems associated with an increase in potato cultivation was a major driver for investigating the historic sources of sediment in the River Arrow catchment. The area of land under potato cultivation increased by over 800% between 1969 and 2004, as illustrated in Figure 6.13.

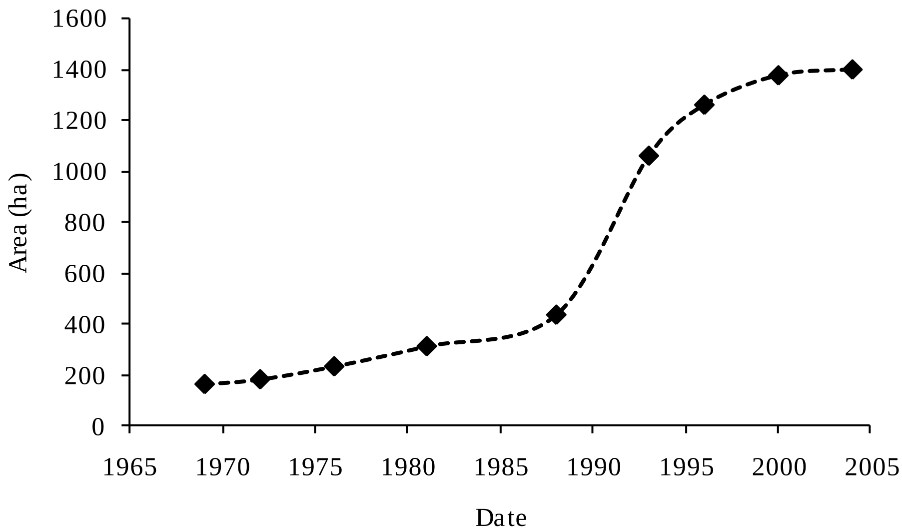

Figure 6.13 *Land cover area for potato cultivation in the River Arrow catchment 1969-2004*

Land cover data for potato cultivation was combined with those of other generally late-harvested crops which are often associated with high erosion risk (Quinton and Catt, 2004; Evans, 2005; Austerwald, 2006; Feiner and Austerwald, 2007), including fodder maize and sugar beet. Data were similarly combined for high erosion risk autumn-sown crops, including wheat, winter-barley and oilseed rape. Temporary grassland and permanent grassland data were also collated for comparative analysis. The combined plots are shown in Figure 6.14. The historic dominance of land cover in the catchment by permanent grassland, mainly used for sheep production, is clearly illustrated. There was a fairly steady increase in the area recorded as permanent grassland from the early 1970s up to the mid 1990s. This may reflect improvement of marginal grassland and the long term establishment of reseeded grass lays on land previously in rotation. The decline in permanent grassland since the mid 1990s appears to correspond with the increase in land under cultivation, perhaps as pasture was ploughed up for more profitable enterprises. Temporary grassland was generally the second largest land use type until the mid 1990s, since when the area under autumn sown crops has increased to form the second largest land use. These patterns serve to illustrate the changes associated with the rotation system of arable cultivation in the catchment as alternative break crops found favor with farms diversifying from livestock production. The rise of potato cultivation since the early 1990s is reflected in the increase of late harvested crops, of which potatoes form an increasing constituent. The increased area under both late harvested crops and autumn sown crops generally correspond to the decline in area previously under permanent and temporary grassland.

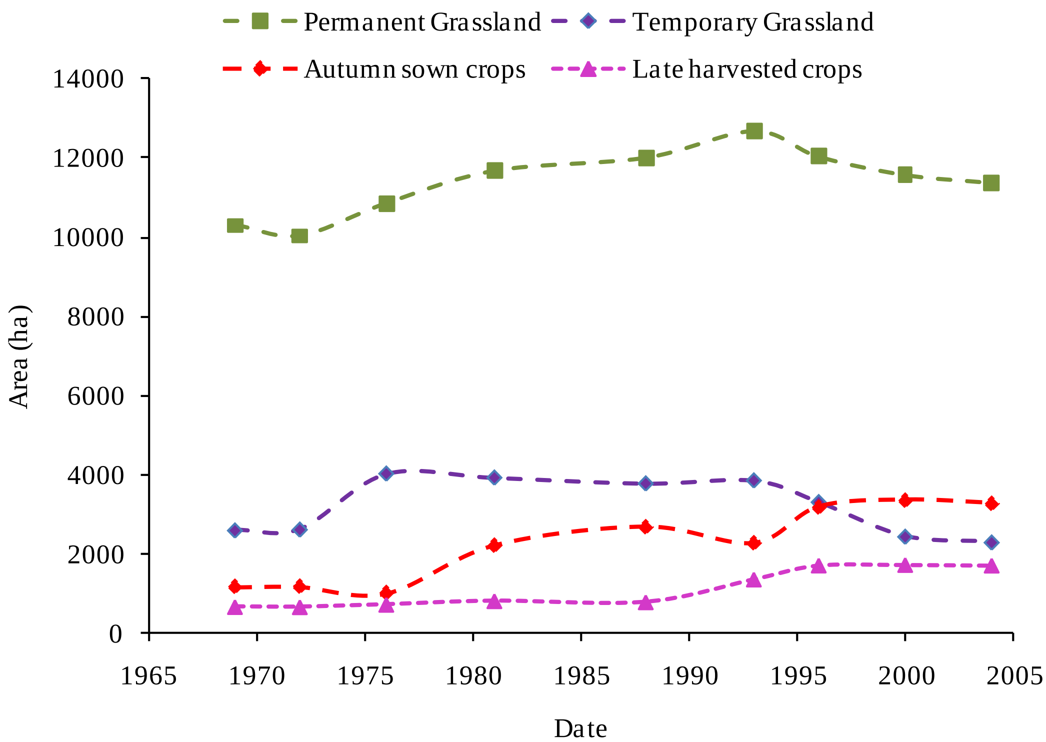

Figure 6.14 *Land cover areas for permanent grassland, temporary grassland, autumn sown crops and late harvested crops in the River Arrow catchment 1969-2004*

Clearly defined relationships between historic land cover changes and the variations in relative source contribution estimates provided by the mixing model are not always easily identified. The percentage area of land within the overall catchment reported under cultivation fluctuated from 18.5% in 1969 to 26.5% in 2004. The average area under cultivation during the study period was 23% which produced an ascribed mean relative contribution of 28%. The results reported for cultivated source contributions over the study period would seem to indicate that although the area under cultivation of late-harvested and early sown crops has increased significantly, when considered on a catchment scale, the impact on sediment source contributions initially appears unaffected. However, it may be worth reconsidering here the comparative analysis of SSA for sources and the floodplain, which indicated that the finer fraction present in the sources was not present in the study floodplain. This finer fraction may represent a greater historic contribution provided by cultivated sources to suspended sediment which was transported over and past the study floodplain. This more detailed information requires a historic resolution which the fingerprinting technique as applied to floodplain cores, unfortunately does not afford.

Fluctuations in stocking patterns within the catchment, calculated from individuals per hectare data are shown in Figure 6.15. Total numbers of cattle and calves over 6 months increased from 22,319 in 1969 to a peak recorded in 1972 of 24,598, from which time total numbers slowly declined to around 14,447 by 2004. This decline is possibly as a result of ever increasing dairy overhead costs and decreasing relative returns due to highly competitive pricing encouraged by major retailers. Farms in the catchment are generally fairly small-scale units and as such are limited in their ability to take advantage of economies of scale. The effects of foot and mouth disease, which hit a number of farms in the catchment, are likely to have had a major contribution to the sharp decline in both sheep and cattle numbers between 2000 and 2004 (Collins, 2009. pers. comm.). Faced with the devastating experience of foot and mouth disease, on-going market conditions and removal of headage payments for livestock due to CAP reform, re-stocking has not been an automatic choice for many farms in the catchment.

For comparative land use impact analysis, stocking densities (LU ha^{-1}) for cattle and sheep were calculated from head per hectare data on the assumption that combined stock grazed the land area under permanent grassland for each associated year. The resolution of data for pig production did not discriminate between outdoor production systems or intensive indoor systems. Pigs were therefore excluded from the combined stocking density calculations on the assumption that their contribution could not be adequately defined. Overall, pig numbers in the catchment were low and no outdoor pig production was observed in the catchment during field visits. Pigs were therefore not thought to have a significant impact on sediment sources.

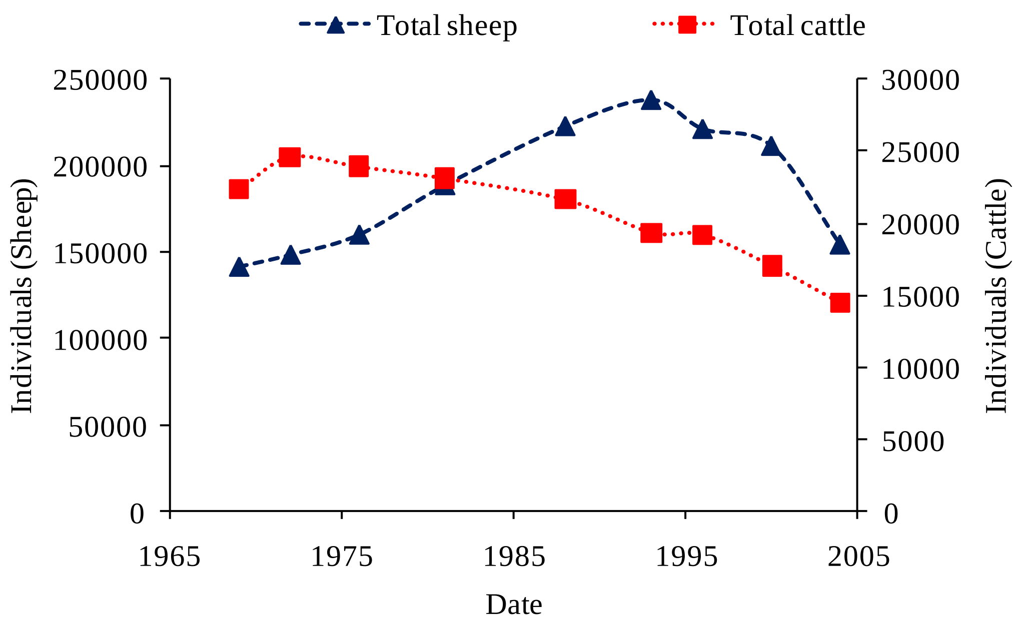

Figure 6.15 *Livestock numbers for cattle and sheep in the River Arrow catchment from 1969 to 2004*

Livestock units (LU), which are commonly used to assess the impact of grazing livestock on pasture by allowing comparison of live stock types, were calculated as detailed in Chapter. As previously observed, the collation and presentation of the Agcensus cattle data in the available datasets are somewhat inconsistent across the time period, with the result that the precise age of cattle cannot be adequately determined for certain years. Consequently, average representative LU figures, as used by Sullivan *et al*. (2004), were applied to all livestock for which data were available. Total LUs were divided across available grassland to provide estimates of stocking densities (LU ha^{-1}) 1969-2004, presented in Figure 6.16.

The percentage area of land within the catchment reported under grassland fluctuated from 63% in 1969, through 77% in 1993, to 64% in 2004. The average area under grassland during the study period was 69% which produced an ascribed mean relative contribution of 31% to catchment sediment sources.

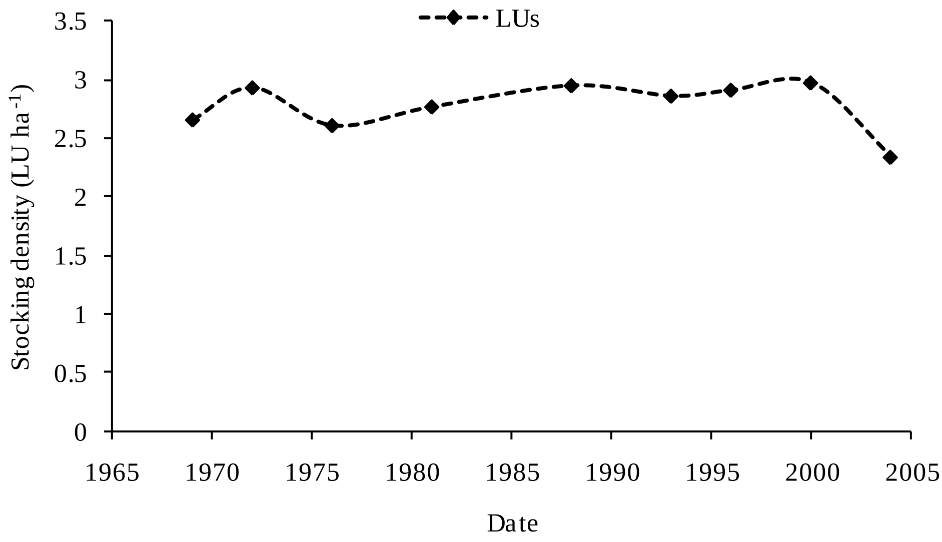

Figure 6.16 *Stocking densities (LU ha^{-1}) in the River Arrow catchment from 1969-2004*

The observed trend of increasing contributions from grassland sources over the period from the early 1960s up to the mid 1980s appears to bear some correspondence with the history of stocking density. After this time, grassland contributions appear to have decreased relative to channel bank contributions, while over the same period stocking densities stabilised and then increased again until 2000. This suggests that when the pressure associated with stocking densities reached a certain point the major impact on sediment sources shifted from grassland to channel banks. Between 2000 and 2004 both stocking densities and relative sediment contributions from channel banks declined substantially, whilst relative contributions from grassland increased once more. This indicates an identifiable relationship between stocking densities and relative sediment contributions from channel bank sources. A large proportion of channel bank sources are incorporated in the many streams and becks which form the upland tributaries of the River Arrow catchment and most of these are unfenced with open access to livestock. It is also apparent that where livestock grazing persisted in the mid and lower catchment riparian boundaries were often in poor repair allowing large-scale erosion at certain favoured drinking points. The large number of and extent of the upland tributaries is undoubtedly a significant reason for the relatively high contribution from channel bank sources. However, the fairly well formed banks in the mid and lower reaches comprised often of fairly light and quite mobile material makes them particularly susceptible to erosion, particularly given the flashy nature of the River Arrow in the study area.

Relatively large-scale bank failures were observed at various points as illustrated in Figure 6.17.

Figure 6.17 *Eroding channel banks in the River Arrow catchment*

It might be considered that the substantial reduction in stocking density between 2000 and 2004 would lead to reduced contributions from grassland as the pressures of livestock related erosion declined. However, it should be borne in mind that the stocking density values are distributed on a catchment-wide basis and do not necessarily reflect localised areas of much greater density of herd or flock populations. Economic pressures to increase herd sizes grew substantially over the period. Whilst CAP reform and the effects of foot and mouth disease may have reduced catchment-scale stocking densities, larger herds and flocks remain more economically viable on an individual farm-scale. Consequently, increased numbers of animals can become concentrated on fewer holdings, as those farmers leaving the livestock and dairy industry lease land for alternative production such as potato cultivation. Cross-compliance for farm payments has encouraged improved riparian fencing, in conjunction with the observations above, these circumstances might increase erosion risk on pasture topsoil whilst concurrently reducing the total area of channel bank at risk from poaching. Further, grassland which is newly ploughed for crop production, such as that favoured by potato producers trying to avoid residual soil borne diseases, may well display many of the geochemical characteristics of a historic grassland function through at least one crop rotation cycle.

Woodland source apportionment is problematic to interpret here in relation to the Agcensus data, as woodland data were only available for years 1972, 1976, 1981, 1988, 2000 and 2004 (Figure 6.18). In addition, no distinction was made between semi-natural ancient woodland and conifer forestry plantations.

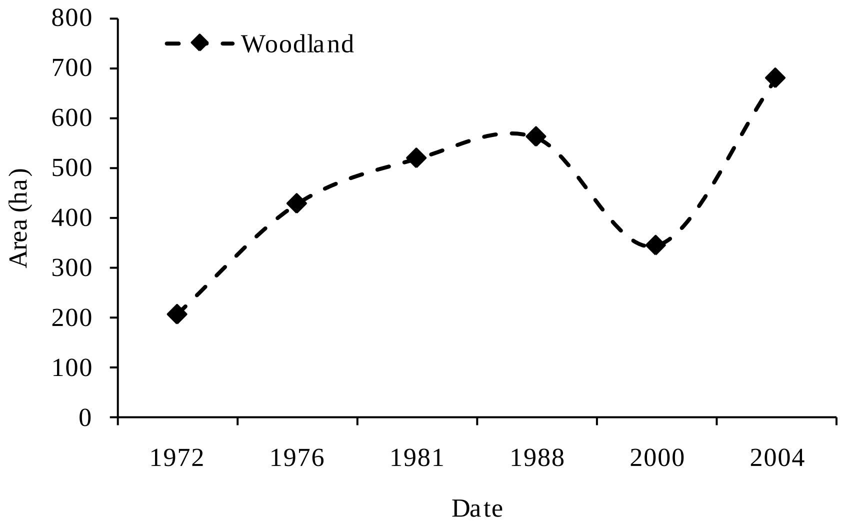

Figure 6.18 *Land cover area of woodland in the River Arrow catchment 1972-2004*

The percentage area of land within the catchment reported under woodland fluctuated from 0.9% in 1972, to 2.9% in 2004. The average area under woodland during the study period was 2% which produced an estimated mean relative contribution of 6%. Throughout the 1970s and 1980s many UK broadleaf woodlands were felled and replanted or ‘converted’ with conifers (Woodland Trust, 2000). This fate befell many Herefordshire woodlands (English Nature, 2009). Although detailed conversion data are not available specifically for the catchment, the age and areas of conifer plantations observed within the catchment appeared to correspond with this timeline and practise. Therefore, perhaps it should not be surprising to see relatively high contributions from woodland sources over this period. Clear felled woodland, preparation for replanting and immature plantations expose bare light woodland soils to erosion and therefore represent a major high risk sediment source (Clark, 2009). After replanting, even fast growing conifers can take some years to replace the canopy cover. During this time, steep sided plantations adjacent to water courses, such as those observed in the catchment, could be expected to be particularly high risk. Woodland cleared and replanted during the 1960s and 1970s may well have taken 10 to 15 years to mature enough to replace the canopy cover and this corresponds with the observed high contributions up to the early 1980s. Contributions are significantly reduced during the mid to late 1980s, 1990s and the first half of the 2000s. The only data available for this period was from 2000 and these indicated a reduced area under woodland at this time. This corresponded with a major change in the way Agcensus data was compiled and is difficult to interpret. The relatively high sediment contribution from woodland sources observed for 2007-2008 may well be due to the combined influence of increased afforestion indicated by the Agcensus data and harvesting of the tress planted during the 1960s and 1970s.

6.10 Conclusion

The Agcensus data interrogation for the River Arrow catchment was complicated by changes in the method of data collection applied since 2000. In 2000, Welsh returns became separately gathered and therefore required separate analysis. There were some associated changes in category types and resolution of detail. Problems previously highlighted with regard to cross-parish land holdings, were further complicated in the River Arrow catchment by problems associated with cross-border holdings. However, as the Welsh section of the catchment was relatively small and limited to upland areas of rough grazing and semi-improved grassland with no significant arable production, the effects of data acquisition changes on consequent analysis were thought to be negligible.

The River Arrow catchment is dominated in the extensive upland area by permanent grassland largely under sheep production, which forms a large part of the study area. Although the area of the mid and lower catchment under arable production supports a large percentage of high risk crops, of which potatoes continue to be an increasing constituent, the overall land cover within the catchment occupied by arable production is relatively small. Notwithstanding a certain lack of resolution, on proportional basis cultivated land sources contributed a much higher percentage of sediment to the flood plain than grassland sources. Woodland sources were also observed to contribute sediment disproportionately to their land area, particularly during the period of afforestation. An identifiable relationship was observed between the level of stocking density and sediment contributions from channel bank sources. The positive benefit of cross-compliance requirements may have helped to reduce the negative impacts of livestock on channel banks, although further data would be required for more recent periods to substantiate this influence. There is possible cause for concern in relation to the onfarm polarizing of livestock, potentially causing localised areas of high stocking density leading to increased impacts on grassland at a farm-scale whilst overall stocking densities appear to be in decline at a catchment-scale. This case study highlights the requirement for the tighter application of sediment source mitigation measures in regard to high erosion risk crop cultivation and the possible requirement for improved site-specific stocking density regulation.

CHAPTER 7 - THE RIVER WAVER CATCHMENT: RESULTS AND INTERPRETATION

7.1 Introduction

The seventh chapter in this thesis presents and interprets the results from the fourth case study and is based on the application of the sediment source fingerprinting technique to floodplain sediment cores from the River Waver Catchment, Cumbria, UK, with the aim of relating relative changes in the source of floodplain overbank sediment to historical land use change over approximately the last 75 years.

The River Waver is one of the designated priority catchments of the ECSFDI (Defra, 2009a). The key land management issues under consideration within the River Waver catchment include the increased connectivity of nutrient rich arable fields to receiving waters due to changes in flood risk management practices and the reported expansion of autumn sown cereals and fodder maize cultivation (Defra, 2009a).

7.2 The River Waver catchment description

The River Waver catchment is situated in the North West of Cumbria, England, close to the border with Scotland. The Waver rises on the Caldbeck Fells at Wavergillhead and flows west and north across the Solway plain, past Wigton, via Waverton, Waverbridge, Lessonhall and Abbytown to discharge into Moricombe Bay on the Solway Firth. The Solway coast has been designated as an Area of Outstanding Natural Beauty since 1964 and encompasses a variety of rare habitats and spectacular landscapes (Solway Coast AONB, 2009). The extent of the catchment identified for this study incorporates the River Waver from its source at Wavergillhead and incorporates all major and minor tributaries down to the designated catchment outlet on the floodplain, above the limit of general tidal influence, at Abbeytown.

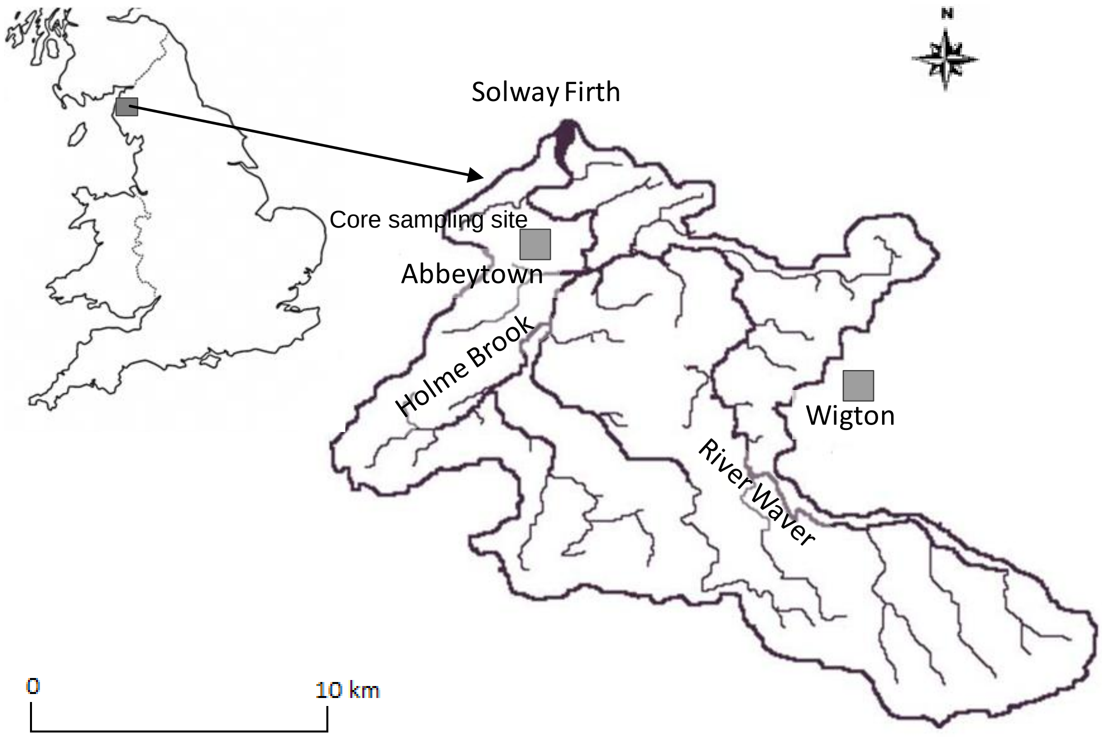

Figure 7.1 *The location and study area of the River Waver catchment, Cumbria, UK*

The geology of the River Waver catchment incorporates red, grey and green mudstones and siltstones, forming part of the Triassic Mercia mudstone group. The drift deposits in the catchment consist of a glacial till consisting of rock clasts of pebble to boulder size and irregular bands or lenses of sand and gravel (Institute of Geographical Sciences 1976).

The soils of the River Waver catchment are characterised in the headwaters by predominantly acid loamy upland soils with a wet peaty surface, which are found along the upland ridge to the south (NSRI, 2010). The slopes towards the plain feature slowly permeable seasonally wet acid loamy and clay soils, which give way to more base-rich loamy and clay soils on much of the plain. The area around the outflow is characterised by loamy and clayey soils of coastal flats with naturally high groundwater. Fertility in the catchment is generally low on the upland slopes and moderate to high on the plain (NSRI,2010).

Land use in the catchment is predominantly grassland (NSRI, 2007). Agriculture in the upland area of the catchment is dominated by sheep production. Throughout the early and mid part of the twentieth century the plain was predominantly under dairy production with numerous small herds, with heavily drained areas on the plain supporting some arable cultivation (e.g. wheat, barley and root crops) much of it for livestock feed (Holme St. Cuthbert History Group, 2009). In the later part of the twentieth century and early 2000s there has been a shift in arable cultivation to include fodder maize cultivation and some small areas of autumn sown cereals (EDINA, 2009)

The woodland in the catchment includes small-scale mixed and coniferous plantations. Woodland areas in the catchment are relatively sparse and generally not particularly well connected to the River Waver or its tributaries. Such pockets of woodland as there are were observed during field visits to support the nationally rare red squirrel.

Considerable clearing of riparian vegetation and bank reprofiling has occurred at various period over the last 20 years under EA flood risk management measures, which have been applied to open field drains, ditches and channel banks throughout the catchment (Cox, 2008. Pers.Comm.). Wooden revetments have been installed along certain reaches in an attempt to reduce erosion due to scour. These engineering practices have increased the connectivity to water courses from fields under both arable cultivation and intensive livestock production.

The flood risk management measures are primarily orientated around reducing flooding on the regions roads and urban centres. Consequently, large areas of the plain can remain saturated for considerable periods of time leading to loss of soil integrity due to livestock poaching and trafficking pressures. These pressures can increase the risk of soil mobilisation and runoff, with associated implications for nutrient transport.

Despite the northerly latitude and westerly aspect of the River Waver catchment, the local CFSO has identified the expansion of autumn sown cereals and fodder maize cultivation as another key cause for concern (Cox, 2008. Pers.Comm.). As identified above, the soils of the plain can remain saturated for considerable periods of time and whilst these is far from ideal conditions for arable cultivation, economic pressures require farmers to pursue such ventures and this leads to increased access to the land by heavy machinery late in the year. This can cause soil compaction and lead to increased erosion and runoff.

These problems were identified as major causes for concern in the River Waver catchment leading to its Priority Catchment designation under the ECSFDI (Defra, 2009a). Figure 7.2 shows some of the sediment associated problems and risks within the River Waver catchment.

Figure 7.2 *Fields adjacent to water courses in the River Waver catchment, exhibiting sediment-associated problems and risks. Clockwise from top left: sheet erosion and runoff from intensively managed grassland; cultivation of maize directly adjacent to main river channel; slurry application directly adjacent to steep re-profiled tributary channel; substantial channel bank collapse*

7.3 Floodplain sampling site selection

Potential floodplain sampling sites were identified for collection of overbank sediment cores through the use of topographic maps, satellite imagery, ground observation and anecdotal evidence. This process pinpointed sites which were regularly inundated by overbank flooding, with associated potential to receive and store sediment representative of fluxes mobilised during flood events. It was important that coring sites were situated above the immediate tidal reach to avoid mixing with recycled estuarine and coastal sediment. Three key potential floodplain coring sites were identified within relatively close proximity to Abbeytown. The sites were situated at Abbey House Farm, Raby Farm and Applegarth Farm respectively, as shown in Figure 7.3. The requirement that the sites had not been cultivated within the recent past, to preserve the historical sedimentation record intact, was substantiated through discussion with the landowners, who had personal knowledge of the sites going back between 40 – 75 years. The anecdotal evidence was combined with a basic ecological appraisal of the sward composition and plant biodiversity at the sites. The species *Soft Rush* (Juncus effusus), often associated with wet or damp uncultivated soils, was observed at the Abbey House Farm and Raby Farm sites. The sward at all sites appeared to contain a diverse combination of grasses, further indicating a general lack of cultivation.

A total of eight cores with potential for use in subsequent sectioned analysis were collected from the identified sites. Nine reference cores were also collected from a nearby undisturbed topographically level site overlooking the floodplain at Roundhill Farm, Aldoth. The reference site was considered to have been subject to neither soil erosion nor sediment deposition and could therefore be considered as representing a ^{137}Cs atmospheric fallout control reference for the immediate area during subsequent radioisotope inventory analysis on floodplain cores.

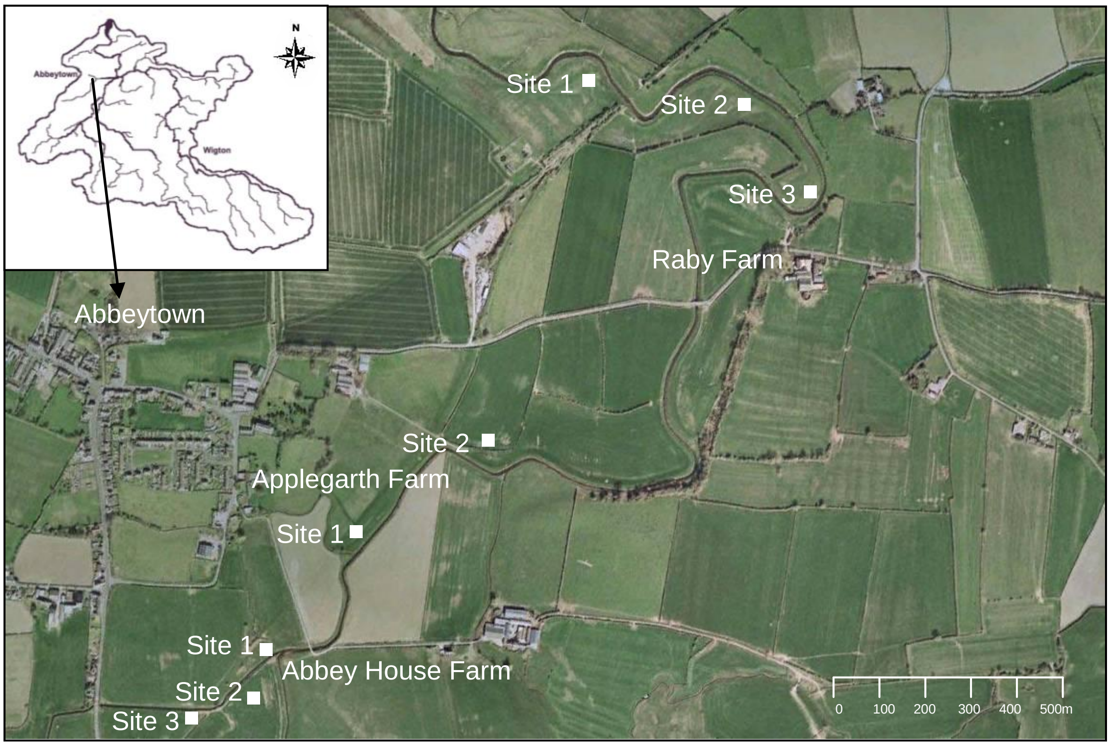

Figure 7.3 *The River Waver catchment floodplain core sampling sites at Raby Farm, Applegarth Farm and Abbey House Farm, Abbeytown, Cumbria, U.K (Google Earth, 2010).*

For each core with potential for use in subsequent sectioned analysis, an adjacent core was extracted for the purpose of estimating the ^{137}Cs bulk inventory for the associated site (see Chapter 2). The bulk cores were dried, then sieved to <2mm and analysed for ^{137}Cs using a gamma spectrometer (see Chapter 2). The bulk inventories were compared with those from the Roundhill Farm reference site. Following comparison of the bulk inventories for the floodplain cores to those of the reference site, illustrated in Figure 7.4, the floodplain site estimated to have received the greatest sediment deposition was identified as Site 3, at Abbey House Farm. The corresponding core from Abbey House Farm Site 3 was accordingly sectioned into 1cm horizons, dried, disaggregated, sieved and prepared for laboratory analysis.

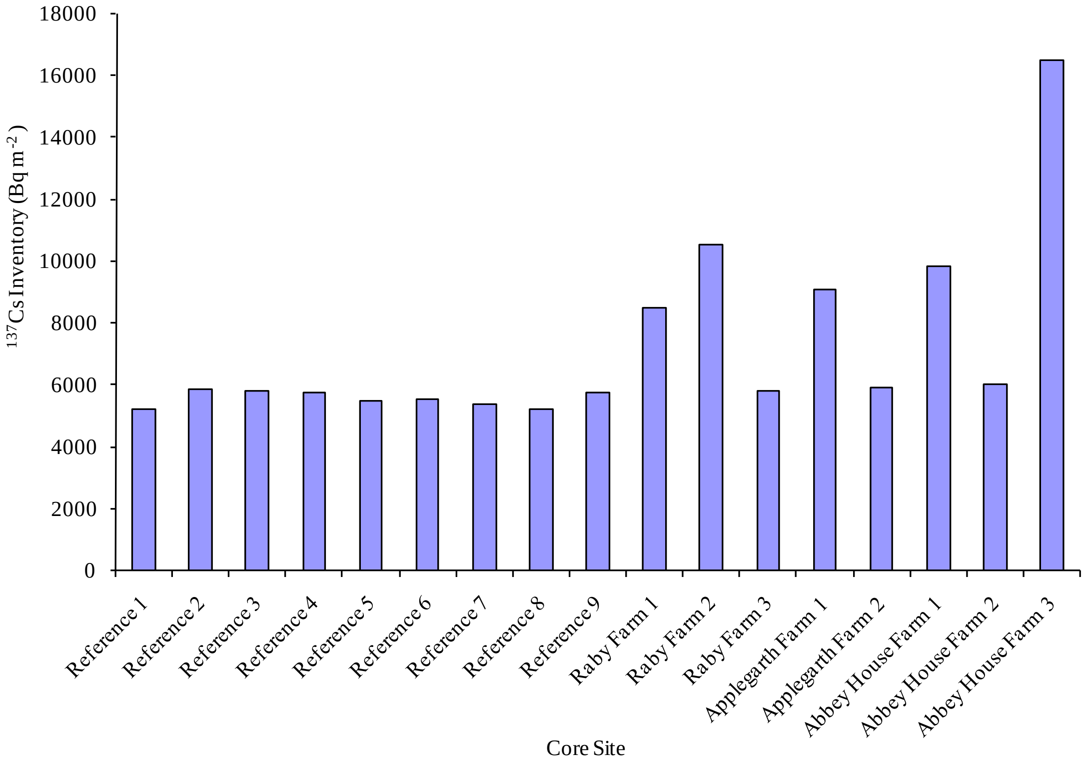

Figure 7.4 *^{137}Cs inventories for the floodplain sediment cores and local reference cores collected from the River Waver catchment*

7.4 ^{137}Cs Radioisotope geochronology

In most regions of the UK it might be acceptable to assume that the peak of ^{137}Cs activity in a core profile corresponded to the peak ^{137}Cs fallout from atomic weapons testing which occurred in 1963. However, following the catastrophic failure and explosion at the Chernobyl nuclear power plant in April 1986, the ensuing plume containing various radioisotopes, but specifically here ^{137}Cs, drifted over Europe. This plume encountered heavy rain as it passed over North West Scotland and Cumbria on May 2nd and this resulted in these areas receiving considerable radioactive fallout over a short time period. Estimates of the resulting levels of activity have varied considerably (Wynne, 1989). Smith *et al.*, (1996) suggests that these inconsistencies may relate to local transport processes immediately following deposition which could have affected distribution and spatial concentrations. Sanderson and Scott (1989) recorded activity in certain locations of over 60,000 Bq/m^2, during an aerial radiometric survey of West Cumbria. Twenty three years after the storm of May 2nd 1986, certain farms in the county were still under government restrictions in 2009 (Hickman, 2009). The Chernobyl incident should therefore be considered explicitly when analysing the ^{137}Cs profiles of any core retrieved from sites in North West Scotland or Cumbria.

^{137}Cs ($T_{1/2}$ = 30.17 yr) assay of individual core sections was undertaken by γ-ray spectrometry, in order to establish the chronology of the sediment core profile. The depth distribution profile of ^{137}Cs activity concentration within the Waver floodplain core is shown in Figure 7.5. The depth distribution of ^{137}Cs within the core was analysed and the horizon containing peak activity was identified at 19 cm. A second, lesser peak was observed at 32 cm. In consideration of the foregoing discussion, it was assumed that the 19 cm peak corresponded to the Chernobyl incident in 1986 and that the 31 cm peak could be realistically associated with the peak in bomb derived fallout in 1963. The apparent lack of clearly defined tail-off after 1963 and before 1986 may be due to subsequent diffusion and migration of ^{137}Cs through the organic fraction of soils at the sample site. There was an apparent increase in sedimentation rates between 1986 and 2008. A time-averaged deposition rate of 0.6 cm $year^{-1}$ was calculated for the core sections between the marker peaks and this was extrapolated down the core from the 1986 peak to provide an approximate chronology for the sections within that range. Similarly, a time-averaged deposition rate of 0.81 cm $year^{-1}$ was calculated for the core sections above the 1986 marker and extrapolated to provide an approximate chronology for the upper sections of the core. The general appearance of the profile suggested that deposition had probably been relatively continuous over time and that the core site was largely undisturbed by modern agriculture (Walling and He, 1992).

Further consideration could be given to potential research opportunities related to the high incidence of Chernobyl fallout over Cumbria. Zheltonozhsky, *et. al*. (2001) reported that ^{60}Co and ^{152} Eu are detectable in trace amounts in bomb derived hot particle fallout but are absent from similar Chernobyl derived fallout, whilst in contrast ^{125}Sb and ^{144}Ce are present in Chernobyl hot particles and not in those from weapons tests. Other studies have also found traceable radioisotope differences between weapons derived and Chernobyl derived fallout (Entwistle *et. al.*, 2003; Ketterer *et. al.*, 2003; Ketterer and Szechenyi, 2008). Determination of identifying radioisotopes within core horizons could potentially help to differentiate between weapons-derived and Chernobyl-derived peaks, and thereby aid in improving chronological estimation. Similarly, there may be potential for increased resolution for studies of erosion rates in areas which have received detectable radioactive particulate fallout from both sources.

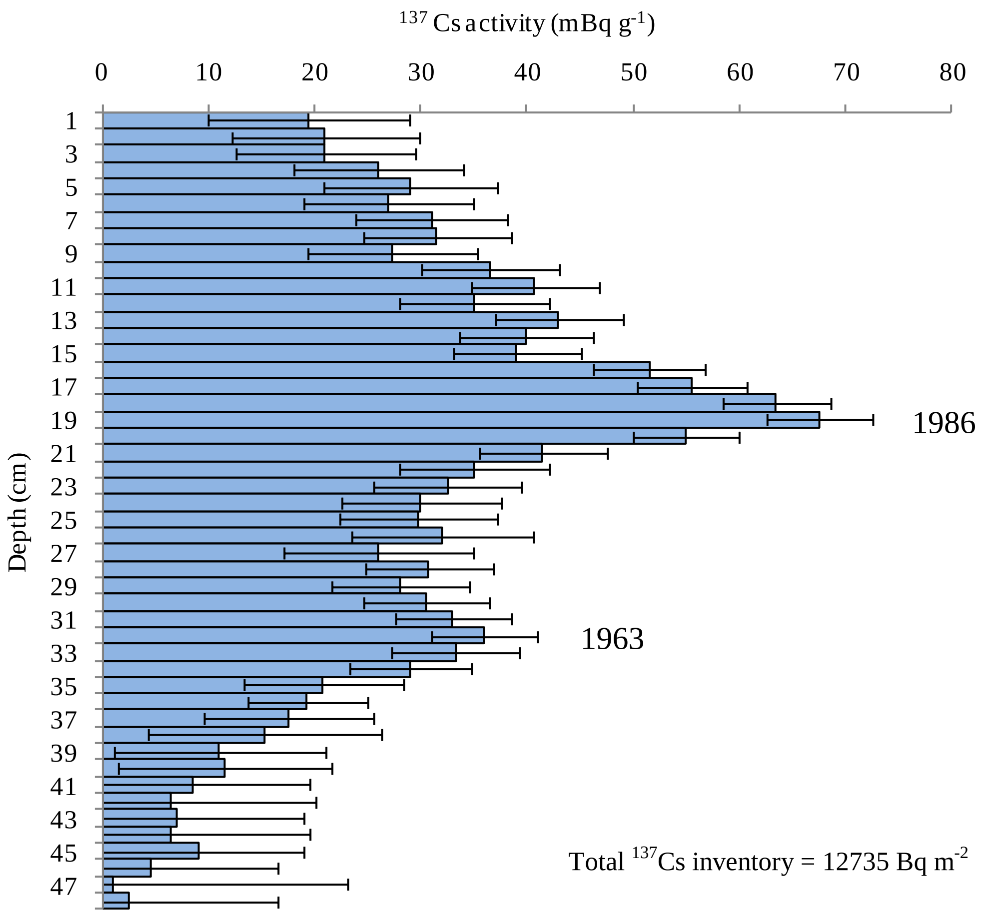

Figure 7.5 *The depth distribution profile of* ^{137}*Cs with associated total inventory from the River Waver floodplain core, Site 3, Abbey House Farm, Abbeytown, Cumbria*.

7.5 The sediment source fingerprinting technique

7.5.1 Source samples

In accordance with the methodology detailed in Chapter 2, surface scrapes (<2cm depth) from 3 distinct potential sediment source groups namely, grassland topsoil, cultivated topsoil and eroding material from channel banks, were retrieved from 90 sites throughout the Waver catchment, providing 30 samples for each respective source group. To improve representation, each source sample comprised around 10 sub-samples, collected from an immediate 0.5 km^2 area. The samples were prepared and analysed, as detailed in Chapter 2. Analysis provided information on particle size composition, SSA and concentration values for a suite of 48 potential geochemical properties, including heavy metals, trace metals, lanthanides and actinides, from which to identify an appropriate composite fingerprint.

7.5.2 Particle size effects

The available suite of 48 properties was tested for correlation between sample SSA and sample fingerprint property concentration within the three source groups using Spearman's rho. A summary of results for correlation between sample SSA and property concentration is shown in Table 7.1.

Based on 147 grouped relationships, 26 (17%) showed significant correlation at $p = 0.01$ and 27 (18%) showed significant correlation at $p = 0.05$. Within the grassland, cultivated land and channel banks source groups, significant correlation, $p < 0.05$, can be observed in 45%, 22% and 41% of cases respectively. Only 2 properties, Ni and Cu had concentration values which exhibited significant correlation with SSA across all three source groups.

After consideration of the correlation results, it was not considered appropriate to apply particle size correction in this instance. It was assumed that by disaggregating and sieving source and floodplain samples to <63 µm during processing, sufficient account had already been taken of any effects of nominal grain size dependencies of property concentrations and thereby an acceptable comparison of concentration values could be undertaken without additional correction.

Table 7.1 *Spearman's rho correlation coefficients and significance for SSA versus property concentration from the grassland, cultivated land and channel bank source groups*

	Grassland		Cultivated		Channel Banks	
Property	Coefficient	Significance	Coefficient	Significance	Coefficient	Significance
Mg	-0.199	0.291	0.378(*)	0.04	-0.214	0.232
Al	0.164	0.388	0.506(**)	0.004	-0.262	0.141
K	0.572(**)	0.124	0.332	0.073	0.438(*)	0.011
Mn	0.614(**)	0.001	0.099	0.601	0.025	0.89
Fe	0.287	0.124	0.545(**)	0.002	0.319	0.07
Li	0.063	0	0.470(**)	0.009	-0.061	0.737
Na	0.173	0.743	0.052	0.786	-0.211	0.238
Sc	0.559(**)	0.361	0.335	0.07	0.663(**)	0
Ti	-0.065	0.001	0.227	0.228	-0.32	0.07
V	-0.103	0.734	0.278	0.137	-.486(**)	0.004
Cr	-0.008	0.588	0.465(**)	0.01	-0.238	0.182
Co	0.488(**)	0.966	0.278	0.137	0.318	0.072
Ni	0.381(*)	0.006	0.444(*)	0.014	0.552(**)	0.001
Cu	0.463(**)	0.038	0.424(*)	0.02	0.459(**)	0.007
Zn	0.194	0.01	0.406(*)	0.026	-0.152	0.399
Ga	0.431(*)	0.304	0.329	0.076	0.111	0.54
Ge	0.487(**)	0.017	0.389(*)	0.033	0.3	0.09
As	0.563(**)	0.006	0.165	0.384	0.274	0.122
Rb	0.522(**)	0.001	0.089	0.639	0.725(**)	0
Sr	0.159	0.003	0.183	0.333	0.196	0.275
Y	0.394(*)	0.401	0.2	0.289	0.487(**)	0.004
Zr	0.154	0.417	0.185	0.328	0.559(**)	0.001
Mo	0.335	0.071	0.297	0.111	0.148	0.411
Pd	0.418(*)	0.022	0.345	0.062	0.232	0.193
Cd	0.390(*)	0.033	0.12	0.527	0.014	0.939
In	0.268	0.153	-0.286	0.126	0.177	0.325
Sn	0.246	0.19	0.308	0.097	-0.241	0.177
Sb	0.015	0.936	0.355	0.054	-0.284	0.109
Cs	0.305	0.101	-0.264	0.159	0.509(**)	0.002
Ba	0.449(*)	0.013	0.31	0.096	0.068	0.708
La	0.073	0.702	0.34	0.066	-0.352(*)	0.045
Ce	0.218	0.247	0.32	0.085	-0.348(*)	0.047
Pr	0.295	0.114	0.353	0.056	0.055	0.761
Nd	0.333	0.072	0.323	0.081	0.182	0.311
Sm	0.451(*)	0.012	0.308	0.097	0.316	0.073
Eu	0.468(**)	0.009	0.308	0.098	0.434(*)	0.012
Gd	0.467(**)	0.009	0.301	0.106	0.420(*)	0.015
Tb	0.438(*)	0.016	0.304	0.103	0.422(*)	0.014
Dy	0.450(*)	0.013	0.298	0.109	0.518(**)	0.002
Ho	0.433(*)	0.017	0.275	0.141	0.468(**)	0.006
Er	0.410(*)	0.024	0.263	0.161	0.426(*)	0.013
Yb	0.455(*)	0.012	0.278	0.136	0.382(*)	0.028
Hf	0.043	0.822	0.143	0.45	0.414(*)	0.017
Tl	0.338	0.067	0.454(*)	0.012	0.455(**)	0.008
Pb	0.225	0.232	0.047	0.804	-0.012	0.948
^{207}Pb	0.226	0.229	0.054	0.778	-0.03	0.869
^{208}Pb	0.215	0.255	0.049	0.796	-0.029	0.873
Bi	0.346	0.061	0.505(**)	0.004	0.059	0.744
U	0.341	0.065	0.309	0.096	0.028	0.876

* Correlation is significant at p = 0.05
** Correlation is significant at p = 0.01

7.5.3 Particle-size distributions

Figure 7.6 illustrates comparisons between the mean particle size distributions of the <63 µm fraction of sediment from the River Waver floodplain core and soil from the samples representing the three source groups. It was apparent that in this instance the source group particle size distributions were very similar to those from the floodplain, particularly those from cultivated and channel bank sources. Based on field observations, the lack of apparent particle size selectivity may be due to the measures introduced on the flood plain for flood risk management. Riparian areas and open field ditches and drains were intensively managed, with all vegetation removed during regular re-profiling and channel clearance work. Heavy grazing had resulted in a low sward height decreasing surface roughness. These practises could lead to rapid transit of water during high magnitude flooding events. Under such conditions the finer fractions of sediment might be expected to remain in suspension until encountering the estuarine environment below the tidal limit.

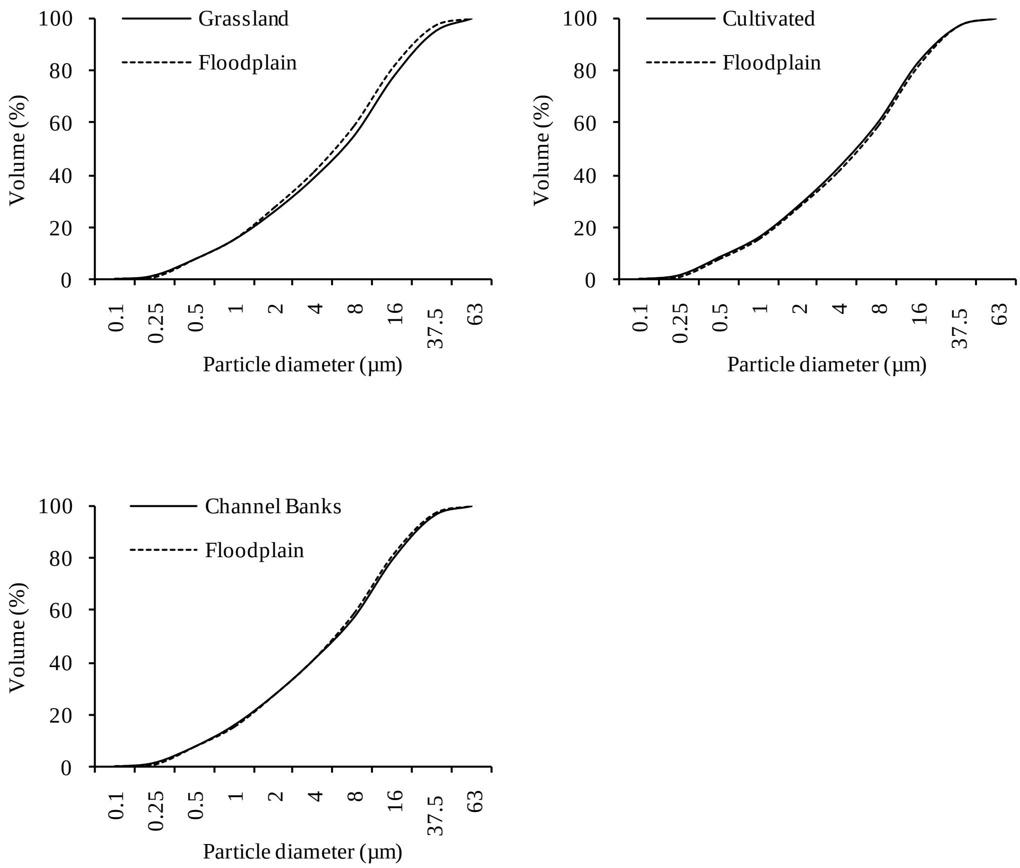

Figure 7.6 *Comparison of the mean particle size distribution (µm) of the <63µm fraction of sediment from the River Waver floodplain core with sample material from the grassland, cultivated land and channel bank source groups*

Figure 7.7 shows the inter-sample group variability of mean and median SSA of the <63µm fraction of sediment retrieved from the floodplain core and sample material from the three source groups. The similarity between the mean and median SSA values for the individual sample groups indicates that the SSA data were likely to be Normally distributed and were not unduly influenced by outliers in this instance. It is apparent that the mean and median SSA values for samples from cultivated land were slightly higher than those of the other source groups and the floodplain sediment samples. This indicates that a proportion of the finer fraction of mobilised sediment from cultivated sources is not being deposited at the floodplain coring point.

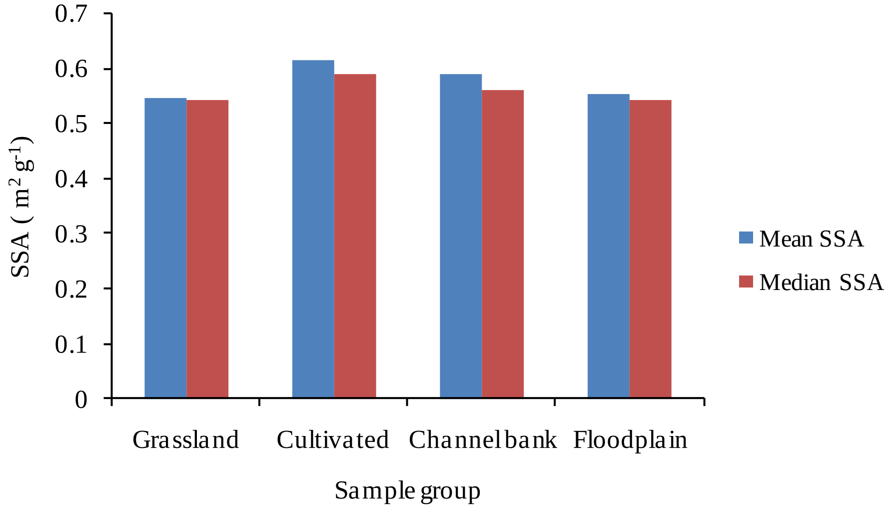

Figure7.7 *Inter-sample group variability of mean and median SSA (m^2 g^{-1}) of the <63μm fraction of sediment from the River Waver floodplain core and source material from the grassland, cultivated land and channel bank source groups.*

Figure 7.8 shows the intra-group variability of SSA of the <63 μm fraction of sediment from the floodplain and sample material from the three source groups. The greatest heterogeneity in SSA can be observed in the grassland samples, whilst the SSA of cultivated samples appears more homogenous, reflecting the influence of tillage. The intra-group variability of SSA from the floodplain core section samples has an identifiable downcore trend of decreasing SSA. This trend possibly indicates an increase in the proportion of finer sediment settling over time or the effects of post-depositional pedogenic processes.

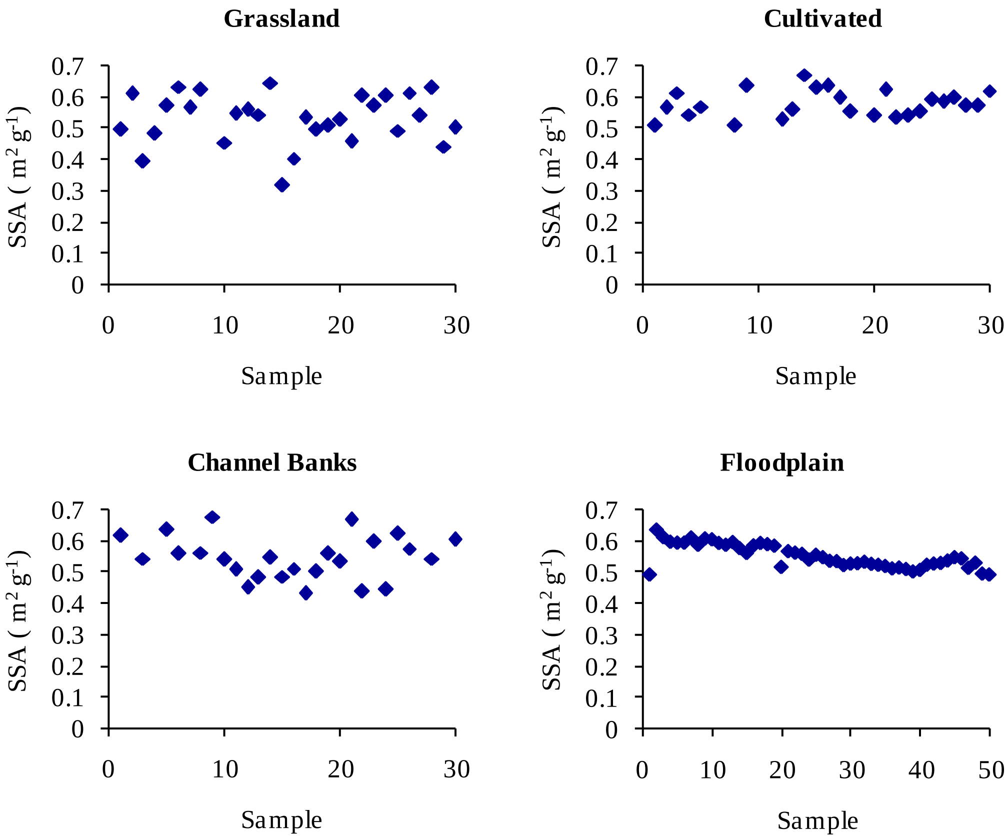

Figure 7.8 The intra-group variability of SSA of the <63µm fraction of sediment from the floodplain core and the sample material from the grassland, cultivated land and channel bank source groups.

7.5.4 The fingerprint property concentration range test

The next stage in the selection of the optimum composite fingerprint was to apply the data to a property concentration range test (see Chapter 3). Table 7.2 displays the initial property range test results for the River Waver catchment. Of the 13 properties (27%) which failed to meet the range test requirement, two properties Fe and Rb had concentration ranges within the core which overlapped the source range minimum concentration value, eleven properties K, Li, Na, Ge, Zr, Pd, Cd, Sn, Hf, Bi and U had concentration ranges which overlapped the source range maximum value. In view of the large proportion of properties which passed the property concentration range test (73%) and the observation that those properties which failed had values which overlapped the floodplain range, it was considered that potential sediment sources in the catchment had been well represented during the sampling process. It also appeared that property concentration values had not been substantially altered following mobilisation, transport and deposition.

Table 7.2 *Results of the property range test for fingerprint property concentrations in the River Waver catchment.*

Core range within source range	Core range overlaps source range min	Core range overlaps source range max
Mg	Fe	K
Al	Rb	Li
Mn		Na
Sc		Ge
Ti		Zr
V		Pd
Cr		Cd
Co		Sn
Ni		Hf
Cu		Bi
Zn		U
Ga		
As		
Sr		
Y		
Mo		
Sb		
Cs		
Ba		
La		
Ce		
Pr		
Nd		
Sm		
Eu		
Gd		
Tb		
Dy		
Ho		
Er		
Yb		
Tl		
^{206}Pb		
^{207}Pb		
^{208}Pb		

7.5.5 Source discrimination: the Kruskal-Wallis H-test

The next stage in the establishment of the optimum combination of tracer properties with which to form the composite fingerprint was conducted to test which properties displayed significant differences between source types. These differences were initially established using the non-parametric Kruskal-Wallis *H*-test, applied to the source sample property value data (see Chapter 3). Table 7.3 presents the resultant *H*-values and asymptotic significance from the Kruskal-Wallis *H*-test applied to confirm the ability of individual tracer properties to distinguish between the three potential source groups.

Table 7.3 *H-values and asymptotic significance from the Kruskal-Wallis H-test utilised to ascertain the ability of individual tracer properties to distinguish between the grassland, cultivated land and channel bank source groups.*

Property	*H*-value	Asymptotic Significance
Mg	8.88	0.01
Al	4.27	0.12*
Mn	3.93	0.14*
Sc	25.24	0.00
Ti	3.08	0.21*
V	20.81	0.00
Cr	8.78	0.01
Co	25.04	0.00
Ni	27.05	0.00
Cu	5.18	0.07
Zn	0.05	0.97*
Ga	8.29	0.02
As	4.08	0.13
Sr	4.69	0.10
Y	19.77	0.00
Mo	2.88	0.24*
Sb	2.69	0.26*
Cs	8.83	0.01
Ba	7.57	0.02
La	8.61	0.01
Ce	14.56	0.00
Pr	26.08	0.00
Nd	28.14	0.00
Sm	33.06	0.00
Eu	30.64	0.00
Gd	30.46	0.00
Tb	29.97	0.00
Dy	25.74	0.00
Ho	25.42	0.00
Er	22.76	0.00
Yb	22.83	0.00
Tl	3.42	0.18*
^{206}Pb	10.43	0.01
^{207}Pb	9.43	0.01
^{208}Pb	10.31	0.01

Critical value = 5.99

* Not significant at p = 0.05

Properties below the critical value of 5.99, at p = 0.05 (Al, Mn, Ti, Zn, As, Mo, Sb and Tl), were subsequently removed from further consideration as viable fingerprint properties at this stage.

7.5.6 Source discrimination: Multivariate Discriminant Function Analysis

A stepwise Multivariate Discriminant Function Analysis (MDFA), using the minimization of Wilks' Lambda, was then applied to the remaining properties. At each step, the property which minimised the overall Wilks' Lambda was entered (see Chapter 3). Maximum significance of F to enter a property was 0.05 and minimum significance of F to remove a property was 0.10. The MDFA tested the ability of the tracer properties to correctly classify the source samples into the appropriate source groups and also provided a quantification of the discriminatory power of the optimum composite fingerprint, as presented in Table 7.4.

Table 7.4 *Results from the stepwise MDFA in identifying the optimum composite fingerprint for discriminating the grassland, cultivated land and channel bank source groups based on the minimisation of Wilks' Lambda.*

Step	Property	Wilks' Lambda	Cumulative original grouped cases correctly classified (%)
1	Sm	0.651246	41.7
2	V	0.520609	55.1
3	^{208}Pb	0.470786	60.6
4	Co	0.423573	64.6
5	Yb	0.384323	66.1
6	Sc	0.34278	66.9

A composite fingerprint containing the six properties Sm, V, ^{208}Pb, Co, Yb and Sc produced a Wilks' Lambda value of 0.34, which was the closest to zero that could be obtained following stepwise inclusion of all available properties. This fingerprint classified 66.9% of the original grouped cases correctly. Table 7.5 shows the predicted sample group against the actual group membership for the three source groups, where it can be observed that grassland was the least discriminated at 53.33% of correctly classified cases. Discrimination for the remaining two source groups was 60% and 93.33% correctly classified cases for cultivated land and channel banks respectively.

Figure 7.9 illustrates the sample distribution around the three group centroids from the first two canonical discriminant functions following stepwise MDFA. The scatter plots further illustrate the relatively poor discrimination offered by the stepwise derived fingerprint. It was considered that this fingerprint offered insufficient discrimination to proceed reliably to the apportionment phase.

Table 7.5 *Results from comparison of predicted sample group membership against actual group membership for the grassland, cultivated land and channel bank source groups, with percentage of correctly classified cases within each group following stepwise MDFA*

		Source Group	Predicted Group Membership			Total
			Grassland	Cultivated	Channel Bank	
Original Group Membership	Count	Grassland	16.00	13.00	1.00	30.00
		Cultivated	9.00	18.00	3.00	30.00
		Channel Bank	0.00	2.00	28.00	30.00
	%	Grassland	53.33	43.33	3.33	100.00
		Cultivated	30.00	60.00	10.00	100.00
		Channel Bank	0.00	6.67	93.33	100.00

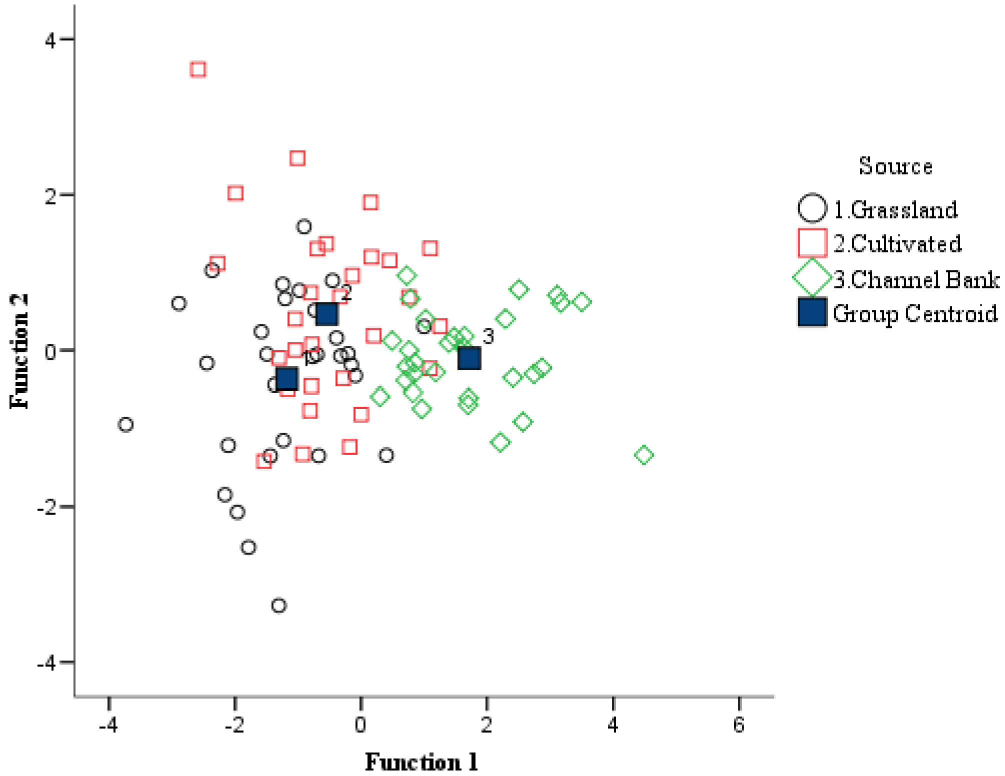

Figure 7.9 *Combined scatter plots showing sample distribution around group centroids from the two canonical discriminant functions applied to the grassland, cultivated land and channel bank source groups following stepwise MDFA.*

An alternative approach was then applied, wherein all properties which had passed the Kruskal Wallis *H*-test were simultaneously entered into MDFA. Consequently, it was possible to lower substantially the Wilks' Lambda to 0.18, as shown in Table 7.6, and to improve discrimination to 85.6% of original grouped cases correctly classified. This fingerprint was derived from an increased number of 26 properties (Cr, Sm, Ga, Pd, Mg, Gd, Li, Eu, Er, Tb, Sr, Fe, La, Hf, K, Ba, As, Mn, Y, Pr, Ti, Ce, Co, Ni, Nd and Zn).

Table 7.6 *Wilks' Lambda Test of Functions for 26 simultaneously entered properties*

Test of Function(s)	Wilks' Lambda	Chi-square	Significance
1 through 2	0.18	129.29	0.00
2.00	0.68	29.41	0.17

Table 7.7 presents the discrimination results for the simultaneously entered 26 property fingerprint. It is apparent that discrimination has improved across source groups grassland, cultivated land and channel banks to 80%, 76.67% and 100% of correctly classified cases respectively. Six each of the misclassified samples, were interchangeably predicted for grassland and cultivated, with just one cultivated sample being misclassified as channel bank. As previously observed, similarities might be to exist in certain geochemical properties for land farmed in rotation between grassland and arable cultivation.

Table 7.7 *Results from comparison of predicted sample group membership against actual group membership for grassland, cultivated land and channel bank source groups, with percentage of correctly classified cases within each group following simultaneous entry MDFA*

<table>
<tr><th rowspan="2"></th><th rowspan="2"></th><th rowspan="2">Source Group</th><th colspan="3">Predicted Group Membership</th><th rowspan="2">Total</th></tr>
<tr><th>Grassland</th><th>Cultivated</th><th>Channel Banks</th></tr>
<tr><td rowspan="6">Original Group Membership</td><td rowspan="3">Count</td><td>Grassland</td><td>24.00</td><td>6.00</td><td>0.00</td><td>30.00</td></tr>
<tr><td>Cultivated</td><td>6.00</td><td>23.00</td><td>1.00</td><td>30.00</td></tr>
<tr><td>Channel Banks</td><td>0.00</td><td>0.00</td><td>30.00</td><td>30.00</td></tr>
<tr><td rowspan="3">%</td><td>Grassland</td><td>80.00</td><td>20.00</td><td>0.00</td><td>100.00</td></tr>
<tr><td>Cultivated</td><td>20.00</td><td>76.67</td><td>3.33</td><td>100.00</td></tr>
<tr><td>Channel Banks</td><td>0.00</td><td>0.00</td><td>100.00</td><td>100.00</td></tr>
</table>

Figure 7.10 illustrates the sample distribution around the three group centroids from the two canonical discriminant functions following simultaneous entry MFDA. The scatter plots help to illustrate the improved discrimination afforded by the simultaneously entered fingerprint. There is greater separation between the source group centroids, with channel bank samples in particular displaying a distinctive grouping around the centroid. The clustered pattern of the points around the channel bank centroid, without any overlapping points from other sources, illustrates the pattern associated with 100% of correctly classified cases. It was considered that this composite fingerprint offered improved discrimination and was acceptable for use in the mixing model during the sediment source apportionment phase.

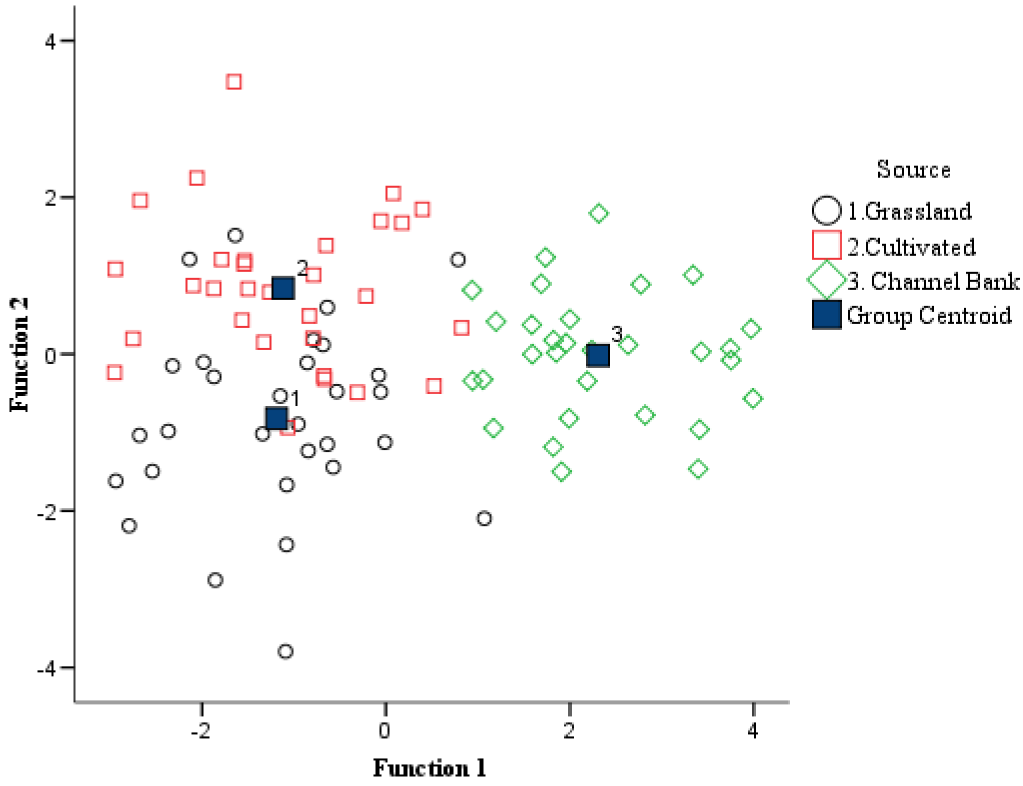

Figure 7.10 *Combined scatter plots showing sample distribution around group centroids from the two canonical discriminant functions applied to the grassland, cultivated land and channel bank source groups following simultaneous entry MDFA.*

7.6 Application of the mixing model

A linear numerical mixing model, as described in Chapter 3, was subsequently employed to provide an estimate of the relative sediment contributions from the three potential source groups to the individual floodplain core sections. The mixing model utilized property-specific weightings, shown in Table 7.8. The weightings were based on the discriminatory power of individual fingerprint properties and were applied to account for the variable contributions made by different properties to overall composite fingerprint discrimination. A Monte-Carlo framework was incorporated into the model to improve representative uncertainty related to source sampling, as described by Collins and Walling (2007). This procedure took explicit account of the uncertainty associated with using a limited number of source samples to calculate the mean input values used in the mixing model.

Table 7.8 *Mixing model property-specific discrimination weightings*

Property	Individual discrimination (%)	Weighting value
Cr	49.60	1.555
Sm	47.90	1.502
Ga	46.20	1.448
Pd	45.40	1.423
Mg	43.70	1.370
Gd	42.90	1.345
Li	42.00	1.317
Eu	42.00	1.317
Er	41.20	1.292
Tb	40.30	1.263
Sr	39.50	1.238
Fe	38.70	1.213
La	38.70	1.213
Hf	38.70	1.213
K	37.80	1.185
Ba	37.80	1.185
As	37.00	1.160
Mn	36.10	1.132
Y	36.10	1.132
Pr	36.10	1.132
Ti	34.50	1.082
Ce	34.50	1.082
Co	32.80	1.028
Ni	32.80	1.028
Nd	32.80	1.028
Zn	31.90	1.000

7.7 Sediment source apportionment and historical catchment land use changes

Table 7.9 presents the apportionment output from the mixing model and shows the relative sediment contributions from the grassland cultivated land and channel bank source groups through successive floodplain core sections during the ca. 75 year study period. The Relative Mean Error (REM) for the apportionment of each core section is also presented. The REM for the combined core sections was 5% giving a goodness of fit of 95% for the combined estimates. This relatively high goodness of fit partially reflects the large number of properties passing the property range test and subsequent discrimination tests to be included in a composite fingerprint comprising 26 individual properties. For comparative purposes the estimates of relative source contributions over time (ca.1932-2008) are illustrated in Figure 7.11.

Table 7.9 *The sediment source apportionment estimate (%) (± standard deviation) for individual floodplain core sections from the River Waver catchment with associated RME (%)*

		Estimated sediment contribution (%)			
Depth (cm)	Estimated date	Grassland	Cultivated	Channel Bank	RME (%)
1	2008	46±20	37±23	17±10	5
2	2007	44±21	38±24	18±11	4
3	2006	35±20	38±24	27±12	4
4	2004	39±23	40±26	21±13	5
5	2003	33±18	34±21	33±10	4
6	2002	33±17	33±20	34±10	4
7	2001	39±18	33±21	28±10	4
8	1999	39±19	37±23	24±11	4
9	1998	32±17	35±20	34±10	4
10	1997	32±18	36±21	32±11	5
11	1996	28±18	35±21	38±11	4
12	1994	39±21	37±24	24±11	5
13	1993	35±21	37±25	28±12	4
14	1992	34±22	37±25	29±13	5
15	1991	37±23	38±26	25±13	4
16	1989	31±20	38±23	31±13	4
17	1988	31±20	38±24	31±12	4
18	1987	28±19	39±22	34±12	4
19	1986	29±20	39±24	32±13	4
20	1984	30±21	41±25	29±13	5
21	1983	37±22	39±25	24±12	4
22	1981	34±20	39±23	27±12	4
23	1979	32±20	40±24	28±12	4
24	1977	35±21	41±25	25±12	4
25	1976	32±22	42±26	26±13	4
26	1974	35±23	44±27	21±14	5
27	1972	36±24	42±27	21±14	5
28	1970	36±22	42±26	22±13	4
29	1969	42±26	46±30	13±14	7
30	1967	32±22	43±26	25±14	5
31	1965	48±22	39±25	14±11	8
32	1963	40±21	40±24	19±12	6
33	1962	42±22	40±25	18±12	6
34	1960	42±22	39±25	19±12	5
35	1958	42±22	40±25	18±13	6
36	1956	38±22	39±26	23±13	6
37	1955	41±23	38±26	21±13	5
38	1953	42±24	40±28	19±14	6
39	1951	49±24	36±27	16±12	8
40	1949	43±24	38±28	19±13	7
41	1948	53±26	35±29	12±12	8
42	1946	30±21	39±26	31±14	6
43	1944	50±27	35±30	15±13	9
44	1942	37±21	37±25	26±13	5
45	1941	33±21	36±24	29±13	5
46	1939	40±22	39±25	24±12	5
47	1937	36±22	39±25	25±13	5
48	1935	40±26	41±29	19±12	7
49	1934	44±24	34 ±27	22±12	6
50	1932	50±26	32±29	19±13	7

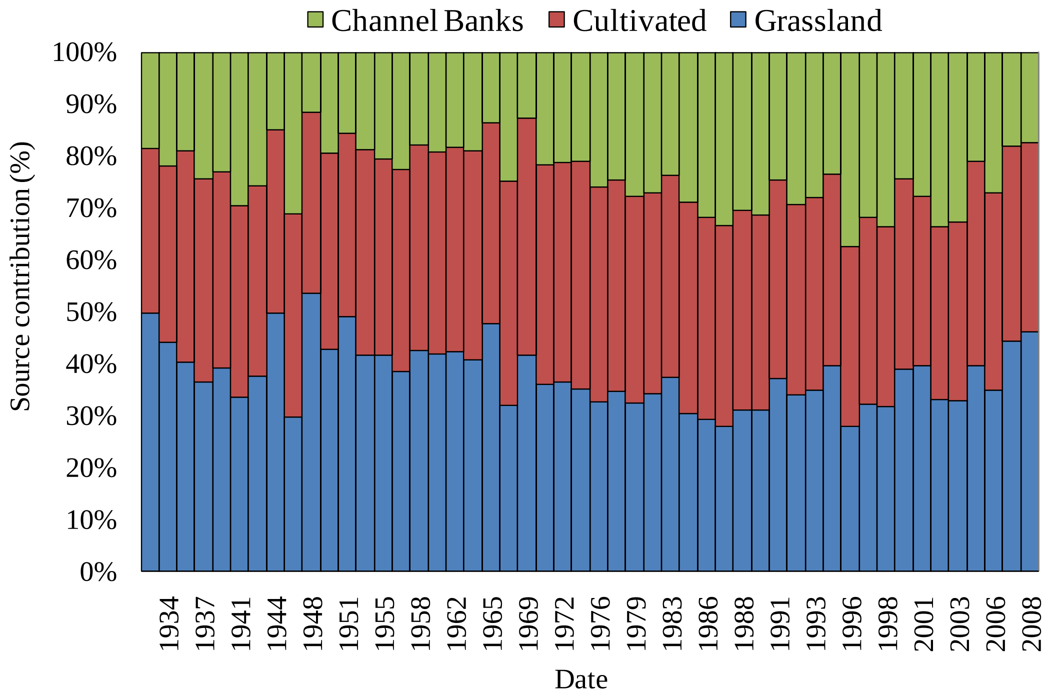

Figure 7.11 *Temporal changes in the relative contributions to floodplain sediment from grassland, cultivated land and channel bank source groups in the River Waver catchment ca. 1933 – 2009*

The apportionment showed general fluctuations in relative contributions from sources over approximately 75 years, 1933-2008. Contributions from channel banks displayed the greatest variation over the period, with a maximum contribution of 38% in the mid 1990s and a minimum of 12% in the late 1940s. Grassland contributions ranged from a maximum of 53% in the late 1940s, to a minimum of 28% in the mid 1980s. Cultivated land exhibited the least variation in sediment contributions over the period, with a maximum contribution of 46% in the early 1970s and a minimum contribution of 32% in the early 1930s. The time averaged contributions for grassland, cultivated land and channel banks were 38%, 38% and 24% respectively.

There was limited variation in the relative sediment contributions from the cultivated sources over the study period. However contributions from such sources increased marginally relative to grassland contributions at the beginning of the 1940s. This relationship may well reflect the effects of the wartime ‘plough-up campaign’. During the 1940s under requirements of the County War Agricultural Committees, a three year rotation was introduced in Cumbria, whereby grassland was ploughed and sown with oats in the first year. The land would then be sown with a mixture of turnips, mangolds, potatoes, carrots and cabbage in the second year. Oats would be sown again in the third year, with grass undersown to reinstate a pasture once the rotation ended (The

Countryside Museum, 2010). Relative contributions from cultivated sources declined slightly during the 1950s and then rose steadily throughout the 1960s and into the 1970s. The rise in relative contributions from cultivated sources corresponds with widespread intensification of agricultural production during this period in response to EU CAP drivers (Robinson and Armstrong, 1987). Relative contributions from channel bank sources also appear to have increased at the beginning of the 1940's. As part of the war effort, field ditches, drains and riparian zones were cleared. This may have potentially exposed channel banks to increased erosion risk. Relative contributions from channel banks were generally reduced during the 1950s and 1960s. However, from the mid 1970s there was an observable trend of increased relative contributions from channel banks. During this period land drainage was heavily encouraged by the government (MAFF, 1970). Large areas of the catchment include open field drains and ditches. From the 1970s onward the channel banks, in conjunction with the catchment drains and ditches, were heavily reprofiled and the riparian areas cleared. The lack of riparian cover may have led to increased erosion risk. During the early 2000's several reaches were reinforced with wooden revetments in an attempt to protect certain vulnerable bank sections from the effects of scour. This modification may partially account for the apparent decline in relative contributions from channel banks from the end of the 1990s onward. There was a significant decline in contributions from grassland throughout the 1930s and early 1940s, perhaps as a result of the areas of conversion already discussed above. However, grassland contributions then rose in the late 1940s and early 1950s, perhaps as a result of increased mechanical erosion on fields prone to saturation in the plain which were liable to extensive flooding or possibly the effects of increased connectivity through improvements to field drains and roadways. From the 1950s relative contributions from grassland sources generally declined until the mid 1980s, since when there has been a trend of increasing relative sediment contributions from grassland sources.

In accordance with the methodology described in Chapter 3, data on changes in land cover, crops and stocking densities were extracted and collated from the Agcensus Database (EDINA, 2009). Data were obtained at 2km x 2km grid resolution from the area of the catchment for the years; 1969, 1972, 1976, 1979, 1981, 1988, 1993, 1996, 2000 and 2004. Existing published information and personal communication complemented the Agcensus data as a source of reference.

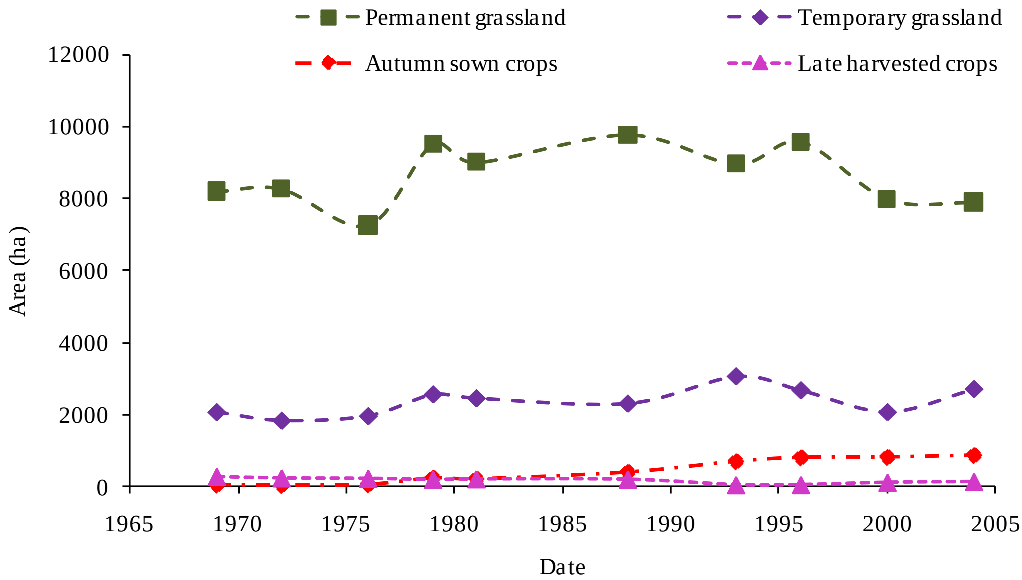

Figure 7.12 *Land cover areas for permanent grassland, temporary grassland, autumn sown crops and late harvested crops in the River Waver catchment 1969-2004*

Land cover data were compiled for late-harvested crops often associated with high erosion risk and included here, potatoes, sugar beet, field beans, turnips, swedes, mangolds and maize. The data were collated at catchment scale between 1969 and 2004. Data were similarly combined for high erosion risk autumn-sown crops, including wheat, winter-barley and oilseed rape. Temporary grassland and permanent grassland data were also individually collated for comparative analysis. The combined plots are shown in Figure 7.12. The historic dominance of permanent grassland, traditionally used for dairy production, as the major land use type in the catchment is clearly illustrated. There was a marked increase in the area reported as permanent grassland throughout the late 1970s. This apparent increase in permanent grassland may reflect the improvement of marginal grassland previously classified as rough grazing, possibly through improved drainage and may have been a response to increasing numbers of livestock in the catchment at this time, encouraged by production based subsidies under the EU CAP. This interpretation is supported by the apparent lack of any appreciable decline in other significant land use which might have, for instance, indicated the long term establishment of reseeded grass lays on land previously in rotation. The decline in permanent grassland since the mid 1990s appears to correspond to some extent with the increase in land under cultivation for autumn sown crops and latterly temporary grassland and also the decline in cattle numbers. Significantly, the initial decline in the recorded area of permanent grassland in the late 1990s, corresponds to a marked drop in sediment contributions from the grassland source during the same period. The increase in permanent grassland in the late 1970s also corresponds to a slight increase in sediment contributions from grassland. However, if the increased permanent grassland area occurred as a result of reclassification of rough grazing as suggested above, then it might be expected that there would be little change in the relative contributions, as the essential land use would have been little changed. Fluctuations in sediment source contributions from grassland sources appear to correspond more closely to changes in the area under temporary grassland. This is perhaps to be expected as the preparation of soils for new leys and the period of time before the new leys are established can leave the soils vulnerable to water erosion.

Figure 7.13 illustrates the total number of sheep and cattle within the River Waver catchment between 1969 and 2004. Numbers of both cattle and sheep generally increased throughout the 1970s and declined slightly during the 1980s.In the first half of the 1990s cattle numbers increased slightly, whilst sheep numbers were more or less stable. From the mid 1990s through to 2004 cattle numbers decreased markedly, whilst sheep numbers have expanded considerably over the same period.

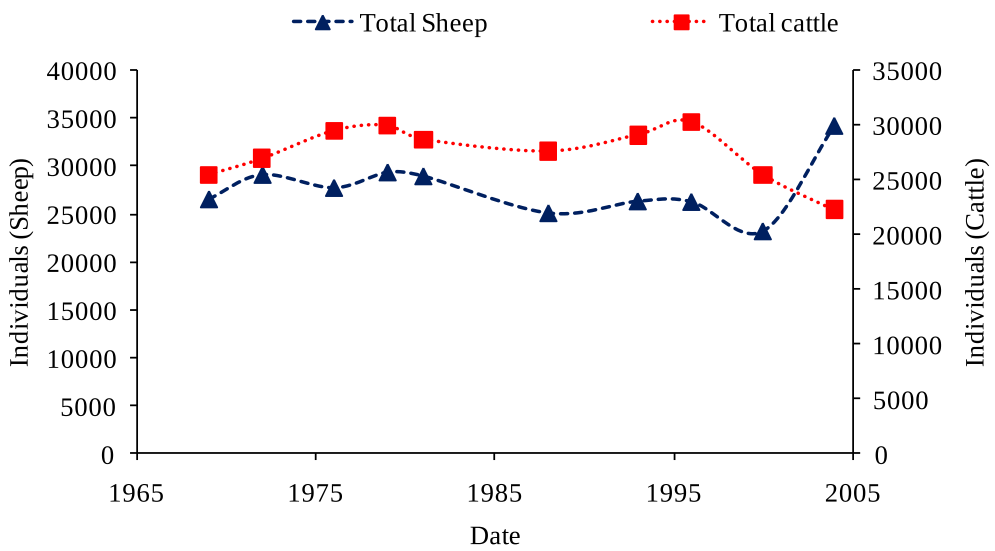

Figure 7.13 *Total numbers of sheep and cattle in the River Waver catchment 1969-2004*

For comparative purposes, cattle and sheep numbers were converted into LUs, as detailed in Chapter 3, and the resultant LUs were divided over the available pasture land to estimate catchment mean stocking densities over the study period. Figure 7.14 shows the mean stocking densities (LUs ha^{-1}) for the River Waver catchment between 1969 and 2004. It is apparent that with the exception of a notable increase in the early and mid 1970s and a decline between 2000 and 2004, stocking densities have remained relatively similar over the study period. There is no apparent relationship between stocking densities and relative sediment contributions from grassland sources over the study period. However, during the peak in stocking densities in the 1970s there is a slight increase in contribution from channel bank sources, also as stocking densities have declined since 2000, relative contributions from channel bank sources have similarly decreased.

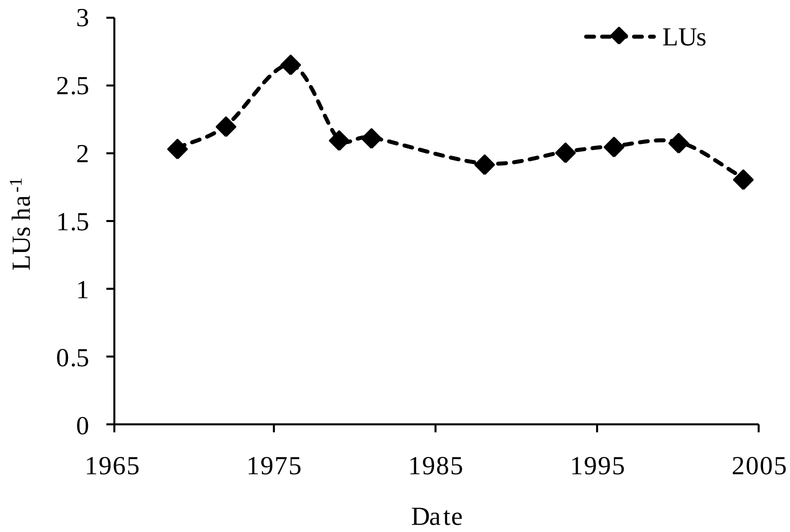

Figure 7.14 *Mean stocking densities (LUs ha^{-1}) for the River Waver catchment between 1969 and 2004.*

Figure 7.15 displays land cover areas for autumn sown crops and late harvested crops (1963-2004) in higher resolution. The pattern of increasing favour for early harvested crops can be clearly seen over crops which would not necessarily finish well in the cold Cumbrian autumn. In spite of the increase in the area of land under cultivation, it should perhaps be considered that even at 2004 levels, the total area of the catchment recorded under cultivation was just 17%, with 82% recorded as grassland.

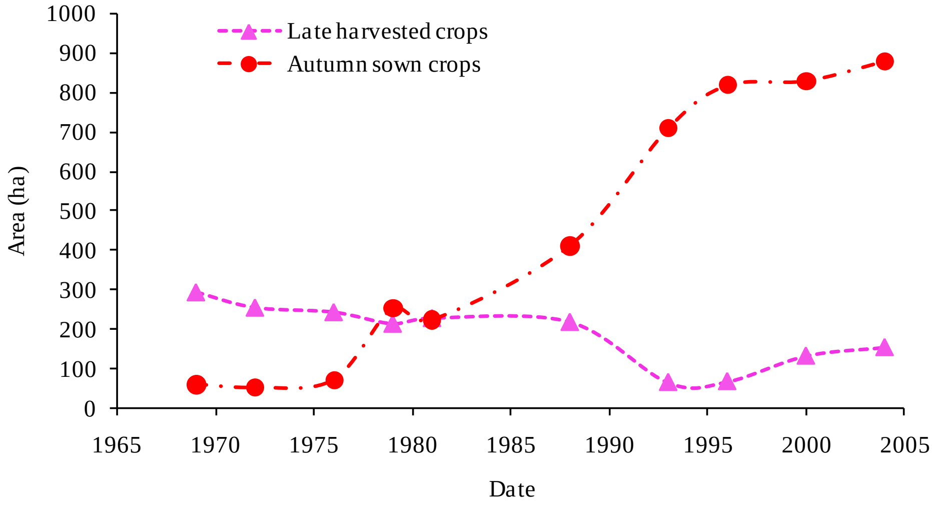

Figure 7.15 *Land cover areas for autumn sown crops and late harvested crops in the Waver catchment 1969-2004*

When considering the variations in areal extent between the grassland and cultivated land sources, it is perhaps not surprising that the apportionment results lack substantial temporal variations over the study period. However, the application of the source fingerprinting technique has proved particularly useful in illustrating the disproportionate sediment contribution derived from cultivated sources to the floodplain core. This relationship is illustrated in Figure 7.16, where the proportion of total land area occupied by grassland and cultivated land is compared to the associated sediment contributions made by the respective source groups to the floodplain core.

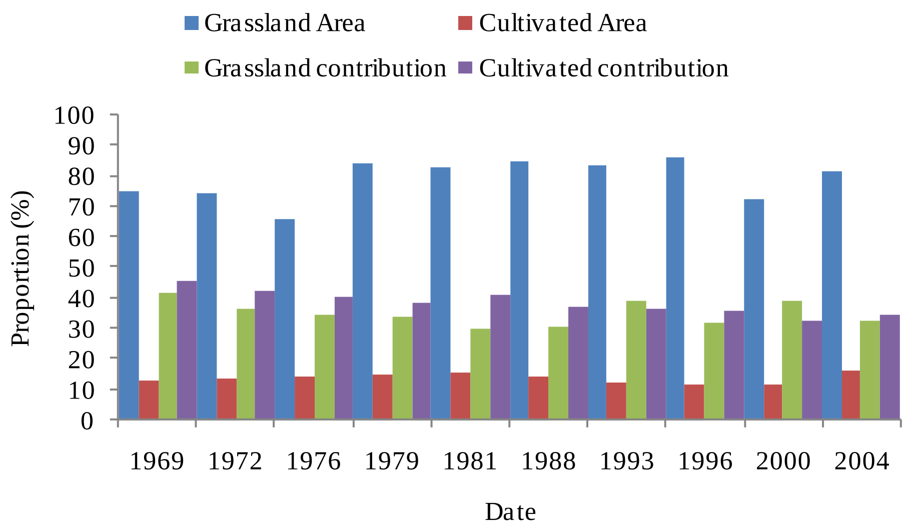

Figure 7.16 *The proportion of total land area occupied and relative sediment contributions to the floodplain core for grassland and cultivated land.*

A final observation and alternative interpretation relates to the extremely close relationship between apportionment estimates for grassland sources and those for channel bank sources. It is perhaps worth considering the flood risk management in the catchment and the associated engineering practices. During channel reprofiling and maintenance, the material which is removed from the channel and channel banks is routinely placed alongside the channel and thereby forms a berm. This effectively disconnects the channel from the floodplain and would restrict the amount of runoff coming from the predominantly grassland riparian fields. In addition, the presence of berms can increase flow velocity, leading to increased channel bank scour during periods of high flows. During periods between channel maintenance, the berms gradually deteriorate and breach, allowing floodplain overland flow to reach the stream channel. This would result in increased sediment ingress from grassland sources and decreased scour of channel banks as the floodplains perform their natural function. Livestock seeking access to water will trample and erode both channel banks and berms which, being comprised of channel bank material, would effectively increase contributions from these sources, particularly during periods of high stocking densities.

7.8 Conclusion

The ECSFDI causes for concern within the River Waver catchment which prompted its selection for investigation included the potential role of increased connectivity between expanding nutrient rich areas of late harvested arable crops (e.g. maize) and receiving water courses. Concerns were related to the potential for high levels of nutrient enriched sediment to be mobilised from cultivated sources and transported in the river channel. However, this study has concluded that the relative area of the catchment area under cultivation has not increased significantly in relation to the total land area and that the overall relative sediment contribution from cultivated sources has not significantly increased over the time period studied. Therefore, in this instance, any significant increase in outlet nutrient content is likely to be due to factors other than increased sediment loads from cultivated land. The areas of intensively managed grassland could be of greater concern, particularly if livestock are introduced to poorly established leys on land prone to saturation. This interpretation tends to support the findings of previous studies which have highlighted the contribution of intensively managed grassland to catchment sediment problems (Billotta *et al.*, 2008; Douglas *et al.*, 2010; Granger *et al.*, 2010). The flood risk management in the catchment follows an approach which has changed little in principle over several decades and is designed to direct high flows downstream as rapidly as possible. However, the consequences associated with this approach can considerably increase channel bank and bed scour and can also lead to catastrophic flood defence failures downstream during extreme high magnitude storm events, as evidenced during the devastating muddy flooding which occurred close to the case study catchment in the Cumbrian town of Cockermouth in 2009.

CHAPTER 8 - THE RIVER RYE CATCHMENT: RESULTS AND INTERPRETATION

8.1 Introduction

The fifth case study in this thesis features the River Rye catchment, North Yorkshire, England. The results from the application of the sediment source fingerprinting technique to floodplain sediment cores from the catchment are presented. Interpretation is offered of the changes in the sources of overbank sediment deposits in response to historical land use change over ca. 100 years.

The key sediment-related issues identified within the River Rye catchment include concerns related to inappropriate arable cultivation, particularly on vulnerable valley slopes and the potential effects of over-abstraction associated with water use in agriculture and fish farming (Environment Agency, 2006; Defra, 2009a) in encouraging sedimentation. Such problems were identified as a cause for concern under the characterisation phase of the England Catchment Sensitive Farming Delivery Initiative (ECSFDI) (Defra, 2009a).

8.2 The study area: the River Rye catchment

The River Rye catchment is situated in the county of North Yorkshire, England. A tributary of the River Derwent, the river rises close to the Hambleton Hills, on the Eastern edge of the North York Moors National Park, near the village of Osmotherley. The river flows through the Ryedale valley passing the villages of Hawnby and Rievaulx. After flowing past the town of Helmsley, it flows on through the Vale of Pickering, via Nunnington, West Ness, East Ness, Butterwick, Brawby, and Ryton. The River Rye joins the River Derwent at a confluence to the north of Malton. The sub-catchment identified for this study encompasses approximately 250km^2, which incorporates the River Rye from its source and includes the sub-catchments of all major and minor tributaries down to a designated catchment outlet below the hamlet of East Ness (Figure 8.1).

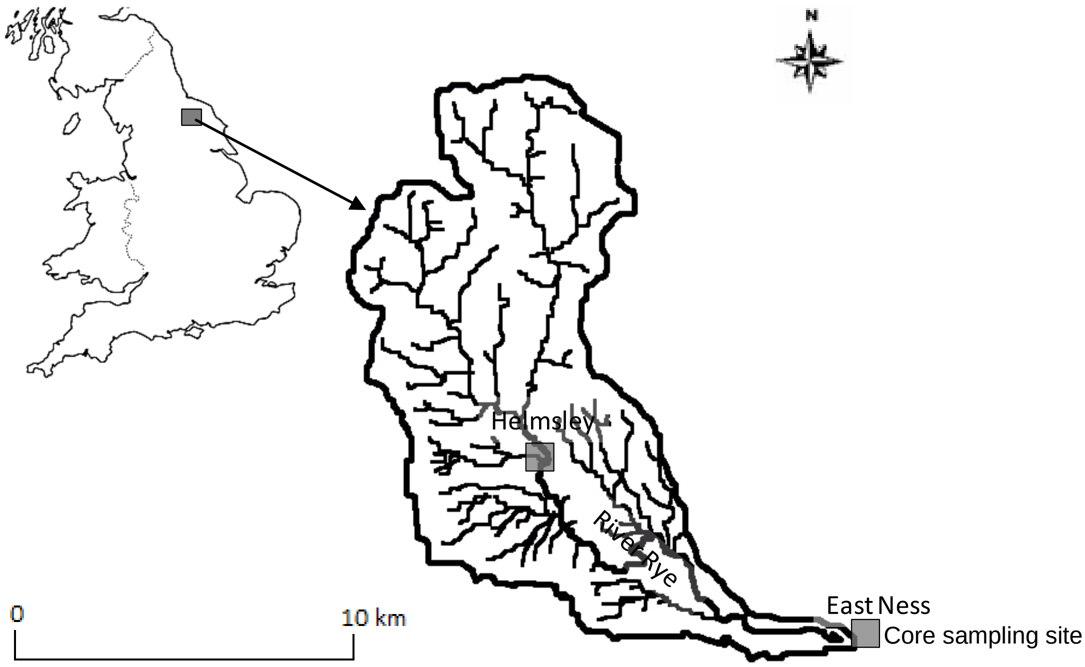

Figure 8.1 *The location and study area of the River Rye catchment, North Yorkshire, England*

The geology of the River Rye catchment incorporates Corallian limestone, which outcrops on the hills surrounding the Vale of Pickering. This deposit incorporates a major aquifer which is exposed in places in the bed of the River Rye. Lower Jurassic calcareous grit occurs in places over underlying Oxford Clay and on certain lower slopes also over the interbedded clay bands in the Corallian succession. The valley floor is underlain by a variety of glacial deposits (EDINA, 2010).

The soils of the River Rye catchment are characterised in the moorland headwaters by predominantly acid loamy upland soils with a wet peaty surface (LandIS, 2010). Soil types along the Howardian Hills ridge and valley slopes include sandy loams and shallow lime rich soils (Defra, 2009). The valley floor is characterised by naturally wet, loamy and clayey floodplain soils with some smaller areas of freely draining, lime-rich loamy soils (LandIS, 2010).

Agriculture in the upland area of the catchment is dominated by grassland for rough and semi-improved grazing. In the mid and lower reaches of the catchment, the land use includes some intensively managed, improved grassland with large areas of the lower slopes and valley floor under mixed arable cultivation (EDINA, 2009). The woodland in the catchment includes stands of mixed deciduous woodland and coniferous plantations. The woodland areas in the catchment represent less than 2% of the available land area (EDINA, 2009).

The head of the River Rye catchment lies in the North York Moors National Park, which is designated as a Special Protection Area (SPA) for a variety of bird species and as a Special Area of Conservation (SAC) for several key habitats which are important for biodiversity. The River Rye catchment contains eleven individual Sites of Special Scientific Interest (SSSIs), five of which are specifically water related (Environment Agency, 2010). In addition, the catchment incorporates the Howardian Hills Area of Outstanding Natural Beauty (AONB), and the Duncombe Park National Nature Reserve (NNR) (Environment Agency, 2006).

The specific concerns ECSFDI priorities for the River Rye catchment include the potential role of increased quantities of enriched sediment delivered from cultivated sources on vulnerable hillside soils and were described thus,

> "Extensive areas of winter wheat, maize, potatoes and other arable crops established on a variety of gradients including steeply sloping land, and soil types including sandy loams and shallow lime rich soils" (Defra, 2009a).

Concerns were expressed that,

> "High rainfall (837-1021mm yr^{-1}) combined with steep gradients and the soil types of the area can result in some agricultural land generating high run off bringing very high volumes of sediment into the River Rye and the Derwent River system" (Defra, 2009a).

Figure 8.2 shows aspects of land use and management observed during field visits which have been associated with sediment-related problems and risks in the River Rye catchment.

Figure 8.2 *Land use and management in the River Rye catchment posing sediment-associated problems and risks. Clockwise from top left: Hillslope sheet erosion; channel bank collapse in pasture field; vertical autumn sown arable crop pattern on hillslope; fish farm adjacent to main river channel.*

8.3 Floodplain site selection

Potential floodplain sampling sites were identified for collection of overbank sediment cores through the use of topographic maps, satellite imagery, ground observation and anecdotal evidence. This process pinpointed sites which were regularly inundated by overbank flooding, with corresponding potential to receive and store sediment mobilised from upstream sources.

Potential floodplain coring sites were identified at three locations. Two of the selected coring sites were within close proximity to the village of Nunnington. The third site was situated immediately downstream of the hamlet of East Ness, shown in Figure 8.3. As previously observed (see Chapter 2), it was important that the coring sites had not been cultivated within the recent past in order to ensure that deposited sediment and the associated geochemical signatures had not been mixed, thereby obscuring the record of source area inputs. The absence of cultivation in the recent past on the coring site at East Ness was substantiated through discussion with the landowners, who had partial field records for the site going back some 120 years and personal knowledge of the site going back 65 years. The recent history of cultivation at the first coring site in Nunnington was harder to confirm and relied on anecdotal evidence from near-by residents with only 20 years knowledge of the site. This confirmed the general regularity and extent of inundation and the lack of cultivation over the previous 20 years. At the second coring site in Nunnington, the lack of cultivation over the previous 40 years was confirmed by the landowners. The associated anecdotal evidence was combined with a basic ecological appraisal of the sward composition and plant biodiversity at the sites. The sward at all sites appeared to contain a reasonably diverse combination of grasses with various herb species, further indicating a general absence of cultivation and introduction of associated monocultures.

Figure 8.3 *The location of the floodplain core sampling sites at East Ness, North Yorkshire, England (Google Earth, 2010).*

Areas at the floodplain sites within meander bends and those featuring shallow topographical depressions were chosen for coring, as these were deemed to be more likely to have received and retained overbank flood waters and to thereby represent the most promising depositional sinks. The potential for the sites to represent sediment sinks was further substantiated following discussions with land owners about the nature and extent of regular overbank inundations during flood events. Environment Agency flood risk maps were also interrogated to confirm the potential extent of any inundations during flooding (E.A., 2007).

A total of eight cores with potential for use in subsequent laboratory analysis were collected from the identified sites. The floodplain cores from the River Rye catchment were collected relatively early in this research project. At this time the procedure of comparing control reference bulk core inventories with floodplain bulk core inventories, to aid in establishing sites which receive maximum sediment deposition, had not been incorporated into the study protocol. Therefore, in this instance, selection of the most appropriate core for laboratory analysis was based on the best available historical, anecdotal and visual evidence of the suitability of the selected sites. On this basis, the floodplain core from East Ness Core Site 1 was sectioned into 1cm horizons, dried, disaggregated, sieved and prepared for laboratory analysis.

8.4 ^{137}Cs radioisotope geochronology

The depth distribution profile of ^{137}Cs activity within the Rye floodplain core is shown in Figure 8.4. Inspection of the depth distribution identified a horizon of peak activity at 17cm. A second, smaller peak was observed at 4cm. In consideration of the discussion of UK ^{137}Cs fallout distribution presented in previous chapters, it is likely that the 4cm peak corresponds to the date of the Chernobyl incident in 1986 and that the 17 cm peak could be realistically associated with the peak in bomb-derived fallout attributed to 1963. There was a small amount of ^{137}Cs downward mobility in the profile tail below the 1963 peak which may be due to leaching through the organic fraction of soils at the floodplain sampling site. The interpretation of the peaks presented above leads to the conclusion that the sedimentation rate at the site diminished considerably in the period from 1986 to the time of core collection in 2007. Time-averaged deposition rates for the years prior to 1963, and including those years between 1963 and 1986, were calculated at 0.54cm year^{-1} and extrapolated over the depth of sediment corresponding with that age range within the core to provide an approximate chronology. Similarly, time-averaged deposition rates for the years between 1986 and 2007 were calculated at 0.14cm year^{-1} and extrapolated to complete the estimated core chronology (see Figure 8.4). Lees *et al.*, (1997) found not dissimilar substantial fluctuations in sedimentation rates for three North York Moor catchments, particularly in relation to notable declining rates over more recent periods. Remobilization of floodplain sediment during high magnitude overbank flood events could offer an alternative interpretation of the apparently diminished sedimentation rate since 1986 (Greenwood *et al.*, 2008). Notwithstanding the above observations, the general appearance of the profile suggested that the core site had been undisturbed by cultivation over the recent past (ca 80 years).

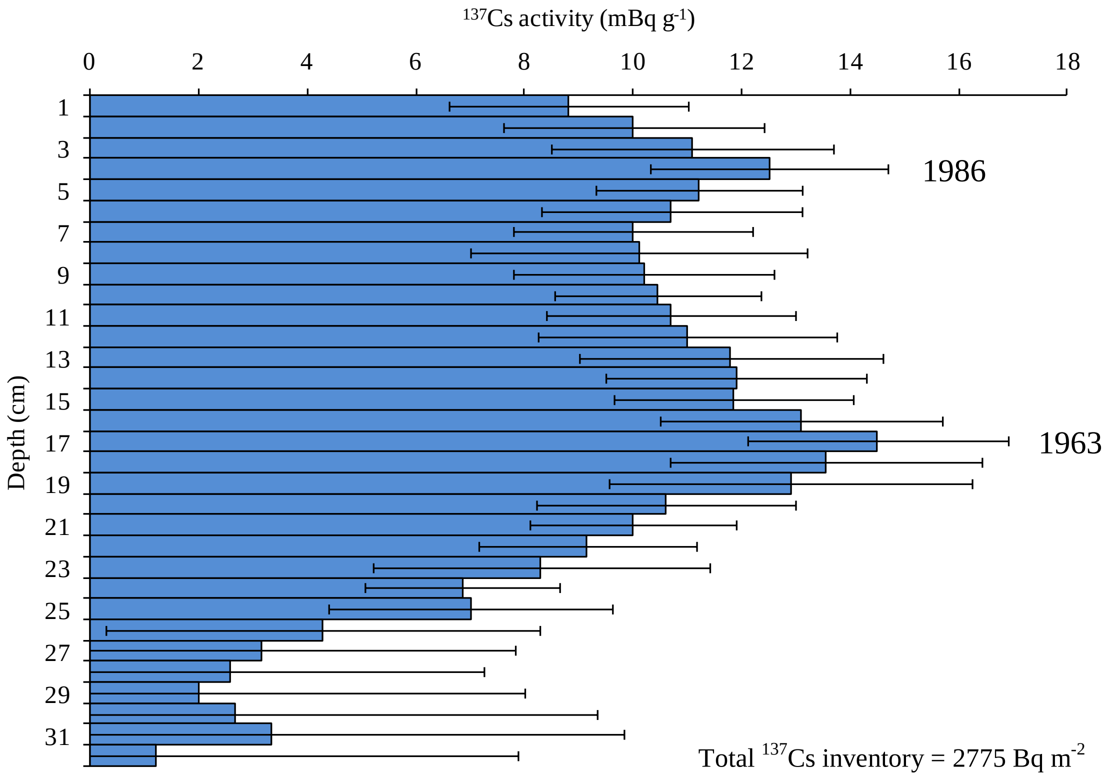

Figure 8.4 *The depth profile of ^{137}Cs with associated estimated chronology and total inventory from the River Rye floodplain core, Site 1, East Ness, North Yorkshire, UK*

8.5 The sediment source fingerprinting technique

8.5.1 Source samples

Surface scrapes from three distinct potential sediment source types namely, topsoil from grassland, topsoil from cultivated land and eroding channel banks, were retrieved from 94 sites across the River Rye study catchment. The samples from the topsoils of grassland and cultivated land were collected from field areas with identified potential for water erosion and mobilisation of sediment, combined with clear connectivity to the river channel system. The surface scrapes provided 30 samples each for the grassland and channel bank source groups and 34 samples for the cultivated land source group.

The samples were prepared and analysed, as described in detail in Chapter 2 to identify an appropriate optimum composite fingerprint.

8.5.2 Particle size effects

The available suite of 48 properties was tested for correlation between property concentration and sample SSA within each of the three potential source groups using Spearman's rho. A summary of results for correlation between property concentration and sample SSA is shown in Table 8.1.

Based on 144 grouped relationships, 14 (9.7%) showed significant correlation at $p = 0.01$ and 41 (28.7%) showed significant correlation at $p = 0.05$. Within the grassland, cultivated land and channel bank source groups, significant correlations ($p < 0.05$), were observed in 12%, 33% and 39% of cases, respectively. The collective results for correlations between the source sample SSAs and property concentrations showed that significant correlation ($p = 0.05$) occurred in 38% of cases. Consequently, it was not appropriate to apply particle size correction in this instance. It was assumed that by disaggregating and sieving source and floodplain samples to <63µm during processing, sufficient account had already been taken of any nominal grain size dependencies of property concentrations and thereby an acceptable direct comparison of concentration values could be undertaken without additional correction.

8.5.3 Particle-size distribution

Figure 8.5 compares the mean particle size distributions of the <63µm fraction of sediment retrieved from the River Rye floodplain core and the three source groups. Differences are apparent between the particle size distribution for the floodplain sediment and that for the grassland source group. However, the particle size distribution for the floodplain sediment and those for cultivated and channel bank sources are quite similar. In comparison with the floodplain samples, cultivated samples were marginally more enriched in fines (<4µm). This may indicate that a proportion of the finer fraction remained in suspension during overbank flood events. This possibility could be related to the rate of flow occurring over the floodplain core sample site during overbank inundation.

Table 8.1 *Spearman's rho correlation coefficients and significance for SSA versus fingerprint property concentration from grassland, cultivated land, and channel bank source groups*

	Grassland		Cultivated		Channel Banks	
Property	Coefficient	Significance	Coefficient	Significance	Coefficient	Significance
Mg	0.083	0.661	0.002	0.99	0.055	0.775
Al	-0.039	0.836	-0.095	0.593	-0.299	0.108
K	0.14	0.461	-0.136	0.444	-0.078	0.682
Mn	0.23	0.222	0.053	0.765	.365(*)	0.048
Fe	.424(*)	0.02	0.076	0.668	0.168	0.374
Li	.429(*)	0.018	-0.021	0.907	0.013	0.945
Na	0.165	0.384	-0.156	0.377	-0.106	0.578
Sc	0.232	0.218	0.108	0.541	0.288	0.123
Ti	0.055	0.773	-.424(*)	0.013	-0.217	0.25
V	-0.091	0.631	-0.092	0.604	-0.314	0.091
Cr	-0.122	0.522	-0.089	0.615	-.403(*)	0.027
Co	.564(**)	0.001	0.125	0.48	0.31	0.095
Ni	.558(**)	0.001	0.116	0.514	0.154	0.418
Cu	.511(**)	0.004	-0.124	0.484	0.185	0.327
Zn	0.331	0.074	0.055	0.757	0.186	0.324
Ga	.380(*)	0.038	0.112	0.527	-0.042	0.825
Ge	0.284	0.129	0.121	0.495	.366(*)	0.047
As	0.132	0.487	0.279	0.11	-0.097	0.609
Rb	0.244	0.195	-0.305	0.08	-0.358	0.052
Sr	.375(*)	0.041	0.125	0.48	0.111	0.558
Y	0.218	0.248	.403(*)	0.018	.373(*)	0.042
Zr	0.153	0.42	0.302	0.083	-0.321	0.083
Mo	0.185	0.328	-0.14	0.43	-0.293	0.116
Pd	0.276	0.14	.386(*)	0.024	.495(**)	0.005
Cd	-0.067	0.725	0.116	0.513	0.294	0.115
Sn	-.421(*)	0.02	-.441(**)	0.009	-0.332	0.073
Sb	-0.341	0.066	-.409(*)	0.016	-.376(*)	0.04
Cs	0.118	0.534	-.437(**)	0.01	-.600(**)	0
Ba	.406(*)	0.026	0.168	0.343	0.149	0.433
La	-0.017	0.93	0.265	0.129	0.302	0.105
Ce	0.062	0.746	0.3	0.085	.391(*)	0.033
Pr	0.109	0.567	.365(*)	0.034	0.36	0.05
Nd	0.138	0.468	.362(*)	0.035	.371(*)	0.043
Sm	0.247	0.188	.384(*)	0.025	.401(*)	0.028
Eu	0.27	0.149	.410(*)	0.016	.443(*)	0.014
Gd	0.277	0.139	.401(*)	0.019	.439(*)	0.015
Tb	0.293	0.116	.387(*)	0.024	.449(*)	0.013
Dy	0.289	0.121	.381(*)	0.026	.451(*)	0.012
Ho	0.285	0.127	.393(*)	0.022	.442(*)	0.014
Er	0.249	0.185	.382(*)	0.026	.430(*)	0.018
Yb	0.249	0.184	.399(*)	0.02	.472(**)	0.008
Hf	0.16	0.398	.349(*)	0.043	-.410(*)	0.024
Tl	-0.055	0.771	-0.091	0.61	-0.174	0.358
Pb	-.527(**)	0.003	-.740(**)	0	-.453(*)	0.012
^{207}Pb	-.511(**)	0.004	-.752(**)	0	-.450(*)	0.013
^{208}Pb	-.526(**)	0.003	-.742(**)	0	-.458(*)	0.011
Bi	-0.133	0.483	-.340(*)	0.049	-.405(*)	0.026
U	0.019	0.921	-0.063	0.725	-0.272	0.145

* Correlation is significant at p = 0.05
** Correlation is significant at p = 0.01

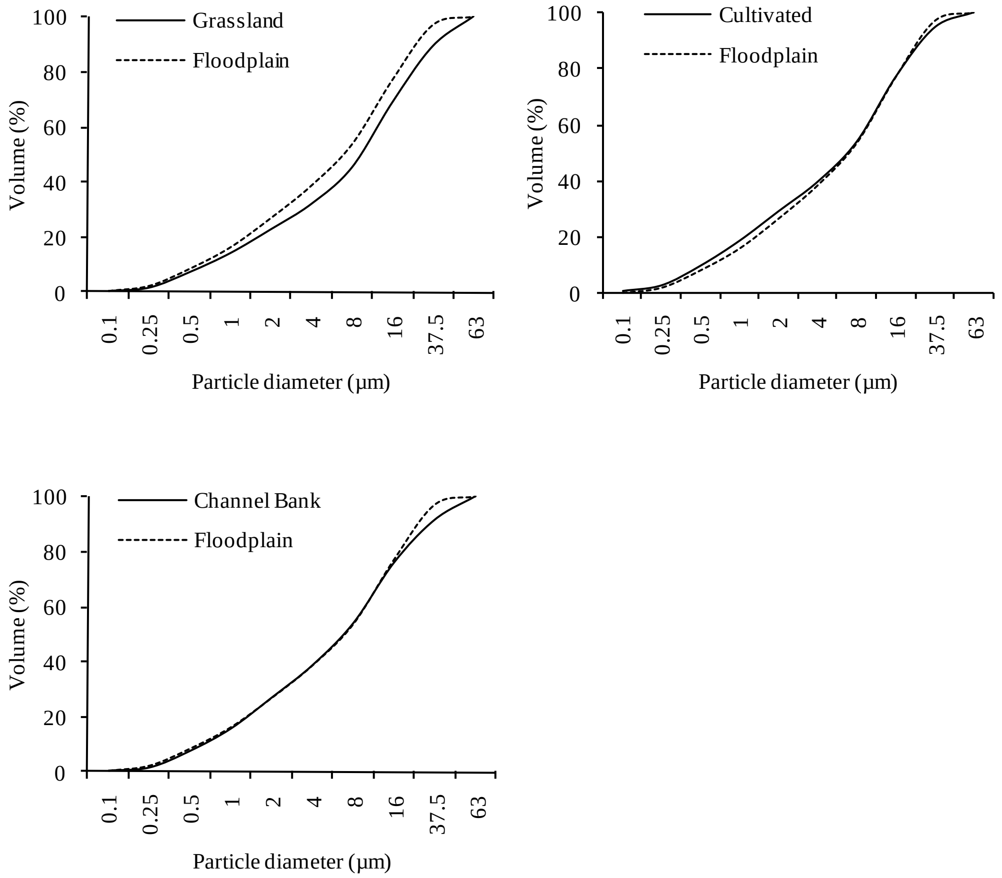

Figure 8.5 *A comparison of the mean cumulative particle size distribution (µm) of the <63µm fraction of sediment from the River Rye floodplain core with corresponding information for grassland, cultivated land and channel bank source groups.*

A relatively dynamic overbank flow rate could limit the proportion of the finer sediment falling out of suspension onto the floodplain at the sample site. The choice of floodplain sampling site within a meander was based on the assumption that such areas are likely to receive regular inundation. However, in a flashy river system, this orientation to the channel could potentially result in a risk of finer fractions being remobilised from the floodplain surface. The distance of the core sample site from the channel could also be a limiting factor in maximising the representativeness of the core sample. Work by Walling *et al.*, (1997) established that the particle size composition of overbank sediment deposited during major flooding can be spatially variable across the floodplain area and can exhibit a strong tendency for particle size to diminish with increased distance from the channel. Therefore, to improve the likelihood of collecting sediment samples containing the finer fractions, the coring site might ideally have been situated at a greater distance from the river channel, as distal areas are more likely to receive fine sediment. Given sufficient resources, a series of cores collected along a transect perpendicular to the channel would be a preferred option to reduce uncertainty associated with the representativeness of the floodplain sediment samples (Walling *et al*., 1997).

The mean and median SSA provide useful parameters for characterizing a particle size distribution and Figure 8.6 shows the inter-sample group variability of mean and median SSA of the <63µm fraction of sediment associated with the floodplain core and the three source groups. The general similarity between the mean and median SSA values from the grassland, channel bank and floodplain samples indicates that the data were likely to be Normally distributed and therefore not unduly influenced by outliers. It is also apparent that the mean SSA values for the source groups were similar and did not differ greatly from those of the floodplain samples.

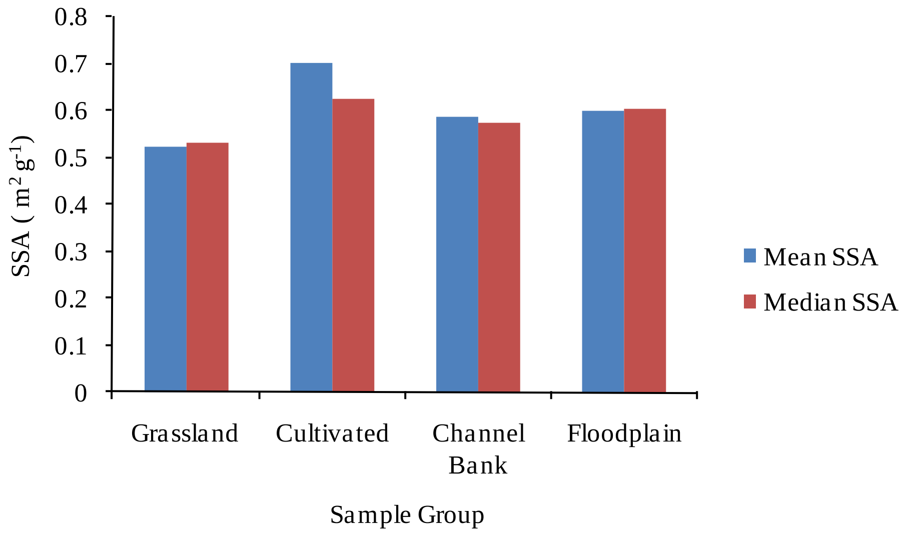

Figure 8.6 *Inter-sample group variability of mean and median SSA (m^2 g^{-1}) of the <63µm fraction of sediment associated with the River Rye floodplain core and the grassland, cultivated and channel bank source groups.*

Figure 8.7 shows the intra-group variability of SSA of the <63µm fraction of sediment associated with the three source groups and the floodplain. This emphasises the relatively heterogeneous nature of the SSA of samples within the source groups when compared to the SSA values for the floodplain samples.

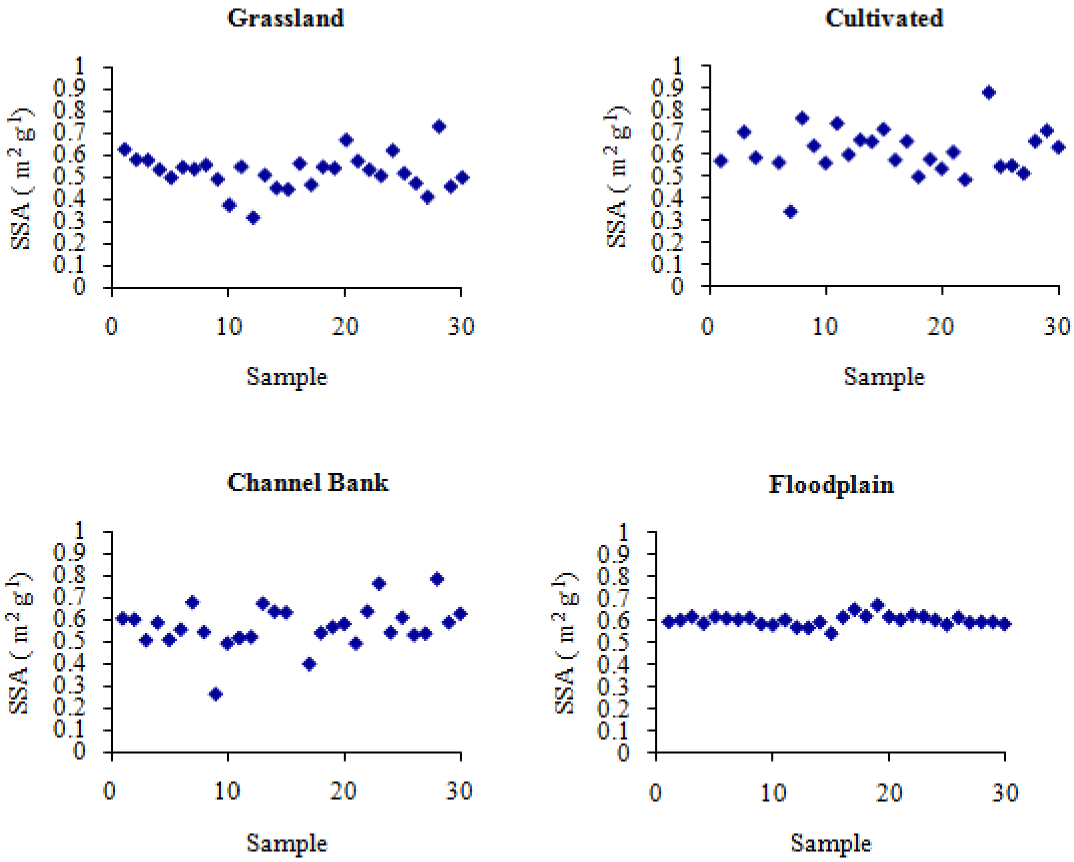

Figure 8.7 *The intra-group variability of SSA of the <63μm fraction of samples associated with the River Rye catchment grassland, cultivated land and channel bank source groups and the floodplain sediment core.*

8.5.4 The fingerprint property concentration range test

The next stage in the selection of the optimum composite fingerprint was to apply a property concentration range test to the data in order to assess the conservative behaviour of sediment properties during erosion, transport, deposition and storage on the floodplain. The range test was also used as a general assessment of whether all potential major sources had been included in the catchment sampling programme.

The source range was derived from the mean property concentration values of the three source groups and spanned from the minimum mean property concentration value minus the associated standard deviation, to the maximum mean property concentration value plus the corresponding standard deviation. The source range included the standard deviation values in order to ensure that the test property values would correspond to the ranges used subsequently during Monte Carlo analysis (See Chapter 3).

Table 8.2 displays the initial property range test results for the River Rye catchment. Of the seventeen properties which failed to satisfy the range test requirement, three properties Al, K and Sc had concentration ranges within the core which overlapped the source range minimum concentration value, and twelve properties Na, Ni, Cu, Zn, Ge, Zr, Mo, Pd, Cd, Ho, Hf and Bi had concentration ranges which overlapped the source range maximum value. For Tl the minimum core value was lower than the corresponding source minimum. The source range for U lies within the core range. These results may suggest that the properties which failed the property range test had become either concentrated or depleted in sediment during transport or storage. An alternative interpretation of those properties failing the property range test suggest that the source samples which were collected may not have fully represented the soil bound sources of those properties within the catchment.

***Table 8.2** The fingerprint property range test results for the River Rye catchment.*

Core range within source range	Core range overlaps source range min	Core range overlaps source range max	Core range below source range min	Source range within core range
Mg	Al	Na	Tl	U
Mn	K	Ni		
Fe	Sc	Cu		
Li		Zn		
Ti		Ge		
V		Zr		
Cr		Mo		
Co		Pd		
Ga		Cd		
As		Ho		
Rb		Hf		
Sr		Bi		
Y				
Sn				
Sb				
Cs				
Ba				
La				
Ce				
Pr				
Nd				
Sm				
Eu				
Gd				
Tb				
Dy				
Er				
Yb				
^{206}Pb				
^{207}Pb				
^{208}Pb				

8.5.5 Source discrimination: the Kruskal-Wallis H-test

The next stage in the selection of the optimum composite fingerprint was conducted to examine the ability of individual properties to clearly distinguish the source type samples. These differences were initially established using the non-parametric Kruskal-Wallis *H*-test (Collins *et al.*, 1997a). Table 9.3 presents the Kruskal-Wallis *H*-values and asymptotic significance. The critical value of 5.99 for 2 *df* of the Chi-Square distribution was used to estimate *H* at $p < 0.05$. Seven properties (Mn, V, Cr, As, Sr, La and Ce) had *H* values below the critical value and were consequently removed from further fingerprint analysis at this stage.

Table 8.3 *H-values and associated asymptotic significance from the Kruskal-Wallis H-test*

Property	*H*-value	Asymptotic Significance
Mg	19.73	0.00
Mn	1.42	0.49*
Fe	15.07	0.00
Li	13.60	0.00
Ti	17.49	0.00
V	4.49	0.11*
Cr	2.84	0.24*
Co	21.29	0.00
Ga	16.29	0.00
As	2.33	0.31*
Rb	8.05	0.02
Sr	4.12	0.13*
Y	6.37	0.04
Sn	23.14	0.00
Sb	41.64	0.00
Cs	24.09	0.00
Ba	18.98	0.00
La	0.22	0.90*
Ce	4.94	0.08*
Pr	6.36	0.04
Nd	9.81	0.01
Sm	15.95	0.00
Eu	17.40	0.00
Gd	14.85	0.00
Tb	14.45	0.00
Dy	12.17	0.00
Ho	10.65	0.00
Er	9.27	0.01
Yb	6.95	0.03
^{206}Pb	36.97	0.00
^{207}Pb	38.38	0.00
^{208}Pb	36.92	0.00

Critical *H* value = 5.99
*Not significant at $p = 0.05$

8.5.6 Source discrimination: Multivariate Discriminant Function Analysis

The geochemical properties which passed the Kruskal-Wallis test were then entered stepwise into Multivariate Discriminant Function Analysis (MDFA) based on the minimization of Wilks' Lambda. At each step, the property which minimised the overall Wilks' Lambda was entered, with maximum significance of F to enter a property at 0.05 and minimum significance of F to remove a property at 0.10. The MDFA tested the ability of the tracer properties to classify the source samples into the correct source groups and also provided a quantification of the overall discriminatory power of the optimum composite fingerprint, as shown in Table 8.4.

Table 8.4 *Results from the stepwise MDFA in identifying the optimum composite fingerprint for discriminating the grassland, cultivated land and channel bank source groups based on the minimisation of Wilks' Lambda*

Step	Property	Wilks' Lambda	Cumulative original grouped cases correctly classified (%)
1	Co	0.73	48.9
2	^{208}Pb	0.56	63.8
3	Cs	0.48	72.3
4	Ti	0.39	73.4
5	^{207}Pb	0.36	73.4
6	Mg	0.32	78.7

A composite fingerprint containing the six properties Co, ^{208}Pb, Cs, Ti, ^{207}Pb and Mg produced a Wilks' Lambda value of 0.32, which was the closest to zero that could be obtained following stepwise inclusion of all available properties. This fingerprint correctly classified 78.7% of the samples collected to represent the individual source groups. Table 8.5 shows the predicted sample group against the actual group membership for the three source groups. It can be observed that grassland topsoil was the most poorly discriminated (53% of samples classified correctly). The majority of the misclassified samples (43%) from the grassland topsoil source group were predicted to belong to the cultivated topsoil source group. This may reflect the use of temporary grassland within the catchments rotational cropping system. The percentage of correct discrimination for the samples from the cultivated land and channel bank source groups was 91% and 90% respectively.

Table 8.5 *Results from comparison of predicted sample group membership against actual group membership for grassland, cultivated land and channel bank source groups, with percentage of correctly classified cases within each group following stepwise MDFA.*

		Source Group	Predicted Group Membership			Total
			Grassland	Cultivated	Channel Bank	
Original Group Membership	Count	Grassland	16	13	1	30
		Cultivated	2	31	1	34
		Channel Bank	1	2	27	30
	%	Grassland	53.33	43.33	3.33	100
		Cultivated	5.88	91.18	2.94	100
		Channel Bank	3.33	6.67	90.00	100

Figure 8.8 illustrates the sample distribution around the three group centroids from the first two canonical discriminant functions following stepwise MDFA. The source group centroids appear to be relatively close to each other and there is observable overlap between samples from all source groups, particularly between grassland topsoil and cultivated topsoil sources.

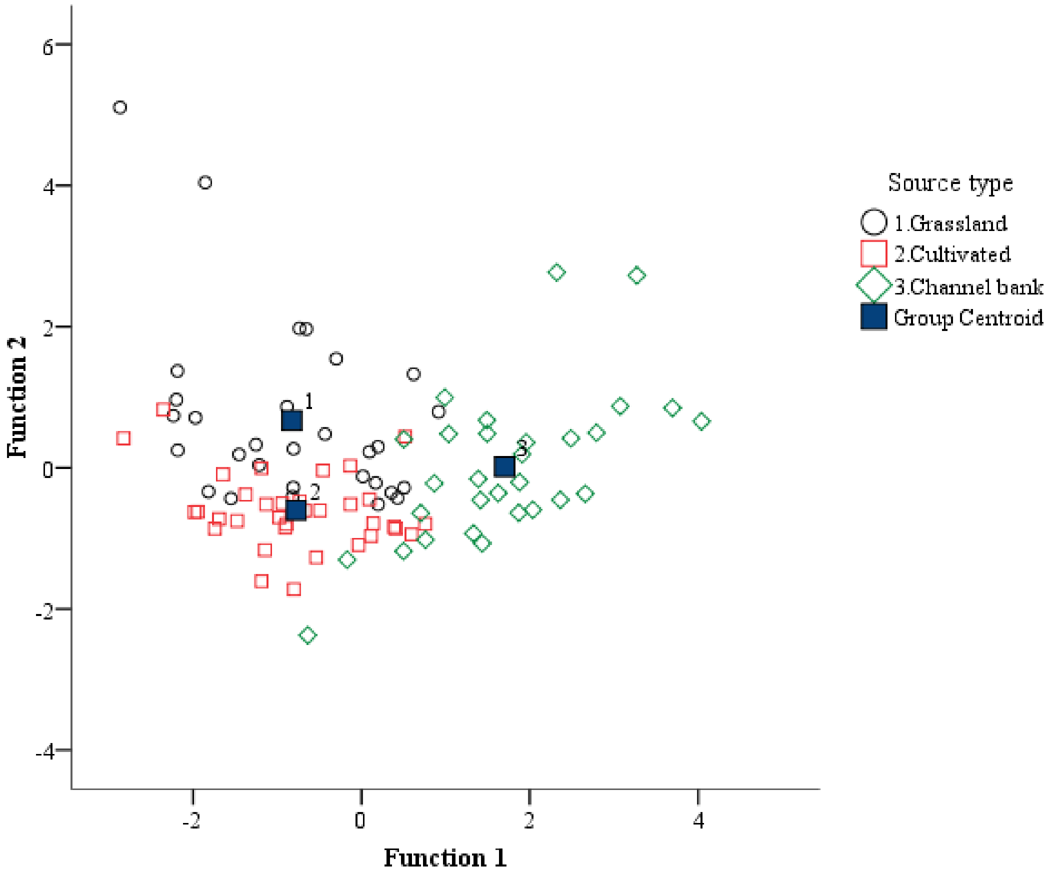

Figure 8.8 *Combined scatter plots showing sample distribution around group centroids from the two canonical discriminant functions applied to the, grassland, cultivated land and channel bank source groups following stepwise MDFA*

In order to ascertain whether discrimination might be further improved, simultaneous entry MDFA was undertaken. The minimum tolerance level for entry was set at a 0.01. Seven properties (Eu, Tb, Dy, Ho, Er, Yb and ^{208}Pb) failed to meet the basic tolerance criteria and were excluded from any further analysis. All properties which passed the tolerance criteria were entered simultaneously into the MDFA.

Following simultaneous entry of all properties which passed the previous screening tests, it was possible to lower the Wilks' Lambda to 0.22. The results of the simultaneous entry MDFA are shown in Table 8.7. The composite fingerprint comprised eighteen properties (Mg, Fe, Li, Ti, Co, Ga, Rb, Y, Sn, Sb, Cs, Ba, Pr, Nd, Sm, Gd, ^{206}Pb and ^{207}Pb) and discrimination across all three source groups was improved to 87.2%.

Table 8.6 displays the discrimination results for the revised composite fingerprint. It is apparent that correct classification improved for the grassland and cultivated topsoil source groups to 80% and 77%, respectively, whilst discrimination of channel bank samples remained consistent with that obtained by stepwise MDFA at 90%.

Table 8.6 *Wilks' Lambda Test of Functions for the properties simultaneously entered into MDFA*

Test of Function(s)	Wilks' Lambda	Chi-square	Significance
1 through 2	0.22	125.78	0.00
2	0.62	39.14	0.00

Figure 8.9 illustrates the sample distribution around the three group centroids from the two canonical discriminant functions following simultaneous entry MDFA. The scatter plots help to illustrate the improved discrimination afforded by the composite fingerprint identified using simultaneous entry MDFA. It can be observed that the separation between the source group centroids increased. However, the within group variance, particularly for grassland topsoil appears relatively high and concurrently the discrimination of grassland topsoil sources remains the lowest of the three source groups at 77% (Table 8.8). The grassland and cultivated land group distributions remained overlapping, which was perhaps due to the rotational cropping regime referred to above. Samples from cultivated land appear to display the closest grouping around the corresponding centroid, which is reflected in the higher level of discrimination (94%) obtained for this specific group (Table 8.7). It was considered that as the composite fingerprint obtained by simultaneous entry MDFA offered improved discriminatory power, that it was preferable for use in the mixing model.

Table 8.7 *Results from comparison of predicted sample group membership against actual group membership for grassland, cultivated land and channel bank source groups, with percentage of correctly classified cases within each group following simultaneous entry MDFA*

		Source Group	Predicted Group Membership			Total
			Grassland	Cultivated	Channel Banks	
Original Group Membership	Count	Grassland	23	5	2	30
		Cultivated	2	32	0	34
		Channel Banks	1	2	27	30
	%	Grassland	77	17	7	100
		Cultivated	6	94	0	100
		Channel Banks	3	7	90	100

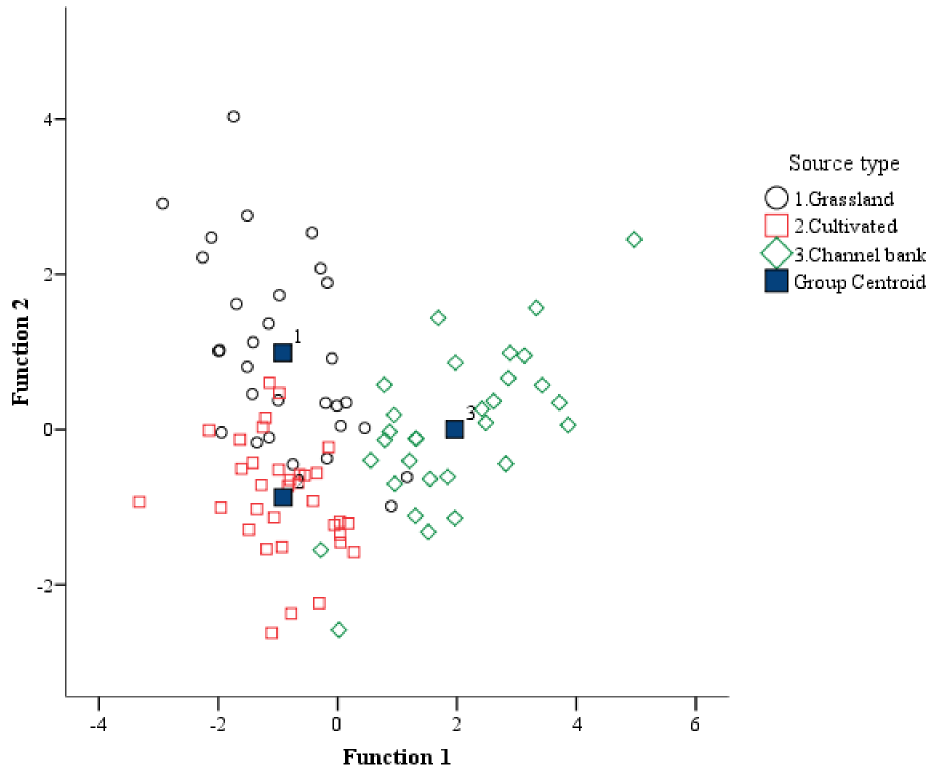

Figure 8.9 *Combined scatter plots showing sample distribution around group centroids from the two canonical discriminant functions applied to the grassland, cultivated land and channel bank source groups of the River Rye catchment following simultaneous entry MDFA*

8.6 Application of the mixing model

A linear numerical mixing model (described in Chapter 3) was subsequently employed to provide an estimate of the relative contributions of the three potential sediment source groups to the individual floodplain core sections. The mixing model algorithm incorporated a weighting factor to reflect individual tracer property discriminatory power. The weightings were based on the discriminatory power of individual fingerprint properties as identified during MDFA (Table 8.8) and were applied to account for the variable contributions made by specific properties to the aggregate discriminatory power of the composite fingerprint.

Table 8.8 *Mixing model property-specific discrimination weighting values*

Property	Individual discrimination (%)	Weighting value
Mg	43.6	1.05
Fe	48.9	1.18
Li	45.7	1.10
Ti	50.0	1.20
Co	48.9	1.18
Ga	50.0	1.20
Rb	43.6	1.05
Y	41.5	1.00
Sn	42.6	1.03
Sb	52.1	1.26
Cs	55.3	1.33
Ba	52.1	1.26
Pr	47.9	1.15
Nd	45.7	1.10
Sm	48.9	1.18
Gd	48.9	1.18
^{206}Pb	60.6	1.46
^{207}Pb	60.6	1.46

The mixing model was incorporated into a Monte-Carlo framework of 5000 simulated input data sets (detailed in Chapter 3). It was considered that in this way, uncertainty associated with using relatively few samples to characterise the mean tracer values for the individual sediment source types would be recognised explicitly.

8.7 Sediment source apportionment and historical catchment land use changes

The apportionment output of the mixing model provided percentage estimates of relative source contributions over time. Table 8.9 shows estimated contributions to floodplain sediment from grassland, cultivated land and channel bank source groups in the River Rye catchment ca. 1918–2007, with associated relative mean error (RME) values. The combined RME for all core sections was 8% and goodness-of-fit was 82%. With the exception of the section from 17cm depth (RME 21.35%), all RME estimates were well within the suggested range of acceptability (i.e. RME <15%) and therefore the mixing model was considered to have provided acceptable predictions of measured property concentrations. The apportionment estimates are illustrated in Figure 8.10 for comparative purposes.

Table 8.9 *Estimated contributions (%) (± standard deviation) to floodplain sediment from grassland, cultivated land and channel bank source groups in the River Rye catchment ca. 1918 –2007 with associated RME (%)*

Depth (cm)	Estimated chronology	Estimated sediment contribution (%)			RME (%)
		Grassland	Cultivated	Channel Bank	
1	2007	6±7	66±11	28±9	8
2	2000	6±6	70±9	24±8	7
3	1993	7±6	72±10	21±8	8
4	1986	15±8	58±10	27±8	7
5	1984	10±7	66±9	24±7	7
6	1982	3±5	69±9	29±8	8
7	1980	5±6	62±9	33±8	6
8	1978	7±6	74±10	18±8	8
9	1976	6±7	59±10	35±8	6
10	1975	11±8	61±10	27±8	6
11	1973	12±7	66±10	22±8	7
12	1971	11±9	51±12	38±9	7
13	1969	6±8	52±11	41±9	7
14	1967	7±7	60±10	33±8	6
15	1965	15±10	38±12	47±9	7
16	1963	4±5	69±9	27±8	7
17	1960	4±5	73±9	23±8	9
18	1957	2±5	71±10	27±9	9
19	1954	1±5	64±15	35±15	21
20	1951	4±5	72±10	24±9	10
21	1948	6±6	57±10	36±8	6
22	1945	5±6	66±9	29±8	8
23	1942	5±5	64±10	32±8	8
24	1939	6±6	56±10	38±8	7
25	1936	8±7	51±11	41±9	6
26	1933	6±6	69±11	26±10	9
27	1930	6±7	57±11	38±10	8
28	1927	7±7	58±13	35±11	8
29	1924	3±5	52±12	45±11	9
30	1921	6±6	45±12	49±10	8
31	1918	2±5	40±11	57±10	9

The source apportionment results presented in Figure 8.10 show general fluctuations in the relative contributions from the potential sources over approximately 90 years (1918-2007). Contributions from channel banks varied over the period from a maximum contribution of 57% around the mid 1920s to a minimum of 18% in the late 1970s. Grassland topsoil contributions ranged from a maximum of 15% in the mid 1980s, to a minimum of 1% in the mid 1950s. Cultivated topsoil varied in contributions over the period from a maximum contribution of 74% in the late 1970s to a minimum contribution of 38% in the mid 1960s. The time-averaged contributions from grassland, cultivated land and channel banks over the study period were 7%, 61% and 33% respectively. Throughout the study period overall contributions from grassland were notably low in comparison to those from channel banks and in particular to those from cultivated sources.

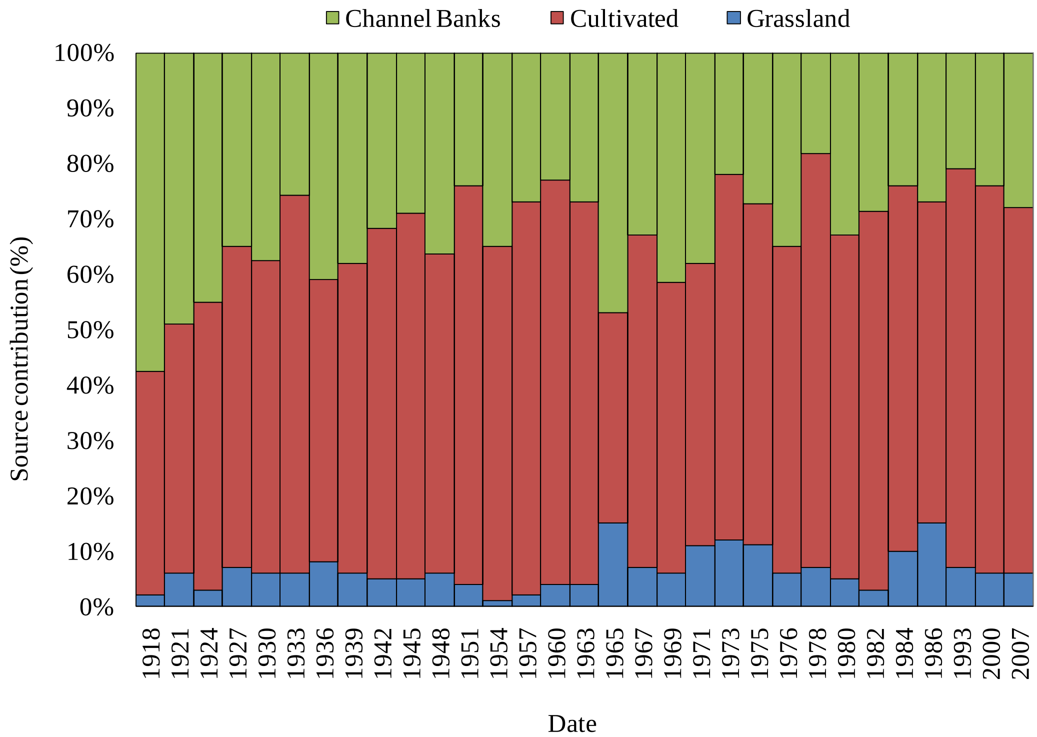

Figure 8.10 *Temporal changes in the relative contributions to floodplain sediment from grassland topsoil, cultivated topsoil and channel bank source groups in the River Rye catchment c.a. 1918 – 2007*

In order to compare ascription estimates to land use change within the catchment, data representing changes in stocking densities, land cover and crop types were extracted and collated from the Agcensus Database (EDINA, 2009). Data were obtained at 2km x 2km grid resolution from the area of the catchment for years; 1969, 1972, 1976, 1979, 1981, 1988, 1993, 1996, 2000 and 2004. Existing published information and personal communication complemented the Agcensus data as sources of historical reference.

Land cover data were compiled for late-harvested crops often associated with high erosion risk (potatoes, sugar beet, kale, beans, peas, turnips, swedes, mangolds and maize). The data were collated at catchment scale between 1969 and 2004. Similarly, data were combined for high erosion risk autumn-sown crops, including wheat, winter-barley and oilseed rape. Temporary grassland, permanent grassland and rough grazing data were also individually collated for comparative analysis.

The combined land cover plots are shown in Figure 8.11. Permanent grassland is the major land cover throughout the study period. The largest fluctuation in permanent grassland occurred from the late 1980s to the mid 1990s when the recorded area increased from 5494 ha to 6373 ha. This increase can be observed to be in almost direct inverse proportion to the area under rough grazing and may therefore be representative of semi-improved grassland. The increase in the area under permanent grassland may have been a response to the growth of livestock numbers (Figure 8.12) and the pressure of increased stocking densities (Figure 8.13) which begin to increase in the period immediately before the expansion of permanent grassland. Similarly, permanent grassland occupied a reduced area over the last decade as stocking densities and livestock numbers declined.

Observation of the source apportionment outputs over the beginning of this time period indicates a marginally increased sediment contribution from grassland sources, as both the area under permanent grassland and stocking densities increased. It should be borne in mind that although livestock numbers and stocking densities increase over this period, the stocking densities concerned could be considered to be relatively low. In addition and perhaps more significantly, much of the livestock within the catchment is likely to be occupying the more marginal land of the uplands, whilst arable production occupies the more fertile lower slopes and valley floor with associated field drainage which is highly connected to the river channel (Robinson and Armstrong, 1987; Chapman *et al*., 2005).

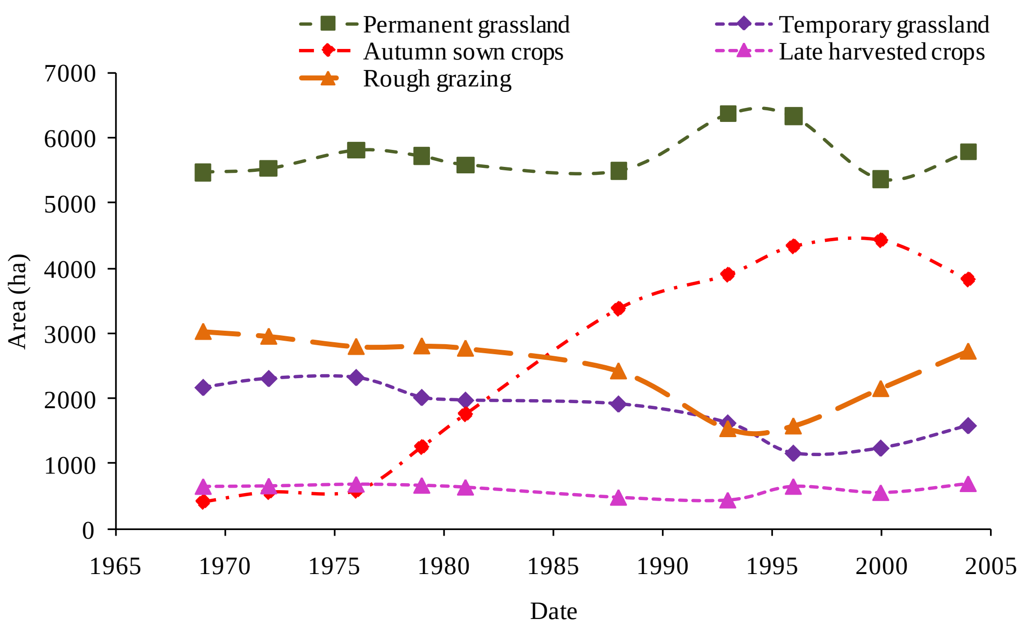

Figure 8.11 *Land cover areas for permanent grassland, temporary grassland, autumn sown crops, late harvested crops and rough grazing in the River Rye catchment 1969-2004*

The most striking observation from the land cover data is the dramatic increase in the area under autumn sown crops from 587 ha in 1976 to 4,435 ha in 2000. Over this time period the estimated relative sediment contributions from cultivated sources rose from 59% in 1976 to 70% in 2000. It could be argued that the general trend representing increased relative sediment contributions from cultivated sources corresponds with the trend of increased land recorded under autumn sown crops. However, some of the variations within the relative sediment contributions from the different source groups during other, shorter time periods are harder to interpret using the available land use data.

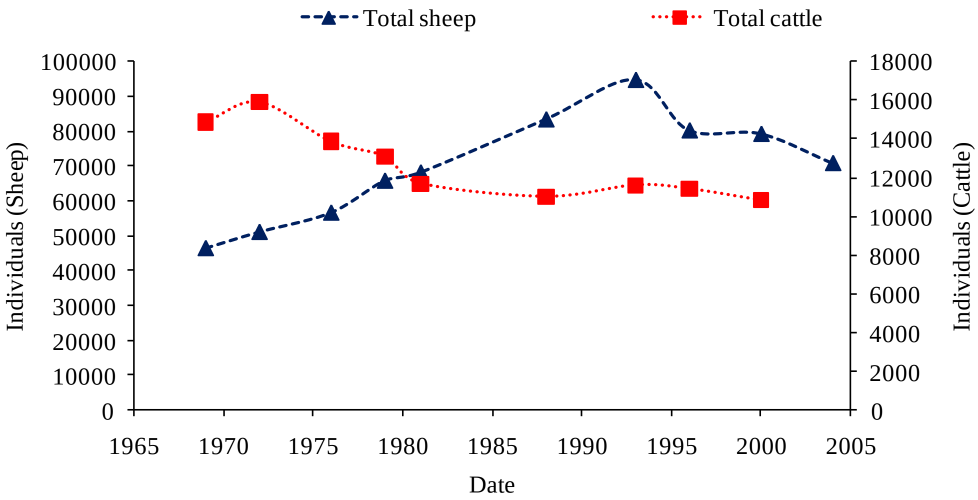

Figure 8.12 *Livestock numbers (sheep and cattle) in the River Rye catchment 1969-2004*

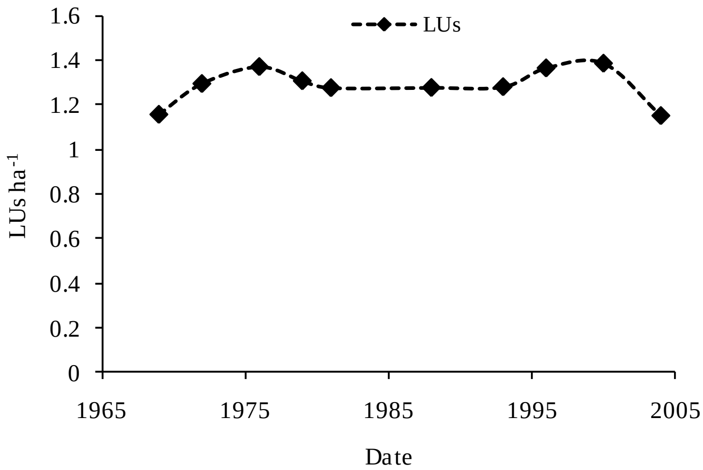

Figure 8.13 *Stocking density estimates (LU ha^{-1}) for the River Rye catchment 1969-2004*

The apparent large-scale reduction in relative contributions from cultivated topsoil sources during the mid 1960s occurs before the Agcensus records begin and is particularly difficult to resolve from available land use information. During the 1960s large areas of the Yorkshire moors were subject to increased drainage (Daelnet, 2009). Field ditches were cut to improve the land for grazing. This land management activity, in combination with a major rainfall event could perhaps have lead to the simultaneous increase in sediment derived from both grassland and channel bank sources. Such circumstances could have led to the apparent relative diminishing of sediment from cultivated topsoil sources. The steepness of the longitudinal profiles of the upland tributaries makes the River Rye a flashy river, which creates the potential for significant erosion of the well formed channel banks in the downstream main stem of the river during high-magnitude rainfall events. This might account for the temporal fluctuations of sediment contributions from eroding channel bank sources throughout the study period.

Figure 8.14 illustrates the proportion of total land area occupied by grassland and cultivated land, with the associated sediment contributions made by both source types to the floodplain between 1969 and 2004. The application of the sediment source fingerprinting technique to floodplain sediment in the River Rye catchment has proved particularly useful in illustrating the disproportionate contribution to floodplain sediment which is derived from cultivated topsoil sources.

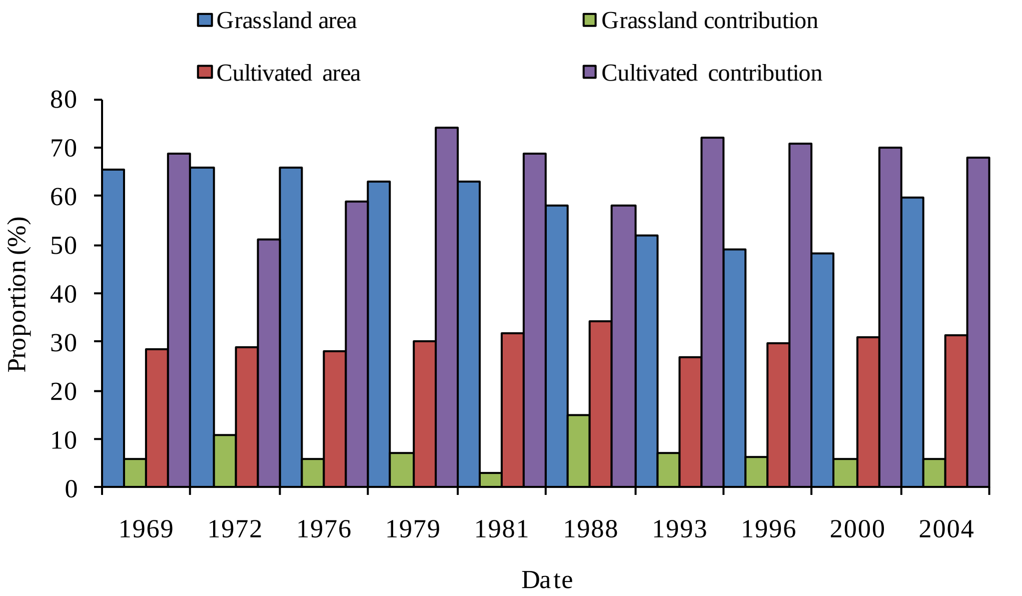

Figure 8.14 *The relative proportions of land cover area and contributions to floodplain ovebank sediment from grassland and cultivated topsoil sources (1969-2004)*

8.8 Conclusion

The sediment pressures reported for the River Rye catchment under the ECSFDI Priority Catchment designation included the reports of increased quantities of enriched sediment delivered from cultivated sources on vulnerable hillside soils. This study has confirmed that throughout the study period the proportion of the catchment area under cultivation has been relatively small when compared to the area under grassland. However, the relative sediment contribution from cultivated topsoil sources has been high in comparison to other sources. The high proportion of sediment derived from cultivated sources appears to remain relatively constant, despite the apparent decline in floodplain sedimentation rates since 1986. This decline might signify reduced sediment loads. Whilst diffuse pollution mitigation measures may have had some influence in this regard, it is perhaps less likely that this influence would have been equally effective across all source types. Concurrent changes in the rainfall patterns and fluvial response within the catchment may have had an influence on both erosion and sediment transport rates. A possible increase in flow rates since 1986 may have limited the deposition of the finer fraction of suspended sediment at the floodplain core sampling point.

In consideration of the results for determination of sources of recent historic sediment contributions to River Rye floodplain, any mitigation measures designed to reduce the excessive sedimentation reported by the ECSFDI should clearly be primarily targeted at the areas of the catchment under arable production.

CHAPTER 9 - THE RIVER WENSUM CATCHMENT:

RESULTS AND INTERPRETATION

9.1 Introduction

This chapter is the last of the case study reports, it presents and interprets the results from the application of the sediment source fingerprinting technique to floodplain sediment from the River Wensum catchment, Norfolk, England, with the aim of relating changes in the relative importance of the sources of the overbank sediment deposits in response to historical land use change over the last 100 years.

The River Wensum catchment has been the subject of some considerable conservation interest over recent years and it has been cited as one of the best examples of an "enriched calcareous lowland river" in the UK (Natural England, 2009). However, it has been under pressure due to excessive sediment ingress prompting the ECSFDI to target the reduction of sediment and P run-off from arable fields in the Upper Wensum as a priority for the Capital Grant Scheme aimed at addressing water quality issues.

9.2 The River Wensum catchment description

The River Wensum catchment is a lowland, predominantly rural, catchment situated to the North East of Norwich in Norfolk, England. The Wensum rises close to the village of Whissonsett, from where it initially flows in a westerly direction passing the villages of South Raynham, West Raynham and East Raynham. The river then turns northward and flows through Sculthorpe Moor nature reserve. Leaving Sculthorpe, the river again changes course to flow eastward through the town of Fakenham. The river then continues in a south-easterly direction through the Pensthorpe nature reserve, featured in the BBC 'Springwatch' television series and onward past the collected villages of Great Ryburgh, Guist, North Elmham, Worthing, Swanton Morely, Lyng, Lenwade and Taverham. The River Wensum then flows through the Norwich suburbs of Drayton, Costessey and Hellesdon before entering the north of the city. After flowing through Norwich, the river flows past Trowse down to its confluence with the River Yare at Whitlingham. The sub-catchment identified for this study incorporates the River Wensum from its source near Whissonsett and all major and minor tributaries down to a designated catchment outlet slightly below Bintree Mill at Bintree, occupying a drainage basin area of approximately 220 km^2.

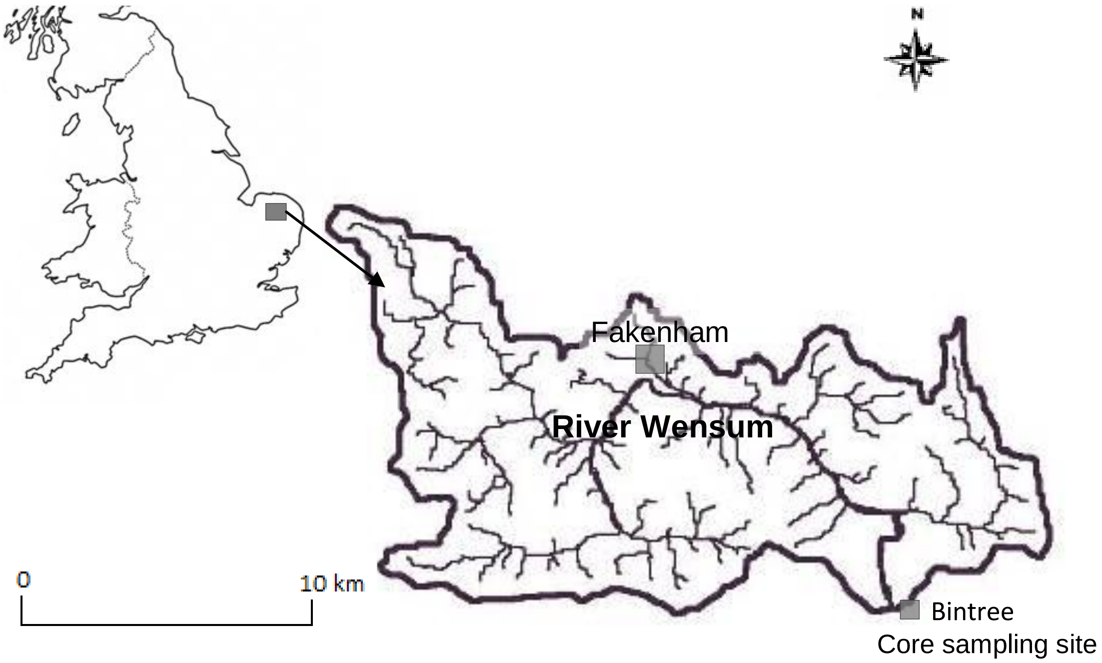

Figure 9.1 *The location and study area of the River Waver catchment, Norfolk, UK*

The geology of the River Wensum catchment is dominated by Senonian Chalk, overlain by a sequence of glacial drift, sands and gravels, which increase in depth towards the confluence with the River Yare below Norwich. The depth of the complex overlying drift sequences often results in the river being separated from the chalk aquifer. Consequently, the River Wensum does not exhibit all of the typical characteristics of many chalk rivers found elsewhere in the south of England. However, the hydrological regime of the River Wensum is essentially that of a groundwater-fed chalk-river. The maximum elevation within the catchment is less than 90m AOD. Consequently, the river is predominantly slow flowing and shallow, with the exception of reaches where channels have been engineered for milling or drainage (Hiscock *et al.*, 2001). The average annual rainfall for the catchment is estimated at 672 mm year^{-1} (Demars and Harper, 2005). The River Wensum flood hydrograph displays a damped response to rainfall events due to the catchment permeability and storage in the local chalk aquifer and this is reflected in a base flow index of 0.83 in the mid-catchment at Fakenham (Institute of Hydrology, 1992).

Land use in the catchment is dominated on the higher ground and shallow sloping valley sides by intensive arable agriculture, whilst some grazing of wet grassland, and areas of marsh, fen, reedbed, scrub and woodland occupy the valley floor and floodplain areas (Natural England, 2009). The woodland in the catchment includes small-scale mixed and coniferous plantations and scrub. In addition, certain riparian areas were planted with stands of white poplars for the production of matches in the 1950's, which have now grown to maturity. The soils of the River Wensum catchment are characterised in the headwaters and higher ground by predominantly sandy loams or silts over clay, whilst some sandy peats and areas of poorly drained course loams on clay occur in the river valleys and riparian areas (Hodge *et al*., 1984; Hiscock *et al*., 2001).

Consistent with the international importance placed on *Ranunculus*-dominated calcareous lowland rivers under the European Habitats Directive (92/43/EEC), fluvial systems such as the River Wensum have been identified as priority habitats by the UK Biodiversity Steering Group (Natural England, 2009). Locally found species with conservation status include Bullhead and Brook Lamprey, the White-clawed crayfish, Desmoulin's Whorl Snail and *Ranunculus*-habitat vegetative species, including water crowfoot and water starwort. The River Wensum is one of 16 rivers in England designated as a European Special Area of Conservation (SAC) and it is one of 31 rivers in England to be designated as a whole river Site of Special Scientific Interest (SSSI) (Natural England, 2009; Norfolk Anglers Conservation Association, 2010).

Although, as described above, the hydrological regime of the River Wensum is essentially that of a groundwater-fed calcareous lowland river, this regime has been extensively affected by anthropogenic modification, including channelisation, dredging, impoundment and embankment. Continued intensive maintenance of certain reaches has resulted in a loss of riparian vegetation and hence reduced ecological and landscape value. The influence of historic obstructions caused by many redundant mill weirs, combined with abstraction rates of up to 14% of the mean weekly flow (Hiscock *et al*., 2001), have had a negative effect on flow rates, which has led to excessive siltation. Intensive arable production is suspected to be contributing considerable quantities of fine sediment to the river. Bank poaching by livestock is also identified as an important local problem. The combination of these factors led to the River Wensum SSSI being regarded in 2009 as being in an "unfavourable and declining condition" (Natural England, 2009). Figure 9.2 illustrates some of the sediment-associated problems and risks in the The River Wensum catchment.

Figure 9.2 *The River Wensum tributaries and main channel, exhibiting sediment-associated problems and risks. Clockwise from top left: Unfenced livestock access to stream channel; large quantities of in-channel sedimentation; reprofiled, defoliated field ditches in pasture field with build up of faecal matter and organic detritus.; eroding channel banks.*

9.3 Floodplain Site Selection

Potential floodplain sampling sites were identified for collection of overbank sediment cores through the use of topographic maps, satellite imagery, ground observation and anecdotal evidence. This process pinpointed sites which were regularly inundated by overbank flooding, with corresponding potential to receive and store sediment mobilised from upstream sources.

Three key potential floodplain coring sites were identified within relatively close proximity to Bintree Mill, Bintree. The locations of the sites are illustrated in Figure 9.3. It was important that the sites had not been cultivated within the recent past, in order to preserve the historical sediment record intact. This requirement was substantiated through discussion with the owner of Bintree Mill, Paul Seaman, who had personal knowledge of the selected sites going back 65 years and was the fourth generation of his family to occupy the mill (pers comm., Seaman, 2008). The anecdotal evidence was combined with a basic ecological appraisal of the sward composition and plant biodiversity at the sites. The species *Variegated (Norfolk) Reed* (Phragmites Variegatus), *Soft Rush* (Juncus effusus), often associated with wet grassland areas prone to frequent inundation, were observed at the Bintree Mill sites. The sward at the potential coring sites appeared to contain a diverse combination of grasses, sedges, herbs and reeds, further indicating regular inundation and a general absence of cultivation.

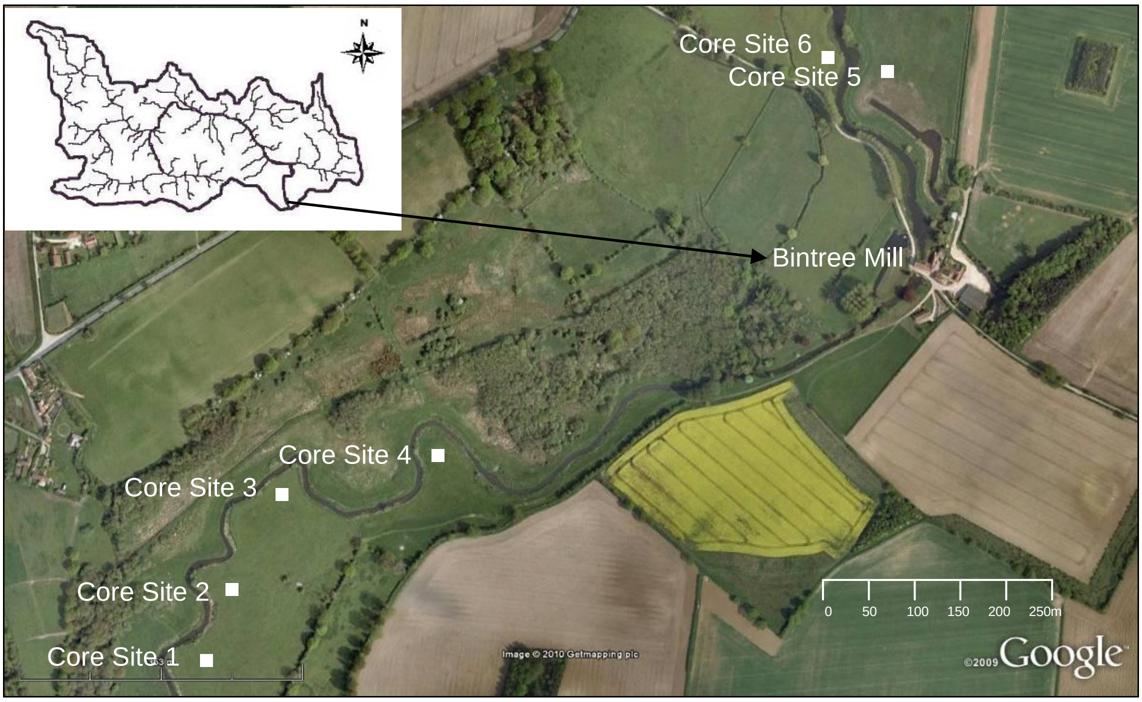

Figure 9.3 *The River Wensum catchment and location of the floodplain core sampling sites at Bintree Mill, Bintree, Norfolk, U.K (Google Earth, 2010)*

Areas at the floodplain sites within meander bends and those featuring shallow topographical depressions were chosen for coring, as these were deemed to be more likely to have retained overbank flood waters and to thereby represent the most promising depositional sinks. The potential for the sites to represent sediment sinks was further substantiated following discussions with the land owner and local fishermen about the nature and extent of regular overbank inundation during flood events.

A total of six cores with potential for use in subsequent laboratory analysis were collected from the identified sites. Nine reference cores were also collected from a nearby undisturbed, topographically level, site overlooking the floodplain on the

Ryburgh Estate. The reference site was assumed to have been subject to neither soil erosion nor sediment deposition and could therefore be considered to represent a control or reference site for quantifying the local ^{137}Cs atmospheric fallout, during subsequent work using the radioisotope inventory for dating the floodplain sediment.

For each core collected for potential use for sectioning and subsequent laboratory analysis, an adjacent bulk core was extracted for the purpose of estimating the ^{137}Cs inventory, as outlined in Chapter 3. The inventories of the bulk cores were compared with the reference inventory established for the Ryburgh Estate reference site. The mean ^{137}Cs inventory from the 9 bulk reference cores was 1837 mBq m^{-2}. Following comparison of the inventories of the bulk floodplain cores with those of the reference site, illustrated in Figure 9.4, the floodplain site estimated to have received the greatest sediment deposition, indicated by a ^{137}Cs inventory of 3339 mBq m^{-2}, was identified as Core Site 4, at Bintree Mill. The corresponding main core was therefore sectioned into 1cm horizons, dried, disaggregated and sieved in preparation for laboratory analysis.

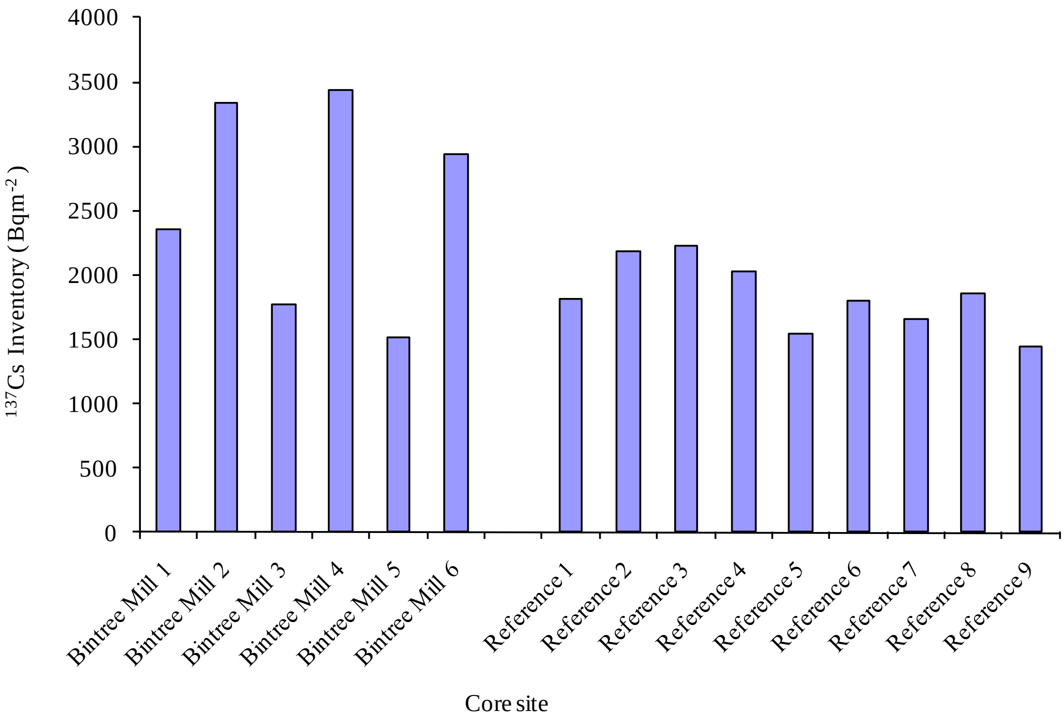

Figure 9.4 *^{137}Cs inventories for the floodplain and local reference cores collected from the River Wensum catchment*

9.4 ^{137}Cs radioisotope geochronology

As noted previously, ^{137}Cs fallout from the 1986 Chernobyl disaster was unevenly distributed across the UK. This patchy deposition reflects in part the fact that the radioactive plume did not reach the upper atmosphere and that the fallout was deposited largely in association with localised precipitation of varying intensities (Cambray *el al.,* 1987; Callaway *et al.,* 1996). Figure 9.5 illustrates the general deposition pattern of Chernobyl-derived ^{137}Cs on vegetation across the UK, as evidenced by a ground vegetation survey undertaken shortly after the accident by the Institute of Terrestrial Ecology (ITE) (Allen, 1986.Cited in Walling *et al.*, 1989).

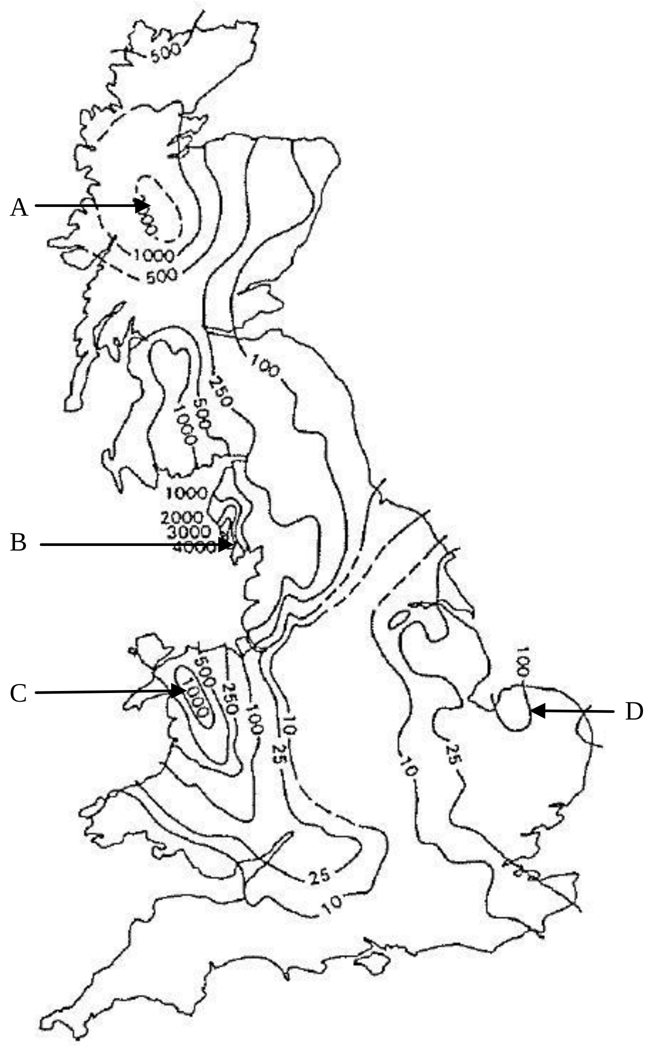

Figure 9.5 *The pattern of Chernobyl-derived ^{137}Cs deposition (Bq m^{-2}) across the UK as evidenced by the ITE vegetation survey (based on Allen 1986. Cited in: Walling et al., 1989)*

The well documented ^{137}Cs fallout hotspots in the West of Scotland (A), Cumbria (B) and North West Wales (C) are clearly visible in Figure 9.5. However, of interest here, is the localised and regionally relatively high deposition recorded for the north Norfolk area, which incorporates the study area (D). Davis (1963) observed that the quantity of fallout radiocaesium absorbed by plants was small; the majority being washed off the vegetation onto the soil surface. Walling *et al.* (1989) proposed that as the ITE survey was based on ground vegetation, it was likely to underestimate the total input, since a proportion of fallout could have already passed through the vegetation canopy onto the topsoil, which was not sampled at the time. This proposition was confirmed by Walling *et al.* (1989) through comparison of Chernobyl-derived ^{137}Cs estimates for the River Severn catchment provided by Cambray *et al*. (1987) based on both soil and vegetation, with those depicted by the ITE map. The comparison confirmed that the estimates based on both soil and vegetation were 100-500% higher than those based on vegetation alone. Therefore, it might be reasonable to assume that localised areas of significant Chernobyl-derived fallout may exist, which could have potential for offering ^{137}Cs markers within sediment profiles (e.g. Foster and Lees 1999; Foster, 2006). Callaway *et al*. (1996) used Chernobyl-derived ^{137}Cs to determine sediment accretion rates at a site on the Norfolk marshes at Stiffkey, some 15 miles from the study core site at Bintree Mill. It was therefore considered appropriate to accept the possibility of an identifiable Chernobyl-derived ^{137}Cs marker being present in the floodplain core profile used for this study.

Caesium-137 ($T_{1/2}$ = 30.17 yr) assay of individual core sections was undertaken by γ-ray spectrometry, in order to establish the chronology of the sediment core profile. The depth distribution profile of ^{137}Cs activity within the River Wensum floodplain core is shown in Figure 9.6. The depth distribution of ^{137}Cs within the core was analysed and the horizon containing peak activity was identified at 10cm. A second, smaller peak was observed at 18cm. Based on the foregoing discussion of documented fallout patterns, it was assumed that the 10cm peak corresponded to fallout from the Chernobyl incident in 1986 and that the 18cm peak could be realistically associated with the peak in bomb derived ^{137}Cs fallout attributed to 1963. Time-averaged deposition rates for the previous, intervening and remaining years were then calculated at 0.37cm year^{-1} and extrapolated over the depth of sediment within the core to provide an approximate chronology.

The general appearance of the profile suggested that a small amount of ^{137}Cs may have leached from the 1963 peak down the profile, possibly as a result of drainage through the peaty soils at the floodplain sampling site. The B horizons in the cores from the floodplain around Bintree Mill were observed to be quite rich in organic peaty material. Radiocaesium has been observed to be more mobile in such peaty soils than in intrinsically mineral soils, although the presence of minimal amounts of certain clay minerals can restrict any such mobility (Hird *et al*., 1996; Mackenzie, 1997). Shand *et al*., (1994) noted that this contrasting behaviour has been attributed to caesium remaining on exchange sites associated with the organic matter, which can limit the rapid fixation by mineral components, particularly clays, which are present in most organic soils, though sometimes in very small quantities (Cremers *el al.,* 1988; Maguire *et al*., 1992). The apparent lack of a continued decline of ^{137}Cs activity between 2-6cm depth may perhaps have been influenced by bioturbation or could reflect recent inputs of sediment-associated ^{137}Cs from the upstream catchment. The fluctuating floodplain water table may also have influenced any apparent upward mobilization of ^{137}Cs, by redistributing any poorly fixed or desorbed ^{137}Cs to finer mineral material up the profile as water table levels rise and the floodplain becomes saturated.

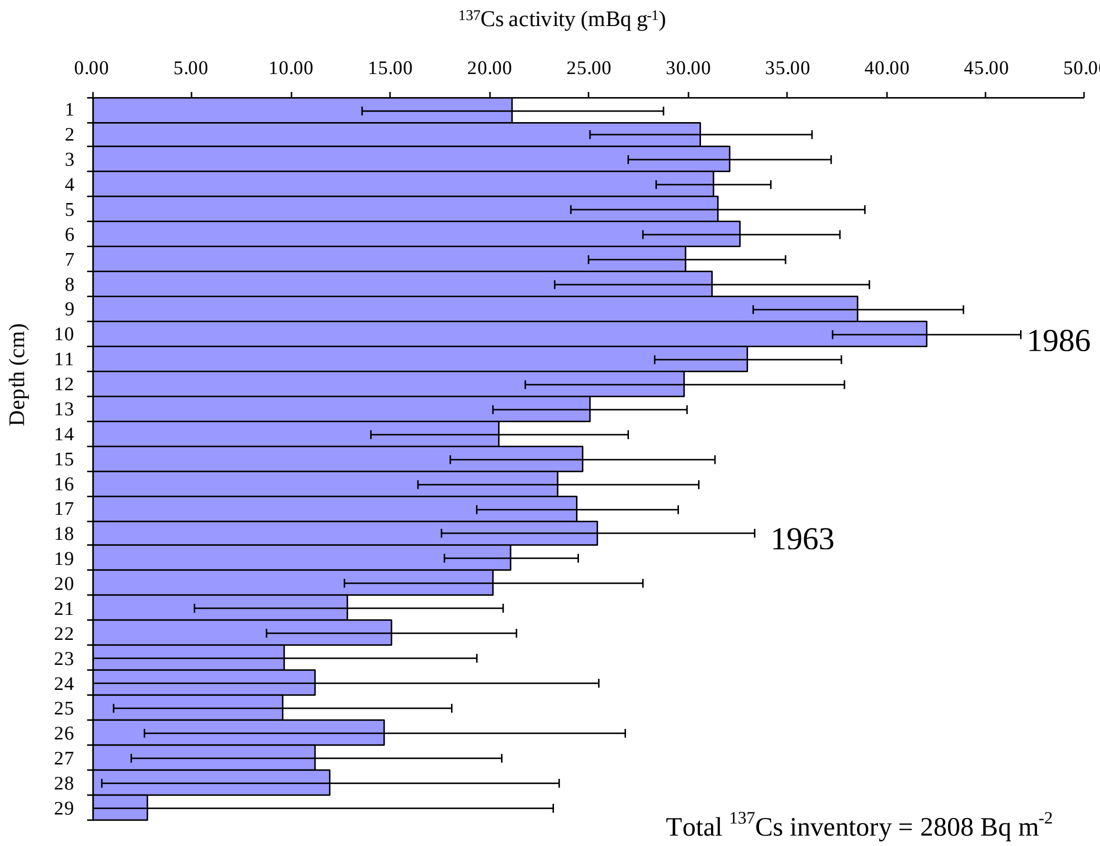

Figure 9.6 *The depth distribution profile of* ^{137}*Cs with associated total inventory from the River Wensum floodplain core, Site 4, Bintree Mill, Bintree, Norfolk, UK*

Notwithstanding any apparent partial ^{137}Cs migration, there was strong chronological agreement between the two peak markers when considered in relation to the surface date at the time of collection which suggested constant sedimentation rates were likely to have occurred. The appearance of the profile indicated that sediment deposition had been continuous over time at a fairly constant rate and that the floodplain core site was likely to have been largely undisturbed over the recent past (ca.100 years).

9.5 The sediment source fingerprinting technique

9.5.1 Source samples

Surface scrapes (<2cm depth) from four distinct potential sediment source groups namely, the topsoils of grassland, cultivated land and woodland and eroding material from channel banks, were collected from 120 sites across the River Wensum study catchment, providing 30 samples for each source group. The samples were collected, prepared and analysed, as described in detail in Chapter 2. Analysis provided information on particle size distribution, specific surface area and concentrations for a potential suite of 48 geochemical properties, including heavy metals, trace metals, lanthanides and actinides, from which to identify an appropriate optimum composite fingerprint.

9.5.2 Particle size effects

The available suite of 48 properties was tested for correlation between property concentration and sample SSA within each of the four source groups using Spearman's rho. A non-parametric test was used, because property concentration data were not assumed to be normally distributed. A summary of results for the correlation between property concentration and sample SSA is shown in Table 9.1.

Based on 196 grouped relationships, 101 (51.53%) showed significant correlation at $p = 0.01$ and 23 (11.74%) showed significant correlation at $p = 0.05$. Within the grassland, cultivated and woodland topsoil and channel bank source groups, significant correlations ($p < 0.05$) were observed in 65%, 65% 73% and 43% of cases, respectively. Twenty-one properties (Mn, Sc, Ti, V, Co, Ni, Sr, Y, Pd, La, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Yb, Tl, and Bi) had concentration values which exhibited significant correlation with SSA across all four source groups.

Based on the above findings, it was considered appropriate to apply a particle size correction to the raw property concentration values used in this study. Details of the particle size correction methodology employed in this study are provided in Chapter 3.

Table 9.1 *Spearman's rho correlation coefficients and significance for SSA versus property concentration for grassland, cultivated land, woodland and channel bank source groups in the River Wensum catchment*

	Grassland		Cultivated		Woodland		Channel Banks	
Property	Coefficient	Significance	Coefficient	Significance	Coefficient	Significance	Coefficient	Significance
Mg	0.520(**)	0.003	0.520(**)	0.003	0.683(**)	0	0.296	0.113
Al	0.410(*)	0.025	0.410(*)	0.025	0.666(**)	0	0.001	0.995
K	0.681(**)	0	0.681(**)	0	0.434(*)	0.016	0.098	0.606
Mn	0.352	0.056	0.352	0.056	0.667(**)	0	0.472(**)	0.008
Fe	0.733(**)	0	0.733(**)	0	0.480(**)	0.007	-0.045	0.812
Li	0.273	0.145	0.273	0.145	0.737(**)	0	-0.11	0.563
Na	0.299	0.108	0.299	0.108	-0.106	0.576	-0.257	0.17
Sc	0.665(**)	0	0.665(**)	0	0.711(**)	0	0.421(*)	0.021
Ti	-0.064	0.737	-0.064	0.737	-0.031	0.872	-0.495(**)	0.005
V	0.562(**)	0.001	0.562(**)	0.001	0.066	0.729	-0.531(**)	0.003
Cr	0.573(**)	0.001	0.573(**)	0.001	0.702(**)	0	-0.256	0.172
Co	0.728(**)	0	0.728(**)	0	0.748(**)	0	0.459(*)	0.011
Ni	0.823(**)	0	0.823(**)	0	0.636(**)	0	0.480(**)	0.007
Cu	0.506(**)	0.004	0.506(**)	0.004	0.251	0.181	0.232	0.218
Zn	0.536(**)	0.002	0.536(**)	0.002	0.455(*)	0.012	0.001	0.997
Ga	0.322	0.082	0.322	0.082	0.574(**)	0.001	-0.174	0.358
Ge	0.326	0.079	0.326	0.079	0.651(**)	0	0.207	0.273
As	0.552(**)	0.002	0.552(**)	0.002	0.202	0.285	-0.012	0.95
Rb	0.345	0.062	0.345	0.062	0.427(*)	0.019	0.166	0.379
Sr	0.525(**)	0.003	0.525(**)	0.003	0.377(*)	0.04	0.778(**)	0
Y	0.677(**)	0	0.677(**)	0	0.794(**)	0	0.643(**)	0
Zr	0.640(**)	0	0.640(**)	0	0.492(**)	0.006	-0.162	0.392
Mo	0.306	0.1	0.306	0.1	-0.380(*)	0.038	0.146	0.441
Pd	0.634(**)	0	0.634(**)	0	0.788(**)	0	0.610(**)	0
Cd	0.601(**)	0	.601(**)	0	0.371(*)	0.043	0.135	0.477
In	-0.03	0.877	-0.03	0.877	-0.011	0.954	-0.167	0.378
Sn	0.297	0.111	0.297	0.111	0.003	0.989	0.239	0.204
Sb	0.039	0.836	0.039	0.836	-0.512(**)	0.004	-0.004	0.983
Cs	0.182	0.335	0.182	0.335	0.084	0.658	-0.075	0.694
Ba	0.214	0.257	0.214	0.257	0.512(**)	0.004	-0.227	0.227
La	0.681(**)	0	0.681(**)	0	0.749(**)	0	0.472(**)	0.009
Ce	0.665(**)	0	0.665(**)	0	0.724(**)	0	0.247	0.187
Pr	0.682(**)	0	0.682(**)	0	0.734(**)	0	.378(*)	0.039
Nd	0.685(**)	0	0.685(**)	0	0.763(**)	0	.387(*)	0.034
Sm	0.682(**)	0	0.682(**)	0	0.770(**)	0	0.349	0.059
Eu	0.706(**)	0	0.706(**)	0	0.772(**)	0	0.428(*)	0.018
Gd	0.722(**)	0	0.722(**)	0	0.762(**)	0	0.424(*)	0.02
Tb	0.692(**)	0	0.692(**)	0	0.760(**)	0	0.433(*)	0.017
Dy	0.700(**)	0	0.700(**)	0	0.779(**)	0	0.458(*)	0.011
Ho	0.691(**)	0	0.691(**)	0	0.784(**)	0	0.498(**)	0.005
Er	0.697(**)	0	0.697(**)	0	0.776(**)	0	0.502(**)	0.005
Yb	0.690(**)	0	0.690(**)	0	0.786(**)	0	0.506(**)	0.004
Hf	0.593(**)	0.001	0.593(**)	0.001	0.502(**)	0.005	0.026	0.891
Tl	0.446(*)	0.013	0.446(*)	0.013	0.612(**)	0	0.365(*)	0.047
Pb	0.309	0.096	0.309	0.096	-0.313	0.093	0.077	0.684
^{207}Pb	0.315	0.09	0.315	0.09	-0.309	0.097	0.077	0.684
^{208}Pb	0.3	0.107	0.3	0.107	-0.302	0.104	0.083	0.661
Bi	0.507(**)	0.004	0.507(**)	0.004	0.001	0.994	0.386(*)	0.035
U	-0.103	0.588	-0.103	0.588	0.219	0.246	0.079	0.68

* Correlation is significant at p = 0.05

** Correlation is significant at p = 0.01

9.5.3 Particle-size composition

Figure 9.7 compares the mean particle size distributions of the <63µm fraction of sediment retrieved from the River Wensum floodplain core and the four source groups. Significant differences are apparent between the particle size distribution for the floodplain sediment and those for the individual source groups, particularly the grassland and woodland surface sources.

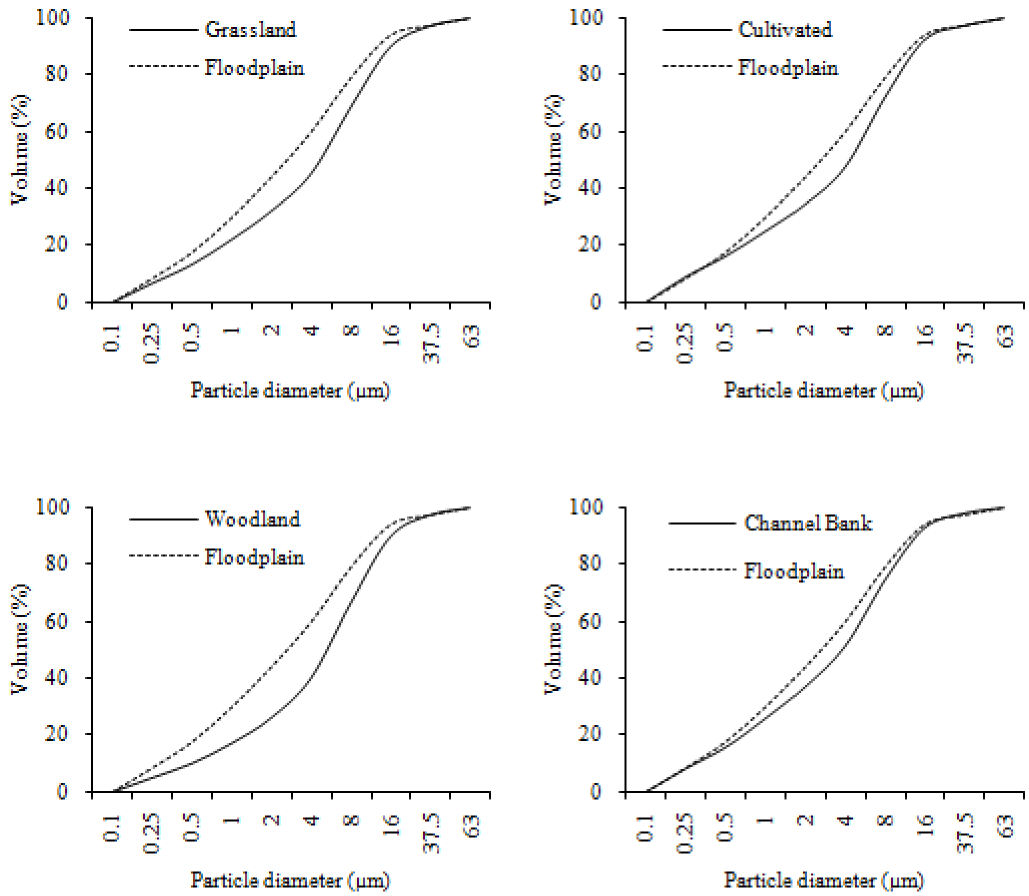

Figure 9.7 *A comparison of the mean cumulative particle size distribution (µm) of the <63µm fraction of sediment retrieved from the River Wensum floodplain core and the sample material from the grassland, cultivated land, woodland and channel bank source groups*

The mean and median SSA provide useful parameters for characterizing a particle size distribution and Figure 9.8 shows the inter-sample group variability of mean and median SSA of the <63µm fraction of sediment associated with the floodplain core and the four source groups. The similarity between the mean and median SSA values for all sample groups, particularly the cultivated and floodplain sample groups, indicates that the data were likely to be normally distributed and therefore not unduly influenced by outliers. It can be noted that both the mean and median SSA values for cultivated topsoil are higher than those from the other source groups and actually slightly higher than those from the floodplain samples. This variation may reflect the choice of land for cultivation based on the finer mineral loamy soils of the higher ground and valley slopes, compared to the soils of the floodplain used for grazing and woodland.

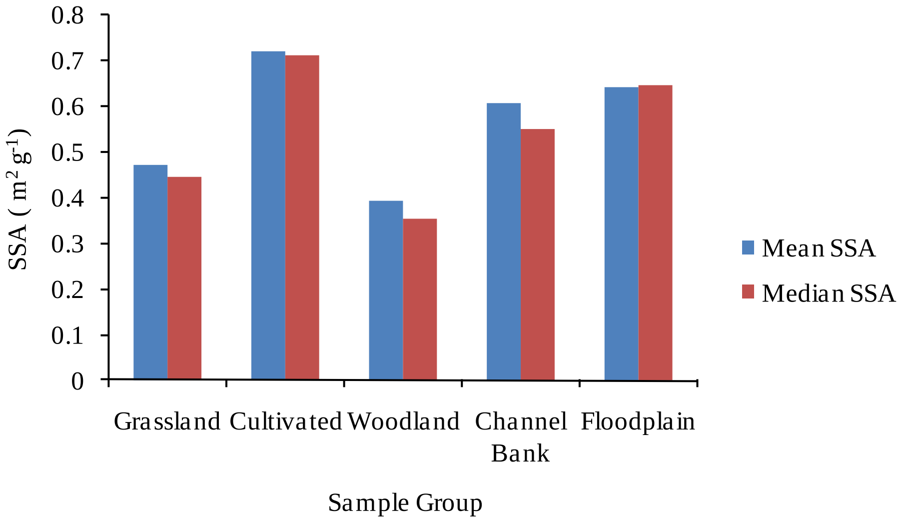

Figure 9.8 *Inter-sample group variability of mean and median SSA (m^2 g^{-1}) of the <63μm fraction of sediment associated with the River Wensum floodplain core and the grassland, cultivated land, woodland and channel bank source groups*

Figure 9.9 shows the intra-group variability of SSA of the <63μm fraction of sediment associated with the four source groups and the floodplain. This emphasises the relatively heterogeneous nature of SSA within each source group when compared to the SSA values for the floodplain sample group. There is an apparent slight downcore trend possibly indicating that finer material had been deposited in the past or alternatively reflecting post-depositional pedogenic processes.

9.5.4 The fingerprint property concentration range test

The next stage was to apply a property concentration range test to the data, to assess the conservative behaviour of sediment properties during erosion, transport, deposition and storage on the floodplain. The test also provided an assessment of whether all potential major sources had been included in the source sampling programme (see Chapter 3).

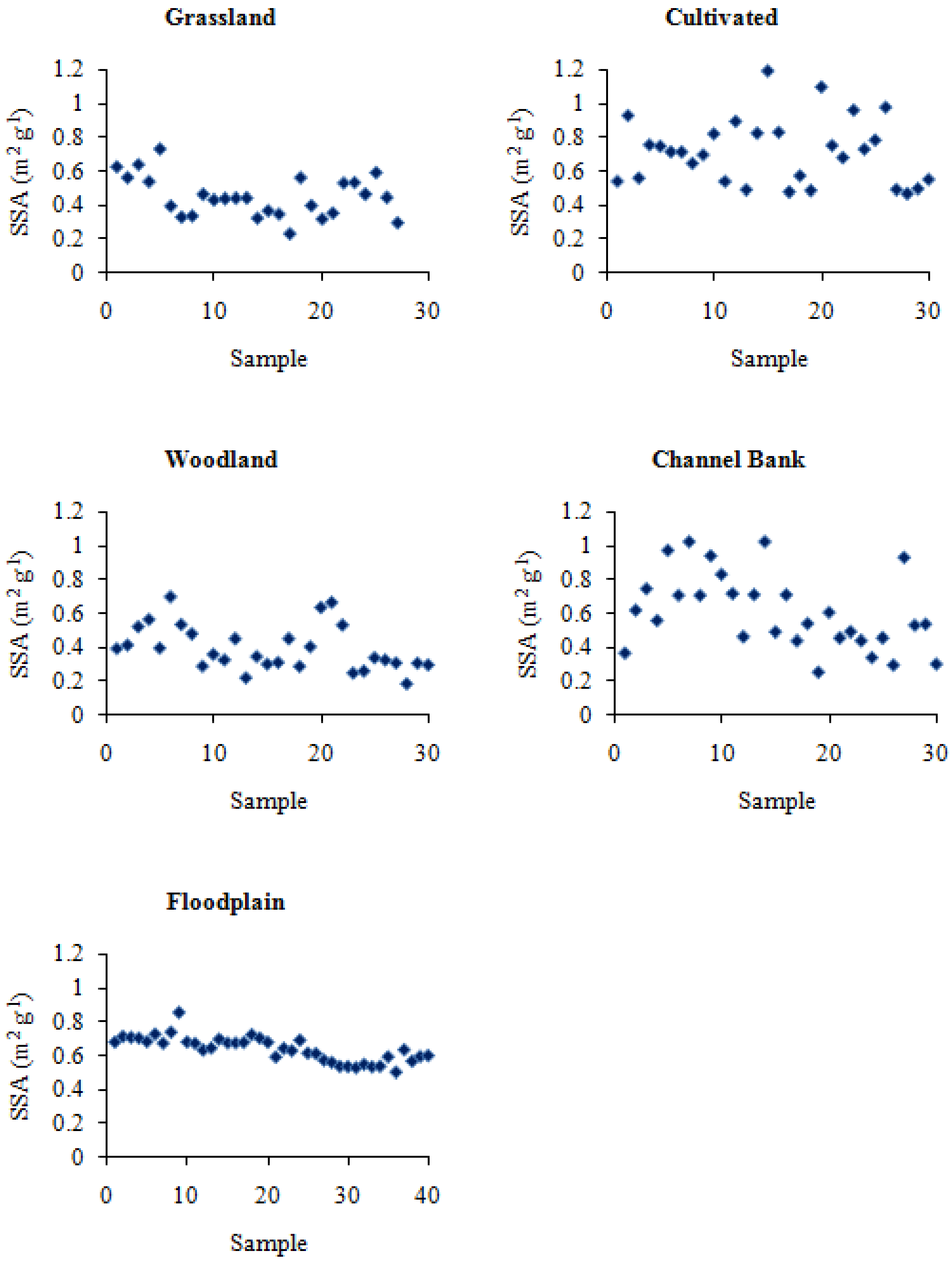

Figure 9.9 *The intra-group variability of SSA of the <63µm fraction of material from the grassland, cultivated land, woodland and channel bank source groups and the floodplain core*

The source range was derived from the mean property concentration values of the four source groups and spanned from the minimum mean property concentration value minus the associated standard deviation, to the maximum mean property concentration value plus the corresponding standard deviation. The source range included the standard deviation values in order to ensure that the test property values would correspond to the ranges used subsequently during construction of the Monte Carlo framework input dataset (see Chapter 3).

Table 9.2 displays the initial property range test results for the River Wensum catchment. Of the twelve properties which failed to satisfy the range test requirement, ten properties (Al, K, Sc, Ti, Cr, Co, Ni, La, Ce, and Tl) had concentration ranges within the sectioned core which overlapped the source range minimum concentration value. One property (Hf) had a concentration range which overlapped the source range maximum value.

Table 9.2 *The property range test results for property concentrations*

Core range within source range	Core range overlaps source range min	Core range overlaps source range max
Mg	Al	Hf
Mn	K	
Fe	Sc	
Li	Ti	
Na	Cr	
V	Co	
Cu	Ni	
Zn	La	
Ga	Ce	
Ge	Tl	
As		
Rb		
Sr		
Y		
Zr		
Mo		
Pd		
Cd		
Sn		
Sb		
Cs		
Ba		
Pr		
Nd		
Sm		
Eu		
Gd		
Tb		
Dy		
Ho		
Er		
Yb		
^{206}Pb		
^{207}Pb		
^{208}Pb		
Bi		
U		

9.5.5 Source discrimination: the Kruskal-Wallis H-test

The next stage in the selection of the optimum combination of tracer properties to form the composite fingerprint was conducted to test which properties displayed significant differences between source types. These differences were initially assessed using the non-parametric Kruskal-Wallis *H*-test, applied to the source sample property value data (Collins *et al*., 1997). The Kruskal-Wallis *H*-test is suitable when the study incorporates two or more potential source groups and the number of observations per group exceeds the total number of groups (Walling and Collins, 2000). Greater *H* values are produced as the significance of inter-group contrasts increases. Table 9.3 presents the Kruskal-Wallis *H*-values and associated asymptotic significance.

Table 9.3 *H-values and asymptotic significance from the Kruskal-Wallis H-test for differences between the grassland, cultivated land, woodland and channel bank source groups*

Property	*H*-value	Asymptotic
Mg	7.47	0.058*
Mn	22.71	0
Fe	9.28	0.026
Li	9.51	0.023
Na	34.14	0
V	17.34	0.001
Cu	13.70	0.003
Zn	9.34	0.025
Ga	12.04	0.007
Ge	4.86	0.182*
As	20.99	0
Rb	13.50	0.004
Sr	42.09	0
Y	9.86	0.02
Zr	9.74	0.021
Mo	36.33	0
Pd	10.26	0.016
Cd	7.92	0.048
Sn	28.36	0
Sb	46.33	0
Cs	15.09	0.002
Ba	8.40	0.038
Pr	9.34	0.025
Nd	9.14	0.027
Sm	8.26	0.041
Eu	7.66	0.053*
Gd	8.26	0.041
Tb	8.44	0.038
Dy	8.21	0.042
Ho	9.15	0.027
Er	9.85	0.02
Yb	9.83	0.02
^{206}Pb	46.43	0
^{207}Pb	46.70	0
^{208}Pb	46.62	0
Bi	29.61	0
U	15.47	0.001

Critical value = 7.81

* Not significant at p = 0.05

The test statistic was distributed as the Chi-Square with K-1 degrees of freedom (*df*) (where K = number of potential source groups i.e. 4). Thereafter, the critical value of 7.81 for 3 *df* of the Chi-Square distribution was used at $p = 0.05$. Properties with *H*-values below 7.81 (Mg, Ge and Eu) were removed from further fingerprint analysis at this stage.

9.5.6 Source discrimination: Multivariate Discriminant Function Analysis

A stepwise multivariate discriminant function analysis (MDFA), based on the minimization of Wilks' Lambda, was applied to the properties passing the Kruskal-Wallis H-test. At each step, the property which minimised the overall Wilks' Lambda was entered. Maximum significance of F to enter a property was 0.05. Minimum significance of F to remove a property was 0.10. The MDFA tested the ability of the tracer properties to classify correctly the source samples into the appropriate source groups and also provided a quantification of the discriminatory power of the optimum composite fingerprint, as presented in Table 9.4.

Table 9.4 *Results from the stepwise MDFA for identifying the optimum composite fingerprint for discriminating grassland, cultivated land, woodland and channel bank source groupss in theRiver Wensum catchment, based on the minimisation of Wilks' Lambda*

Step	Property	Wilks' Lambda	Cumulative original grouped cases correctly classified (%)
1	Sr	0.610	42.5
2	Cs	0.361	51.7
3	Mo	0.328	58.3
4	Zr	0.289	65
5	V	0.276	67.5

A composite fingerprint containing the five properties Sr, Cs, Mo, Zr and V produced a Wilks' Lambda value of 0.276, which was the closest to zero that could be obtained following stepwise inclusion of all available properties. This fingerprint correctly classified 67.5% of the samples collected to represent the individual source types. Table 9.5 shows the predicted sample group against the actual group membership for the four source groups. It can be observed that grassland was by far the most poorly discriminated (43% of samples classified correctly). Eleven of the misclassified grassland samples were predicted to belong to the cultivated topsoil category, with just two cultivated samples being misclassified as grassland. The respective percentage correct discrimination for the samples collected to represent the remaining three source groups (cultivated and woodland topsoils and channel banks) was 86%, 60% and 80%.

Table 9.5 *Results from comparison of predicted sample group membership against actual group membership for grassland, cultivated land, woodland and channel bank source groups, with percentage of correctly classified cases within each group following stepwise MDFA*

		Source Group	Predicted Group Membership				Total
			Grassland	Cultivated	Woodland	Channel Banks	
Original Group Membership	Count	Grassland	13	11	2	4	30
		Cultivated	2	26	1	1	30
		Woodland	5	5	18	2	30
		Channel Banks	3	2	1	24	30
	%	Grassland	43.33	36.67	6.67	13.33	100
		Cultivated	6.67	86.67	3.33	3.33	100
		Woodland	16.67	16.67	60.00	6.67	100
		Channel Banks	10.00	6.67	3.33	80.00	100

Figure 9.10 illustrates the sample distribution around the four group centroids from the first two canonical discriminant functions following stepwise MDFA. The scatter plots further illustrate the relatively poor overall discrimination offered by the stepwise derived fingerprint. The group centroids for grassland and woodland appear to be particularly close to each other and there is overlap between samples from channel banks and grassland. However, it is grassland and woodland which display the most disparate distributions, further illustrating the poor discrimination of these source groups by the stepwise MDFA in this instance. On the above basis, it was considered that this composite fingerprint selected using stepwise MDFA offered insufficient discrimination to proceed reliably to the sediment source ascription phase.

As an alternative to the stepwise MDFA procedure, simultaneous entry MDFA of all properties which had passed the previous screening tests was next considered. The minimum tolerance level was set to 0.01 and all properties passing the tolerance criteria were entered simultaneously into the analysis. Seven properties which failed the tolerance test were, Nd, Ho, Er, Yb, ^{207}Pb, ^{208}Pb and Bi. Through the simultaneous inclusion of the remaining properties it was possible to lower substantially the Wilks' Lambda to 0.117, as shown in Table 9.6, and to improve discrimination to 81.7%. The composite fingerprint obtained by simultaneous entry MDFA was derived from 27 properties, Mn, Fe, Li, Na, V, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Mo, Pd, Cd, Sn, Sb, Cs, Ba, Pr, Sm, Gd, Tb, Dy, ^{206}Pb and U.

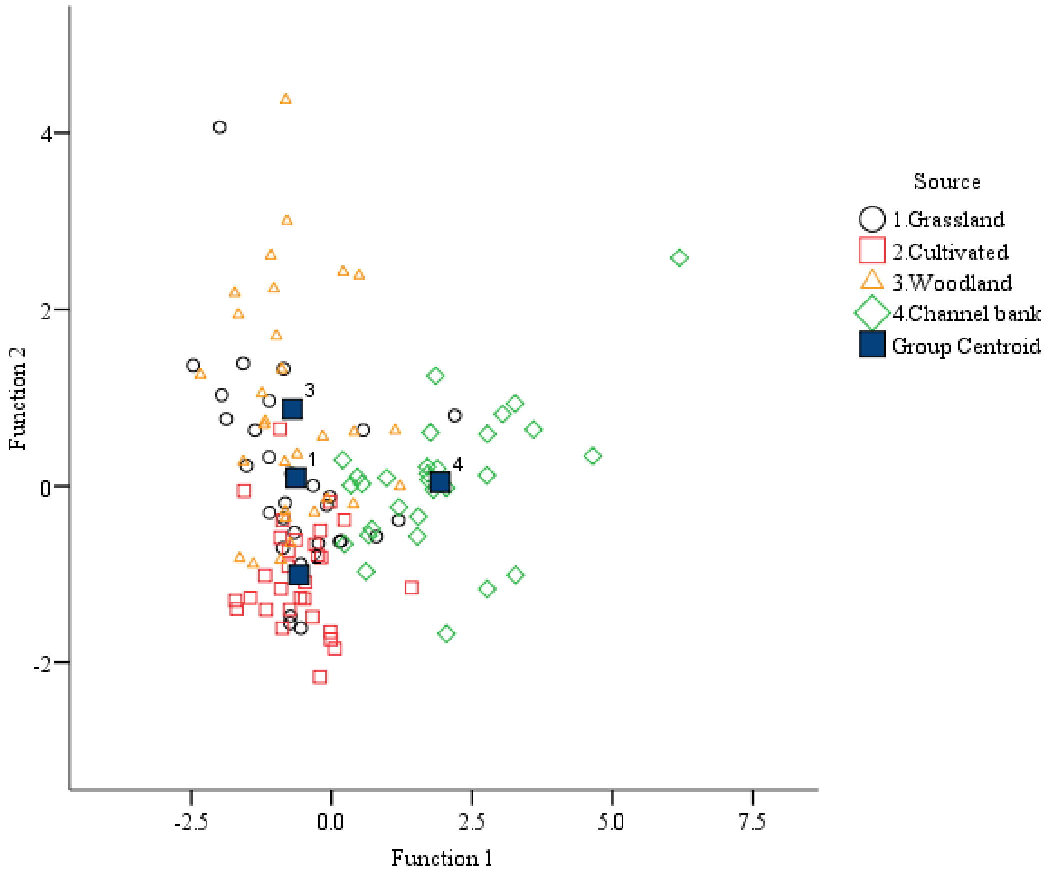

Figure 9.10 *Combined scatter plots showing sample distribution around group centroids from the two canonical discriminant functions applied to the grassland, cultivated land, woodland and channel bank source groups from the River Wensum catchment following stepwise MDFA*

Table 9.6 *Wilks' Lambda Test of Functions for 27 simultaneously entered properties*

Test of Function(s)	Wilks' Lambda	Chi-square	Significance
1 through 3	0.117	221.687	0
2 through 3	0.409	92.597	0
3	0.777	26.133	0.401

Table 9.7 displays the discrimination results for the simultaneously entered 27 property fingerprint. It is apparent that correct classification improved across all four source groups to 66.7%, 90%, 73.3% and 96.7%. Five of the misclassified grassland samples were assigned to the cultivated topsoil source, whilst conversely, two cultivated samples remained misclassified as grassland. The difficulty of obtaining higher levels of discrimination between grassland and cultivated land is consistent with other catchments in this study and most likely reflects the influence of rotation in local farming systems. Similarly, more recent stands of woodland will have been established

on land which was previously under either grassland or cultivation and soil samples from these locations may therefore still retain certain property characteristics of former land use.

Table 9.7 *Results from comparison of predicted sample group membership against actual group membership for grassland, cultivated land and channel bank source groups, with percentage of correctly classified cases within each group following simultaneous entry MDFA*

			Predicted Group Membership				Total
		Source Group	Grassland	Cultivated	Woodland	Channel Banks	
Original Group Membership	Count	Grassland	20	5	2	3	30
		Cultivated	2	27	0	1	30
		Woodland	4	3	22	1	30
		Channel Banks	0	1	0	29	30
	%	Grassland	66.7	16.7	6.7	10	100
		Cultivated	6.7	90	0	3.3	100
		Woodland	13.3	10	73.3	3.3	100
		Channel Banks	0	3.3	0	96.7	100

Figure 9.11 illustrates the sample distribution around the four group centroids from the two canonical discriminant functions following simultaneous entry MDFA. The scatter plots help to illustrate the improved discrimination afforded by the simultaneously entered fingerprint. There is visibly greater separation between the source groups centroids, although grassland and woodland samples still have relatively poor grouping around the group 1 and group 3 centroids, respectively. This overlapping and inter-dispersal of points is reflected in the total discriminatory power (81.7%) of the composite fingerprint based on simultaneous entry. On the basis of its greater discriminatory power, this composite fingerprint was selected for use in the mixing model during the sediment source ascription phase.

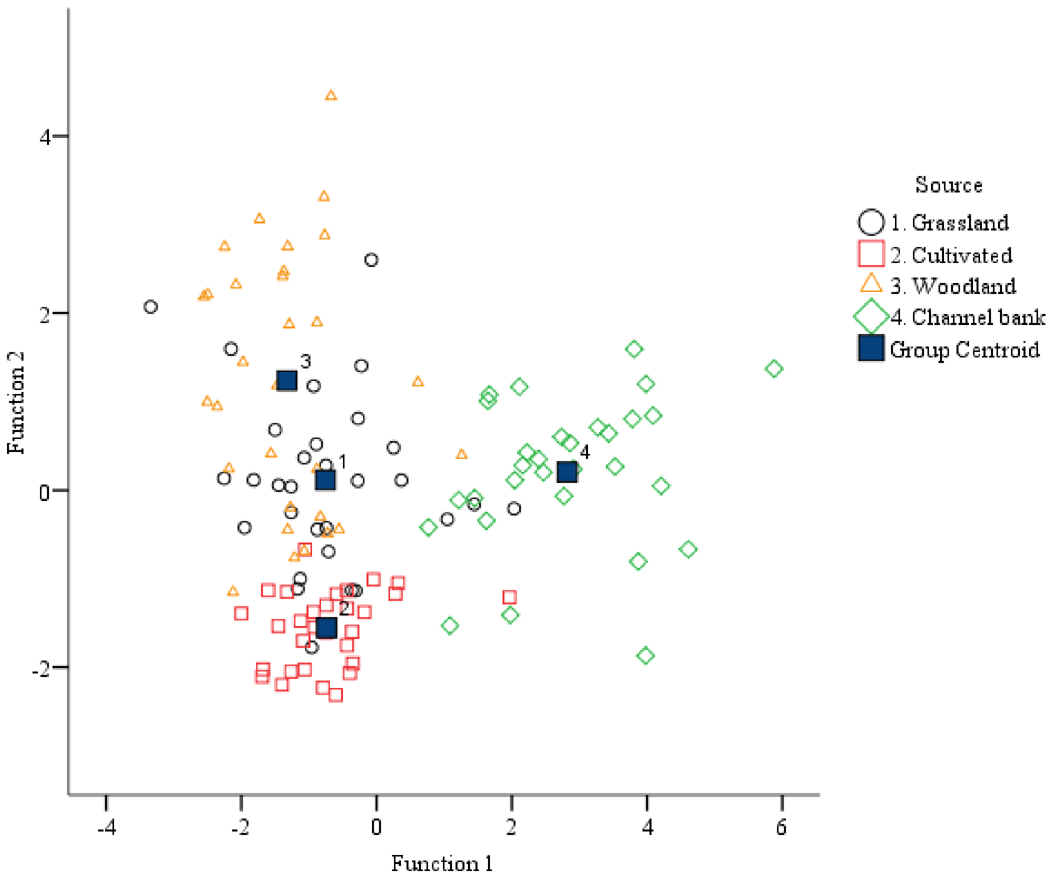

Figure 9.11 *Combined scatter plots showing sample distribution around group centroids from the two canonical discriminant functions applied to the grassland, cultivated land, woodland and channel bank source groups of the Wensum catchment following simultaneous entry MDFA*

9.6 Application of the Mixing Model

A linear numerical mixing model, as described in Chapter 3, was subsequently employed to provide an estimate of the relative contribution of the four potential sediment sources to the individual downcore floodplain sections. The mixing model utilized property-specific weightings, as shown in Table 9.8. A Monte-Carlo framework was used to provide explicit representation of the uncertainty associated with using relatively few samples to characterise the individual sediment source types.

Table 9.8 *Mixing model property-specific discrimination weightings*

Property	Individual discrimination (%)	Weighting value
Mn	32.5	1.025
Fe	35.8	1.129
Li	37.5	1.183
Na	38.3	1.208
V	42.5	1.341
Cu	31.7	1.000
Zn	33.3	1.050
Ga	35.0	1.104
As	38.3	1.208
Rb	35.8	1.129
Sr	43.3	1.366
Y	36.7	1.158
Zr	34.2	1.079
Mo	40.8	1.287
Pd	35.0	1.104
Cd	40.8	1.287
Sn	38.3	1.208
Sb	33.3	1.050
Cs	42.5	1.341
Ba	40.0	1.262
Pr	38.3	1.208
Sm	38.3	1.208
Gd	35.0	1.104
Tb	35.0	1.104
Dy	36.7	1.158
^{206}Pb	43.3	1.366
U	31.7	1.000

9.7 Sediment source apportionment and historical catchment land use changes

The output from the mixing model, applied to individual sediment horizons from the floodplain core, provided percentage estimates of relative source contributions from the four source groups over time and relative mean error (RME) for each section estimate presented in Table 9.9. The mean RME for the combined sections was 19% giving a mean goodness of fit for combined section estimations of 81%. The RME is slightly high in this instance; Walling and Collins (2000) suggest that a RME of <15% indicates that the mixing model has provided an acceptable prediction of the measured fingerprint property concentrations of a given sediment sample. However, analysis of the RME for apportionment estimation of individual sections shows that the RME was skewed by the influence of the four deepest sections of the core. Consequently, the RME was acceptable for the majority of the floodplain core sections. Figure 9.12 illustrates the source apportionment estimations for the four source groups ca. 1904-2008.

Table 9.9 *Estimated sediment contributions (%) (± standard deviation) with associated relative mean error (RME) (%)*

		Estimated sediment contribution (%)				
Depth (cm)	Estimated date	Grassland	Cultivated	Woodland	Channel Bank	RME(%)
1	2008	15±28	50±35	2±11	33±30	6
2	2006	18±32	38±39	3±13	41±38	4
3	2004	17±31	42±37	3±13	38±3	8
4	2001	20±35	33±39	4±16	43±41	10
5	1998	15±28	52±33	3±11	30±26	6
6	1995	17±30	51±35	3±13	29±28	5
7	1993	21±30	51±32	4±14	24±22	4
8	1990	16±29	54±33	3±12	27±25	4
9	1987	15±29	61±33	2±11	21±22	4
10	1985	16±29	52±34	3±12	29±26	4
11	1982	17±29	50±33	3±13	30±25	6
12	1979	17±28	47±31	4±13	32±23	8
13	1977	18±32	40±38	3±14	39±36	9
14	1974	16±30	49±36	3±13	32±29	5
15	1971	18±34	31±41	3±15	47±44	11
16	1968	15±30	49±38	2±12	34±33	7
17	1966	14±29	50±38	2±12	34±33	7
18	1963	15±30	58±36	2±12	25±26	6
19	1960	17±32	39±41	3±13	42±41	7
20	1958	14±30	48±40	2±12	36±36	8
21	1955	17±29	47±35	3±12	33±29	6
22	1952	14±29	53±38	2±11	32±33	8
23	1950	13±28	61±35	2±10	24±26	4
24	1947	15±31	39±42	2±13	44±42	6
25	1944	14±29	52±37	2±11	32±31	6
26	1941	17±31	45±38	3±13	35±34	8
27	1939	16±28	54±32	3±12	27±25	7
28	1936	16±28	53±32	3±12	27±24	8
29	1933	22±31	46±33	5±15	27±25	6
30	1931	24±32	41±31	7±16	28±24	5
31	1928	26±33	40±31	10±19	24±22	7
32	1925	23±30	42±30	8±17	27±23	5
33	1923	26±32	38±29	14±22	21±19	6
34	1920	26±31	39±28	17±23	17±16	14
35	1917	25±31	47±30	12±20	17±18	12
36	1914	29±32	23±23	27±25	22±18	14
37	1912	23±37	29±38	6±20	42±39	38
38	1909	20±39	23±41	5±21	52±49	120
39	1906	19±37	29±42	4±17	48±46	124
40	1904	18±34	32±41	4±15	46±44	249

The sections of the profile between 37- 40cm, represented 10% of the total profile depth and produced 68% of the total RME. Conversely, the sections within the upper 36cm of the profile represented 90% of the total depth and produced 32% of the total RME. The RME for the profile excluding the lower 4cm was 7%, giving a goodness of fit of 93%. In consideration of the foregoing, it was assumed that the relative contributions apportioned down the profile to a depth of 36cm, estimated to represent 1914, provided acceptable predictions of the fingerprint property concentrations. However, the predictions of the source proportions from a depth of 37cm – 40cm, (1904–1912), should be interpreted with some caution.

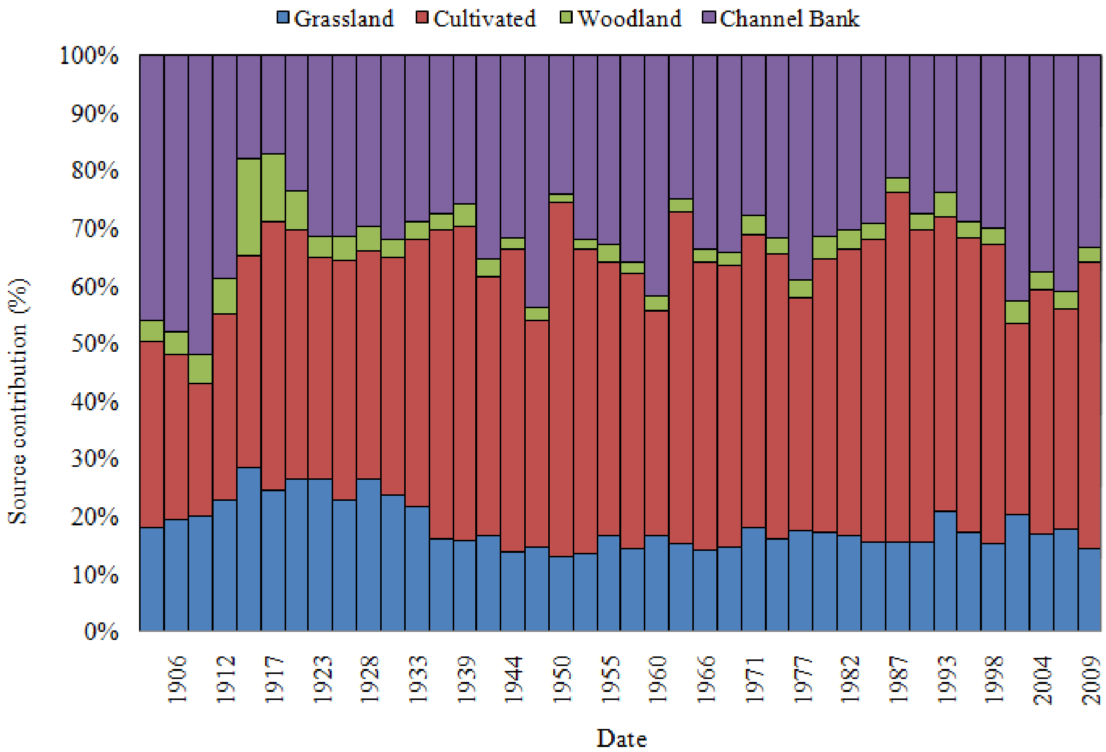

Figure 9.12 *Temporal changes in the relative contributions to floodplain sediment from grassland, cultivated land woodland and channel bank source groups in the River Wensum catchment ca. 1904 – 2009*

The sediment source apportionment showed general fluctuations in relative contributions from sources over approximately the last 100 years. The greatest variation in relative source contributions occurred between cultivated land and channel bank sources. Contributions from cultivated topsoil varied from a minimum contribution of 23% around 1910, to a maximum contribution of 61% in the mid to late 1980s, with a mean contribution over the study period of 44%. The corresponding mean contribution from channel bank sources was 33%, with a minimum contribution of 17% around 1917 and a maximum of 51% occurring earlier around 1909. Contributions from grassland topsoil sources varied less than cultivated topsoil and channel bank sources, with a minimum of 13% in the late 1940's, and a maximum of 28% around 1914, with a mean contribution of 18%. Woodland source contributions and fluctuations were found to be significantly lower than those from the other sources, with a minimum contribution of 1% around 1950 and a maximum contribution of 17% around 1916, with an overall mean contribution over the study period of just 3%.

It can be observed that relative contribution from cultivated land increased sharply around the time of the First World War. Nationally, the area of tilled land increased from 3,468,000 ha in 1914 to 4,055,500 ha in 1919 and this wartime 'plough-up' affected large areas of Norfolk (Sheail, 1973). The increase in arable cultivation was partly in response to wartime conditions, but was perhaps more specifically linked to the price guarantee for wheat introduced by the war cabinet in 1917 (Sheail, 1976). Similarly, contributions from woodland show a considerable peak around the time of the First World War. In 1900, forest cover in the UK stood at around only 5 per cent, and it fell further still during the First World War. The felling of woodland exposes woodland topsoil to increased runoff and erosion (Evans, 1990). The relative contributions from cultivated areas appear to decline throughout the mid to late 1920s and 1930s, during the years of the great depression. The cultivated contributions rise significantly again in the 1940s and into the 1950s. This pattern may possibly reflect the effects of the Second World War 'plough-up' campaign, which once again reintroduced the plough to fields which had lain fallow or been converted to grassland during the inter-war years. Apparent marked increases in contributions from channel bank sources over periods including the mid to late 1940's, 1960, 1977 and the late 1990's could perhaps represent periods of increased drainage or drainage maintenance leading to the mobilisation of sediment from these sources.

Data on changes in land cover, crops and stocking densities were extracted and collated from the Agcensus Database (EDINA, 2009). Data were obtained at 2km x 2km grid resolution from the area of the catchment for years; 1969, 1972, 1976, 1979, 1981, 1988, 1993, 1996, 2000 and 2004.

Figure 9.13 shows livestock numbers for cattle and sheep in the River Wensum catchment from 1969 to 2004. There was a steady decline in cattle numbers over the study period, which was generally mirrored by an overall increase in sheep numbers.

This appears to indicate an observable substitution of cattle production by sheep production on available grazing land.

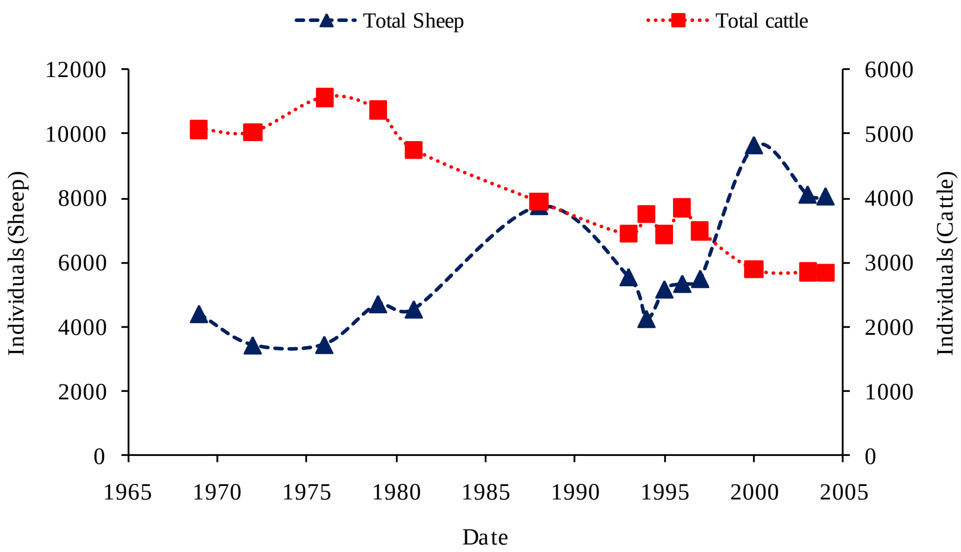

Figure 9.13 *Livestock numbers for cattle and sheep in the River Wensum catchment from 1969 to 2004*

Figure 9.14 shows the stocking density (LUs ha^{-1}) estimated from livestock units divided by available pasture land, from 1969 to 2004. The peak in stocking density observed around 1976 appears to correspond to an increase in channel bank contributions and a small increase in grassland contributions around the same period observed in Figure 9.12 Similarly, the second highest stocking density peak around 2000 appears to correspond with a particularly high channel bank contribution and a concurrent increase in the contribution from grassland sources.

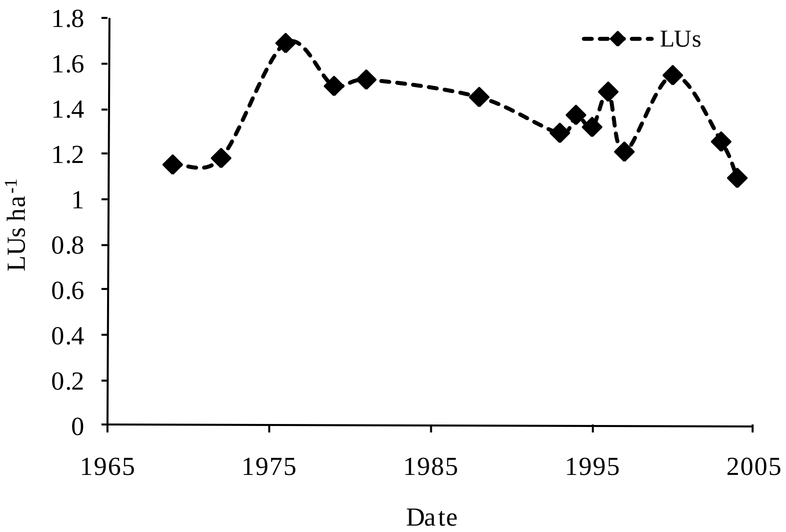

Figure 9.14 *Stocking density (LU ha-1) in the River Wensum catchment 1969 – 2004*

The overall mean area under pasture is relatively small at 14% over the study period when compared to the area under cultivation at 82%. However, as previously observed the land which is grazed tends to occupy the valley floors and is often adjacent to the water course. This land use practice could potentially focus livestock pressure in the riparian zone leading to associated potential for increased poaching of channel banks and riparian pasture land. The poached soils would be vulnerable to subsequent mobilisation and the areas concerned would have direct connectivity to the river channel. Consequently, although the area devoted to pasture land use area appears small, the effects of land management practices on sources of sediment may be significant.

Land cover data were compiled for late-harvested crops often associated with high erosion risk, including potatoes, sugar beet, beans, peas, turnips, swedes, mangolds, maize and linseed. The data were collated at catchment scale, between 1969 and 2004. Data were similarly combined for high erosion risk autumn-sown crops, including wheat, winter-barley and oilseed rape. Temporary grassland and permanent grassland data were also individually collated for comparative analysis. The combined plots are shown in Figure 9.15.

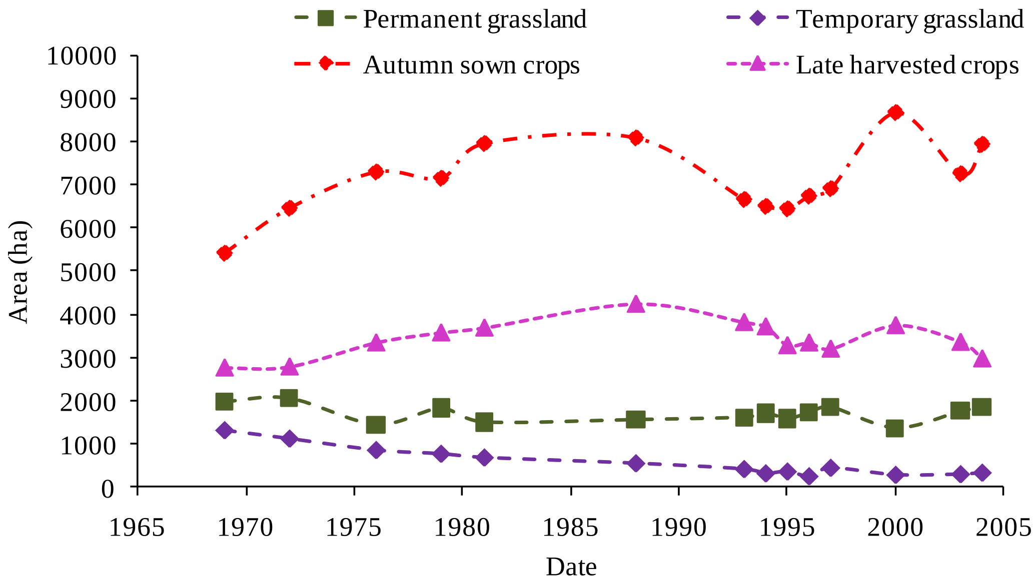

Figure 9.15 *Land cover areas for temporary grassland, autumn sown crops, late harvested crops and permanent grassland in the River Wensum catchment 1969-2004*

The historic dominance of arable production as the major land use type in the catchment is clearly illustrated. There was a marked increase in the area under cultivation throughout the 1970s and into the mid 1980s. This apparent increase in cultivation is largely mirrored by an observable decline in temporary grassland and a fairly stable area under permanent grassland during the same time period. Improvements in the frost tolerance of certain species, including autumn sown wheat and barley led to a huge expansion in the popularity of such autumn sown varieties. Similarly, the cultivation of oilseed rape also increased in popularity, both as a break crop and as a main crop, following the increased demand for vegetable oil over the period from the late 1960s (Gunstone, 2002). Strains were improved and transferred into agronomically adapted cultivars with higher yield quantities and qualities (Przybylski and Mag, 2002).

The area recorded as permanent grassland in the catchment remained relatively consistent over the study period. However, certain periods with a marginal increase in the area under permanent grassland and decrease in area under high risk crop cultivation, during the late 1970s and early 1990s, appear to correspond to observable modest increases in proportion of sediment contributions from grassland sources at those times. Comparison of Figure 9.12 and Figure 9.15 in relation to the period extending from the mid 1990s to 2000, appears to indicate that although the area under high erosion risk crops increased and the grassland area decreased, there was no observable increase in relative sediment contributions from cultivated sources. This may be related in part to the corresponding growth in the area under set aside as shown in Figure 9.16, which illustrates the area of land under set-aside or fallow and the area of land under autumn sown and late-harvested crops.

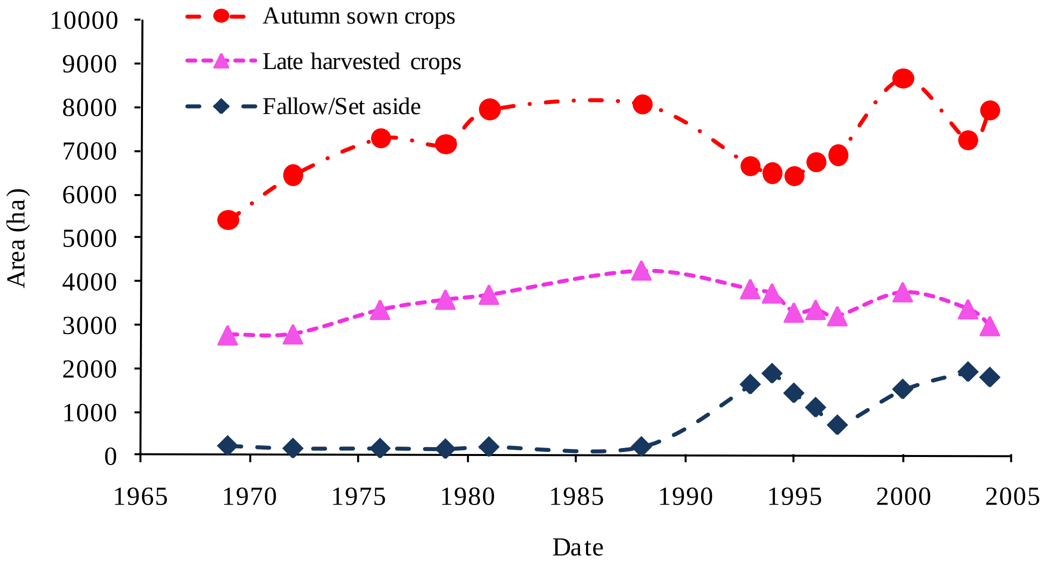

Figure 9.16 *Land cover areas for late harvested crops, autumn sown crops and fallow/set-aside land in the River Wensum catchment 1969-2004*

Full implementation of EC 1094/88 occurred in England during the early 1990s. This European regulation was developed to reduce surplus-production by the set-aside of arable land and the conversion and extensification of farm production techniques (Robinson, 1991). During the initial year of the set-aside scheme, farmers were required to set-aside a minimum of 15% of their cultivated farmland for the harvest year of 1993. This figure had dropped to 10% by the end of the 1990s. Set aside land was often sown with some form of permanent green cover and was widely incorporated into cultivated fields in the form of extended field margins, as shown in Figure 9.17. These could potentially act as buffers for any sediment mobilised from cultivated land moving towards into water courses. Following the delivery of four independent reports, in 2009 Defra, concluded that amongst other attributes set-aside had, “reduced sediment and phosphorus run-off in catchments where there were significant areas of farmland at high risk of erosion” (Defra, 2009b).

Figure 9.17 *Examples of extended field margins adjacent to water courses in cultivated fields in the River Wensum catchment*

Following significant rises in grain prices across Europe in 2007 and concern related to food security, combined with increasing pressure for bio fuel production, the EU decided that the compulsory set-aside requirement for harvest 2008 would be zero. The set-aside requirement has subsequently been completely abolished. This study did not have access to specific data relating to the extent of loss of set-aside in the catchment following this change in policy, although shortly after the change was applied Defra announced that following its annual survey of farmers, the area of arable land left uncultivated nationally was anticipated to halve from its previous level of nearly 400,000 hectares (Jowit, 2009). It can be observed in Figure 9.12 that there is an increase of over 10% in the relative contributions from cultivated sources around 2008/9 over those from the previous period. This proportional increase may be a response to the influence of an increased area under cultivation combined with a reduction of buffering capacity following the loss of set aside.

9.8 Conclusion

The potential scale of the land use change associated with the loss of set-aside, combined specifically with the type of land use concerned i.e. arable cultivation, could have significant effects on sources of sediment in river catchments throughout the EU. The fingerprinting technique could offer a very useful tool in analysing the relative effects on sources of sediment following such a potentially high impact paradigm shift in policy, particularly in predominantly cultivated catchments such as the River Wensum.

A final consideration relates to the large number of water mills which previously occupied many reaches of the River Wensum catchment and the sharp decline of water milling on the river over post-war decades to virtually zero by the 1960s (Hiscock *et al*., 2001). When in operation, the water which flowed through the turbines and over the mill wheels would have flushed out sediment from behind the mill-structures (Natural England, 2009). Despite the decline of milling, many relict mill-structures remain in place across the river channels and the sluices attached to these structures are generally no longer operated. Consequently, the mill-structures are responsible for slowing flow rates, leading to increased sediment deposition and possibly prolonged in-channel storage. The scale of the in-channel storage has not been estimated here, however, the influence of the historic dam structures may have the potential to produce a substantial buffering effect on the transport of suspended sediment loads. This buffering effect could be masking the true extent of the influence of changes in intensive agricultural practices on relative suspended sediment loads and thereby damping or delaying the temporal response in the floodplain sediment record. In addition as sediment backs up behind the redundant structures it will cause highly negative impacts in the upstream ponded reaches.

A recent River Wensum restoration strategy report commission by Natural England identified alterations to the mill-structures as an essential component of the proposed restoration strategy (Natural England, 2009). This work was considered to be a pre-requisite of any channel restoration work and involved lowering the water levels at mill structures and thereby reducing the upstream ponded lengths of the river. Additional measures included bed-raising and other channel enhancements such as recreating meanders in some upper reaches and the creation of berms by redistributing sediment along channel margins to narrow channel width in certain over wide downstream reaches (Natural England, 2009).

CHAPTER 10 - CONCLUSIONS

10.1 Introduction

In recent years there has been an increasing awareness of the detrimental influence of diffuse sources of pollution on aquatic systems and of the integral role played by sediment in the mobilisation and transport of pollutants. Land management practices can exacerbate the erosion risk to soils. Over the last century, land management has undergone considerable change in many parts of the UK, leading to increased sediment-related environmental impacts. The influence of the war time plough-up campaigns were an early manifestation of centralised agricultural policy resulting in major land use change. Widespread intensification of agricultural production practices since the 1960s increased the risk of soil erosion and sediment mobilisation, with deleterious consequences for the aquatic environment. An increased awareness of the environmental, societal and economic importance of the ecological health of aquatic environments led to a paradigm shift in agricultural and environmental policy. To implement successful delivery of emerging policy requirements, it is necessary to have catchment-scale management planning and an enhanced understanding of the relationship between different forms of land use and sources of diffuse pollution, particularly sources of fine sediment. To understand and interpret the effects of current and future land use changes and mitigation measures on sources of sediment, it is useful to consider them within a longer-term context.

A number of recent studies have used the source fingerprinting technique applied to floodplain overbank sediment cores to estimate changes in the relative sediment contributions from differing sediment source types over time (Passmore and Macklin, 1994; Collins, 1995; Foster *et al*., 1996; Collins *et al*., 1997b; Foster *et al*., 1998; Botterill *et al*., 1999; Owens *et al*., 1999; Nicholls, 2000; Owens and Walling, 2002). The sediment source fingerprinting technique offers several advantages over more traditional methods for estimating relative sediment contributions from varying sources, particularly when retrospective information is required at the catchment scale.
The work presented in this thesis has successfully applied the source fingerprinting technique to floodplain overbank sediment cores in a retrospective study of six river catchments with identified sediment problems. The resulting estimates of the variation of the relative sediment contributions from differing sources have been compared to

known land use change within the study catchments over concurrent time periods, to explore any associations which might be apparent. The design of the source fingerprinting methodology used in this work was based on an established successful approach, and this was developed further through the incorporation of a number of refinements designed to improve the robustness of the technique and expedite its implementation.

This chapter presents, an appraisal of the refinements to the fingerprinting technique which were introduced during this research; a summary of the main conclusions from the case studies featured in chapters 4 – 9; a brief summary of the main influences of land use change on sources of suspended sediment identified by the research and suggestions for their mitigation; an appraisal of the main limitations of the approach and finally suggestions for further work and development.

10.2 Summary of results obtained from the individual case studies

10.2.1 The Upper River Torridge catchment

Chapter 4 featured a case study from the Upper River Torridge catchment, in Devon, UK and specifically considered the potential effects of land drainage, changes in stocking density and maize cultivation on sources of fine sediment, in the catchment over the last ca. 100 years. The ^{137}Cs and ^{210}Pb radioisotope geochronology estimates derived from the Upper River Torridge floodplain core compared favourably with each other, thereby confirming the appropriateness of their application in this work. The sediment source apportionment results reflected the general changes recorded in the historic land use data. Increases in the relative contributions from channel bank and sub-soil sources appeared to correspond with certain known periods of increased field drainage. Field observations confirmed that sediment appeared to be discharged from field drains emptying directly into stream channels, leading to channel infilling and widening. However, additional source sampling and fingerprinting to target field drains as an individual source type would be required to reliably attribute the increased proportion of sediment derived from the channel bank source group to field drain sources. Relative sediment contributions from grassland and channel bank sources did not appear to fluctuate in relation to changes in recorded stocking densities, and this could reflect a number of possible con-current factors. Agri-environment schemes which encouraged improved livestock management and mitigation of impacts to water courses may have had a positive influence through the increased use of riparian fencing and buffer strips. The potential positive buffering influence of agri-environment schemes would be in addition to any buffering and attenuation afforded by the enclosed field systems and high incidence of impermeable field boundaries in the Devon landscape. It might also be concluded that the apparent lack of catchment-scale sediment source changes in response to fluctuations in livestock numbers indicates that the stocking densities have been within the carrying capacity of the catchment in terms of sediment-related environmental sustainability. Alternatively, the relative increase in contributions from cultivated sources could have been sufficiently high to reduce the significance of any increases from other sources. The apportionment of contributions from any source is relative to contributions from other sources, rather than necessarily indicative of changes in absolute sediment yield. Increases in the proportion of sediment deriving from cultivated sources in the River Torridge catchment appeared to coincide with the incidence of increased cultivation of autumn sown and late harvested crops. Although the expansion of high erosion risk crops has occupied a relatively small area of the total catchment, the climate of the region is highly likely to compound the vulnerability to erosion and mobilisation caused to exposed soils. The apparently disproportionate sediment contribution from cultivated sources is cause for concern, given the potential economic pressures for further expansion of such production and the higher intensity rainfall rates predicted in coming years due to climate change. Conversely, the recent general decline in English livestock numbers and a shrinking dairy industry may yet temper the future expansion of fodder crop production in the South West. In the absence of such an eventuality, mitigation measures suitable for the Upper River Torridge catchment might include under sowing late harvested crops with a winter cover crop that can be used as livestock forage or ploughed into the soil in the following spring. Laloy and Bielders (2010) estimated that following the maize harvest, the presence of cover crops such as Rye and Ryegrass can reduce erosion by more than 94% compared to bare soil during the intercropping period. The use of cover crops can also generally improve the physical quality of soil and thereby reduce erosion during the main crop. In addition, farmers could be encouraged to restrict cultivation of high erosion risk crops to land with appropriate topography, combined with increased use of mitigating buffer strips to reduce connectivity between fields and water courses. However, a longer term view of sustainable soil management in conjunction with emerging water quality and river habitat policy might require consideration of the appropriateness of high erosion risk crop cultivation in areas subject to high rainfall rates.

10.2.2 The Upper River Axe catchment

The case study presented in Chapter 5 featured the Upper River Axe catchment, in South West England and examined the historical changes (ca. 100 years) of sediment sources. This case study specifically considered the potential impact of intensive livestock production practices and fodder maize cultivation on sediment sources. The Upper River Axe catchment is dominated by permanent grassland under intensive dairy production; however, the major cause for concern within the ECSFDI Priority Catchment designation was the perceived impact of maize cultivation on fine sediment ingress to the river system, particularly in the upper catchment. Although the area under arable production supports a large percentage of high erosion risk crops, the overall land area occupied by arable production, and maize in particular, is relatively small. The relative proportions of the catchment area under the varying land uses were generally reflected by the sediment source apportionment results. These results served to confirm the observations from previous studies of the potential for intensively managed grassland to represent an important sediment source (Foster and Walling, 1994; Collins *et al*., 1997; Russell *et al*., 2001; Walling *et al*., 2003; Owens *et al*., 2005; Bilotta *et al*., 2007). However, the interpretation drawn here cannot be extrapolated to represent the wider River Axe catchment without further research. Specifically, this interpretation does not preclude the potential for maize cultivation in the mid and lower reaches of the catchment and tributary sub-catchments to have a substantially greater influence on localised or more general downstream sediment problems.

Another important cause for concern with the Upper River Axe catchment was the effect of stocking densities on the erosion of channel banks. The case study results showed that relative sediment contributions from channel banks appeared to increase during recorded periods of higher stocking densities. This appeared to confirm the influence of poor land management, as described in the recent Natural England report, which suggested that widespread stock access to stream channels was causing bank erosion, which could be exacerbated by high stocking rates (Natural England, 2010). As noted above, this is a particularly good example of the utility of the fingerprinting technique applied retrospectively, to inform and confirm the basis for current management priorities. Appropriate mitigation in this instance could include the installation of fencing along channel banks and the construction of appropriately designed livestock drinking access points. This would decrease the effects of direct erosion from cattle traffic and encourage the growth of riparian vegetation which would improve overall bank stability and resistance to scour.

The floodplain at the sampling site at Broad Bridge is less developed than the downstream floodplains, where the River Axe valley widens and the gradient reduces towards the estuarine reaches. The riparian fields forming the flood plain are bordered on one side by a railway embankment and on the other by a road embankment. This topographic detail could potentially influence the nature of the flow and sedimentation patterns during high magnitude flood events, particularly as the flow backs up against the bridge structure. The application of the fingerprinting technique to floodplain sediment cores only allows an investigation of changes in the source of sediment deposited during flood events, as opposed to changes in the source of the sediment load transported by low and moderate flows or even high flows which do not exceed bankfull, Without further specific analysis, it is not possible to estimate the proportion and representative qualities of the total sediment load being represented by overbank sediment stored on the study sub-catchment floodplain.

10.2.3 The River Arrow catchment

Chapter 6 presented a case study which examined the recent historical changes (ca. 50 years) of sediment sources in the River Arrow catchment, Herefordshire, UK. The catchment was included in the wider River Wye Priority Catchment under the ECSFDI. Particular concerns were raised in relation to the downstream effects of excessive sedimentation on the breeding habitats of Salmonid species. The primary cause for concern in this case study was the expansion of intensive potato cultivation within the River Arrow catchment. Whilst the area of land under high erosion risk cultivation increased considerably between 1969 and 2000, with the specific land area under potato cultivation increasing by over 800%, this did not appear to influence the relative proportion of sediment contributions from cultivated sources. However, when viewed in terms of the area occupied by arable fields, these areas contributed a much greater amount of sediment to the flood plain than grassland sources. Similarly, but to a lesser extent, woodland topsoil sources contributed a higher proportion of sediment than the proportion of total land area which they occupied. The variation in contributions from woodland sources over the study period appeared to bear some relation to documented shifts in the land area under woodland. A clearer relationship was observed between stocking density and sediment contributions from channel bank sources. There was a possible tipping point in stocking density at which point the primary source of sediment shifted from grassland sources to channel bank sources. In recent years, cross-compliance requirements may possibly have helped to reduce the negative impacts of livestock on channel banks, although as stated above, further data would be required for more recent periods to substantiate this influence. Notwithstanding a certain lack of resolution, The River Arrow catchment case study highlighted the efficacy of the fingerprinting technique in retrospectively identifying and tracking the influence of the major land use changes in the catchment on sediment sources. Based on the higher proportion of sediment derived from cultivated and woodland sources relative to land area occupied by such sources, there is possibly a requirement for the tighter application of sediment source mitigation measures in regard to high erosion risk crop cultivation and the impacts of afforestation. The recent relative increase in sediment contributions from grassland sources, whilst stocking densities estimated at the catchment scale have been falling, may indicate possible requirement for improved site-specific stocking density regulation and monitoring.

10.2.4 The River Waver catchment

The case study presented in Chapter 7, featured the River Waver catchment, Cumbria, UK and related relative changes in the source of floodplain overbank sediment to historical land use change over ca. 60 years. The potential influence of flood risk management practices such as channel re-profiling and bank maintenance were specifically considered in the context of increasing connectivity between fields and watercourses and potential impacts on sources of sediment. In addition, the increased cultivation of fodder maize within the catchment was cited as a major concern in the designation of the River Waver, as a Priority Catchment under the ECSFDI. The key land use issues under consideration within the River Waver catchment include the increased connectivity of nutrient rich arable fields to receiving waters due to changes in flood risk management practices and the reported expansion of autumn sown cereals and fodder maize cultivation.

In considering the rate of sedimentation from 1963-1986 and the rate between 1986 and 2008, the year of core collection, there was an apparent increase sedimentation rates in the latter period. There was minimal variation in the relative sediment contributions from the respective sources over the study period. However, there did appear to be relative increases in the sediment contribution from channel bank sources during periods of known drainage improvement, involving the clearing of vegetation from field ditches, drains and riparian zones and the reprofiling of channel banks. This type of floodrisk management exposes channel banks to increased risk of erosion and scour. During the early 2000’s, several reaches were reinforced with wooden boarding in an attempt to protect certain vulnerable bank sections. This modification may partially account for the apparent decline in relative contributions from channel banks from the end of the 1990s onward. However, it should be noted that stocking densities also experienced a marked decline during the same period.

10.2.5 The River Rye catchment

Chapter 8 presented a case study of the River Rye catchment in North Yorkshire, UK and examined the potential impacts on sediment sources of land use change over ca.90 years. The ECSFDI priorities for the River Rye catchment indicated specific concerns, including the potential role of increased quantities of enriched sediment delivered from cultivated sources on vulnerable hillside soils. This study has confirmed that the proportion of the catchment area under cultivation has been, and remains, relatively small when compared to the area under grassland. However, the overall relative sediment contribution from cultivated topsoil sources to the floodplain has been particularly high in comparison to other sources throughout the study period. The high proportion of sediment derived from cultivated sources appears to remain relatively constant, despite the apparent decline in floodplain sedimentation rates since 1986. Whilst diffuse pollution mitigation measures may have had some influence in this regard, it is perhaps less likely that this influence would have been equally effective across all source types. More detailed interpretation might ideally include consideration of concurrent changes recorded in the rainfall patterns and fluvial response within the catchment. A possible increase in flow rates since 1986 may have limited the deposition of the finer fraction of suspended sediment at the floodplain core sampling point. A multiple core transect approach to the sediment sampling might have provided greater resolution in this respect, however research resource limitations precluded further exploration of these various possibilities within this study.

10.2.6 The River Wensum catchment

The case study presented in Chapter 9 investigated the effects of land use changes over ca. 100 years, within the River Wensum catchment in Norfolk, UK and specifically considered the impacts of intensification of arable production systems on sediment sources. In addition, the influence of the introduction and abolition of compulsory set-aside was discussed. The potential for historical in-channel engineering structures to act as temporary buffers to the transport of suspended sediment storage was also considered.

It was observed that sediment contributions from cultivated land and woodland increased sharply around the time of the First World War. This coincided with a national campaign to increase arable production and the requirement of timber to line the trenches in France. The peak in stocking density in the catchment in the mid 1970s corresponded to an increase in channel bank contributions and a small increase in grassland contributions. In common with many areas of Eastern and Central England, the land which is grazed in the catchment tends to occupy the valley floor and is often adjacent to the water course. This land management practice can focus livestock pressure in the riparian zone, leading to associated potential for increased poaching of channel banks and riparian pasture land. Any such poached soils, would be vulnerable to subsequent mobilisation and represent high risk sediment sources due to their direct connectivity to the river channel. Consequently, although the land use area under pasture is not extensive, the effects of land management practises on sources of sediment may be significant. Although the area under high erosion risk crops increased relative to the area under grassland during the mid to late 1990s, there was no observable increase in sediment contributions from cultivated sources. It is suggested that this may be related in part to the mitigating effects of the corresponding growth in the area under set aside, which was often incorporated into extended field margins with the potential to offer increased sediment transport buffering capacity.

The River Wensum has a history of extensive numbers of mills along the river. Despite the decline of milling, many relict engineering structures remain in place across the river channel and these are responsible for slowing flow rates, leading to increased sediment deposition and in-channel storage. Although the scale of the in-channel storage has not been estimated, it may have the potential to produce a substantial buffering effect, thereby masking the true extent of the effects of changes in intensive agricultural practices on sediment sources over time and consequently dampening or delaying the observable temporal response in floodplain deposits. A recent River Wensum restoration strategy report commission by Natural England identified alterations to the mill-structures as an essential component of the proposed restoration strategy (Natural England, 2009). The work to reduce the levels of sedimentation was considered to be a pre-requisite of any channel restoration work and involved lowering the water levels at mill structures and thereby reducing the upstream ponded lengths of the river.

10.3 Objectives revisited

10.3.1 Identification of suitable study catchments

The selection of appropriate study catchments was driven by the requirements that they should have experienced identified sediment related problems and have documented land use histories. Budget limitations and the need for expediency precluded extensive field-based catchment appraisals. The ECSFDI priority catchment reports (Defra 2009a) offered an available resource of key catchments identified by catchment officers as suffering from various sediment related issues. Similarly, the Agcensus database (EDINA, 2009) offered a useful means of analyzing basic land use changes within the study catchments over recent time. On this basis, six geographically diverse catchments with differing land use histories were selected as being appropriate for inclusion in this study.

In order to ensure that a reasonable number and variety of case study catchments could be included in this project, it was necessary to restrict the size of the study sub-catchments to that which could be representatively sampled within the available project resources (i.e.<300 km^2). Consequently, the sub-catchment outlet locations of the floodplain core sampling sites were often situated on floodplains in the middle reaches of larger river systems. The sedimentation rates at these locations were relatively low and this limited the temporal resolution of the core slices. In addition, it became apparent that the temporal and spatial scale of the sediment problems reported in the initial ECSFDI priority catchment reports may have been particularly localized and of limited duration e.g. a single crop cycle, over a relatively small number of fields, such as that reported for the River Rye catchment and possibly the River Axe catchment. Under such circumstances, the utliisation of the sediment source fingerprinting technique applied at a catchment-scale, over a time-scale of several decades, as represented by floodplain cores, does not nessesarily offer sufficient resolution for establishing firm land use change linkages. Moreover, an alternative stratagey incorporating a nested approach, based on identified contemporary field-scale problem areas, which might use targeted sampling stratagies and suspended sediment fingerprinting might be more appropriate. Any information gained on such a basis could then be extrapolated to provide a current localised snapshot with which to compare both the wider catchment and also with more historical information such as that provided by this study.

In relation to analysis of historical records of land use change, the study highlighted some problems related to the spatial and temporal resolution of the Agcensus datasets as compiled by EDINA (2009), not least of which were those of shifting boundaries and changing survey criteria over the study timespan. Greater resolution of land use change patterns could possibly have been obtained by interrogation of individual parish returns. However, the time required to extract and collate such detailed information for six individual catchments over an historic period of between 50 to 100 years made this option logistically unfeasible.

10.3.2 Identification of optimum composite fingerprints

Substantial research and development time was spent considering the robustness of the identification of optimum composite fingerprints. By considering the application of different aspects of these techniques across six case studies, this study concludes that the hitherto prolific technique of applying stepwise MDFA produces a fingerprint of reduced discrimination when compared to simultaneous entry MDFA. The latter is far more effective at not only improving discrimination but also in producing a more robust multivariate fingerprint. The simultaneous entry MFDA includes properties in the fingerprint which, whilst not necessarily improving the overall discrimination, do not reduce discrimination by their inclusion. This produces a fingerprint containing more properties, albeit of similar discriminatory power. Utilising a fingerprint comprised of multiple and disperate properties has long been considered the most effective and reliable method for effective source apportionment.

Of the 48 potential diagnostic geochemical properties used in this study, only one property, Y, was selected for use in all six catchment case study composite fingerprints, whilst four properties, Mg, Ba, Li and Pr were selected in five of the case study composite fingerprints, Ten properties, Mn, Ti, Co, Zn, Sr, Nd, Tb, Sm, Gd and Ti were selected for inclusion in four of the case study composite fingerprints. This study had the benefit of sufficient resources to allow sample analysis by ICP-MS, which allowed the simultaneous analysis of 48 properties. However, for studies utilizing more time consuming analytical procedures the ability to predict those tracer properties which are most likely to effectively discriminate sources could be of great advantage. Similarly, properties which consistently fail to discriminate could be dropped from consideration in future analytical suites. Any such comparative work should only be considered on studies which use identical statistical selection procedures.

10.3.3 Refinements to the fingerprinting technique

Aspects of the research and development work on the fingerprinting technique within this study are reflected in the refinements detailed below.

Particle size correlation test

The potential influence of sediment particle size on geochemical property concentration has been discussed in some detail in Chapter 3. The significance of the variation in the proportion of the finer fractions between source material and floodplain sediment may not be as acute as that between source material and suspended sediment, due to the effects of selective settling. This was borne out to a certain extent by the similarity of the particle size distributions and mean SSA for source material and floodplain sediment in a number of the case study catchments (e.g. the River Arrow, the River Waver and the River Rye). Whilst it is accepted here that the simplified particle size correlation test applied in this work is no substitute for in-depth analysis of the behaviour of the geochemical properties across various fractionated ranges of particle size and chemistry for individual samples, this was deemed prohibitive due to resource limitations. However, it is considered important that the influence of particle-size on geochemical property concentrations within the individual source types should be tested statistically (Wang and Chen, 2000), to inform the decision of when to apply particle size correction. In relation to the basic non-parametric correlation approach based on Spearman's rho used in this study, the vast majority of samples appeared to exhibit no significant correlation between SSA and property concentration.

Particle-size correction

On the basis that the application of a particle-size correction factor alters the resultant property concentration value, when particle-size correction was required during the study, it was undertaken prior to testing the data for compatibility of concentration ranges and source discrimination. Logically, any particle-size correction factor applied to data which have been previously tested (e.g. for source/sediment concentration range comparability and source discrimination), could render any such testing unreliable, due to the correction factor altering the values which predicate the test results. Any such correction could clearly significantly alter the values and assumptions upon which the selection of the resulting composite fingerprint has been based and would consequently lead to the application of a composite fingerprint within the mixing model of effectively unknown discrimination capabilities and untested range boundaries. The approach applied here was based broadly on that utilized by Gruszowski *et al*. (2003) and ensures that the property values which are used in the subsequent range test and source discrimination analysis are the same property values which are used to provide the inputs into the mixing model. Further, by correcting to the median SSA of all samples being considered, rather than the mean, the effect of any skew within each source group may be reduced. Further refinement might include particle size correction based on fractionated analysis of individual property dependencies derived from a sub-set of source and sediment samples from across the range of individual property concentration values.

Property concentration range test

The introduction of the property concentration range test as an explicit threshold is not a refinement of the fingerprinting technique *per se*. The compatibility for which it tests is a fundamental requirement for the successful performance of the mixing model. The mixing model is founded on the assumption that the concentrations of the properties which comprise the composite fingerprint, measured in the floodplain sediment core sections, represent the product of the corresponding concentrations in the catchment sources and the relative inputs contributed by those sources (Collins *et al.*, 2007). The range test utilised an array approach which allowed the relationships between the source material and floodplain sediment concentration range values for all properties to be assessed very quickly. The introduction of this test as an explicit threshold, rather than implicit generalised condition, had two major effects on the development of the fingerprinting technique utilized in this study. Firstly, it removed potentially non-conservative properties from further consideration, which reduced the number of properties available for the discrimination assessment, leading potentially to lower rates of discrimination. Secondly, by ensuring the compatibility of the concentration ranges, the mixing model apportionment estimates generally produced an excellent goodness of fit.

10.3.4 Redesigning the mixing model

The redesigned mixing model increased the speed of the apportionment phase of the work dramatically, compared to the earlier model configuration, primarily by replacing the large number of data transfers between the Excel Solver, the macro and the spreadsheet with a more efficient approach based on algebraic matrices. Additional benefits were achieved by automating the input of data, the analysis of successive core sections and the output of results. Similarly, by incorporating the random number generator into the same Excel workbook as the mixing model, the time required for the generation and compilation of the Monte Carlo synthesised database was greatly reduced. Ultimately, this refinement rendered the application of the floodplain sediment source fingerprinting technique to the six case study catchments feasible within the time available. It also allowed for experimental work to be carried out, which would have been prohibitive due to time restraints using the original model design. It is hoped that this innovation will prove of considerable value for the further development and application of the fingerprinting technique.

10.3.5 Some aspects of uncertainty

The utilization of Monte Carlo frameworks and the incorporation of discrimination weightings within the fingerprinting technique applied in this study, explicitly addressed aspects of uncertainty related to the representative nature of catchment sampling and the variations of discriminatory power afforded by different fingerprint properties.. However, experience gained during the undertaking of this study has identified additional areas for consideration. One such area of uncertainty relates to the application and results from the property concentration range test. As discussed within the individual catchment results and discussion chapters, there is a potential equifinality related to the results from the range test. Any property failing the range test might be behaving in a non-conservative manner during mobilization, transport or storage on the floodplain, as the test was primarily designed to establish. However, a property value might also fall outside of the range of the test if either the catchment source or floodplain sediment samples were not fully representative of the range of possible concentrations within the catchment. There will always be a desire for a more robust and representative sampling regime and whilst the application of the Monte Carlo technique is designed to synthesise a more fully representative sample database, any framework will only be as representative as the initial property concentration values that seed it. In this regard, it is clearly vital that initial sampling stratagies are carefully conceived and robustly executed, in order to properly reflect the processes and relationships under consideration.

10.4 The influence of land use change on sources of suspended sediment

In reviewing the evidence of the impact of land use change in the recent past on floodplain sediment sources provided by the case studies, a number of key observations can be made. These are presented below, with suggestions for effective mitigation options.

Firstly, the cultivation of high erosion risk crops, such as those which are harvested late in the season (e.g. maize) and those which are sown in the autumn (e.g. winter wheat), has contributed disproportionately to the total sediment load relative to the area of land occupied by such cultivation. As the cultivation of such crops has expanded since the 1980s there has been a marked increase in the sediment derived from these sources. Soil erosion by rainfall on land under these forms of cultivation can be reduced over the winter months by growing cover crops, such as stubble turnips or rye and by ensuring that autumn cereal drilling takes place as early as possible (e.g. September rather than late October) (Chambers *et al*., 2000). Erosion can also be effectively reduced through the use of use of conservation (or noninversion) tillage techniques. This practice maintains a residue straw cover on the soil surface after drilling, thereby reducing the risk of soil erosion, conserving soil organic matter and improving soil structural stability (Morris *et al*., 2010). Runoff can be reduced by the utilisation of grass buffer strips.

Secondly, increased stocking densities can often result in increased relative sediment contributions from grassland sources. Although overall UK livestock numbers have been in decline since the CAP reforms removed headage based payments, fewer herds of larger size have focused pressures on grassland systems. Poaching and runoff can be reduced by ensuring that livestock are removed from pasture fields over the winter.

Thirdly, it is also apparent that variations in stocking densities have had a major influence on the relative sediment contributions derived from channel bank sources. Livestock access to watercourses leads to increased bank erosion through trampling and poaching impacts. It also removes protective vegetation cover and increases hydraulic roughness which can enhance the shear stress on bank faces (Collins *et al*., 2010b). Bank fencing permits vegetation growth as grazing pressures are removed and this can stabilise channel bank morphology (Collins *et al*., 2010b).

Fourthly, the installation and maintenance of drainage for agriculture or for flood risk management has resulted in increased relative sediment loads from channel bank and associated sub-surface sources. Potential mitigation options tend to affect the efficient functioning of drainage systems. Sediment traps can be installed at the outflow of drainage pipes, but these require regular maintenance, without which they can block and cause increased flood risk. Vegetated ditches and open field drains can trap sediment and pollutants but also require regular attention to ensure that they maintain their drainage function.

10.5 Limitations of the study and suggestions for improvements

The possibility of higher resolution interpretation of the case study results was constrained by a variety of factors including the broad timescales represented by both the individual floodplain sediment core sections and the land use data used throughout this project. In order to ensure that a reasonable number and variety of case study catchments could be included in this project, it was necessary to restrict the size of the study sub-catchments to that which could be representatively sampled within the available project resources (i.e.<300 km^2). Consequently, the sub-catchment outlet locations of the floodplain core sampling sites were often situated on floodplains in the middle reaches of larger river systems. The sedimentation rates at these locations were relatively low and this limited the temporal resolution of the core slices. Greater resolution of land use change patterns could possibly have been obtained by interrogation of individual parish returns. However, the time required to extract and collate such detailed information for 6 individual catchments over the study period made this option unfeasible.

10.5.1 Representative sample resolution

As identified above, resolution within the application of the technique could be negatively affected by the limited number of source samples, despite attempts to recognise explicitly such uncertainties in source sample distributions through the incorporation of the Monte Carlo framework. Enlarging the sample sets could make source data more spatially representative. However, incorporating larger numbers of source samples would require considerably more resources to cover increased collection time, processing time and additional laboratory analysis. Similarly, with both resource limitations and analytical facilities restricting analysis of potential tracers to a geochemical suite, the level of discrimination which can be achieved between sources is reduced, as it is well known that utilising tracers from different property subsets generally provides more robust fingerprint (Walling *et al.*, 1993; Collins *et al.*, 1997a; Collins and Walling, 2002).

10.5.2 Floodplain spatial variation and selective sedimentation

Floodplain core sites are subject to spatial variation in sediment deposition rates (Walling and He 1993, 1994; Walling et al. 1996) and this variation needs to be taken into account when selecting the point for core collection. Measurements of the ^{137}Cs inventory of bulk cores were used to identify those points which had received the maximum sediment deposition and were therefore likely to provide the optimum sediment record. However, concerns have arisen during this study regarding the possible preferential deposition of specific size fractions of sediment at different locations within the varying case study floodplains (e.g. the River Axe, the River Arrow and the River Wensum catchments). This influence has important potential implications for the ability of floodplain cores to represent a robust record of historic suspended sediment mobilised from throughout the catchments (Walling, 2005). If a significant proportion of the finer fractions of sediment remain in suspension during overbank flood events and are transported over the floodplain without settling, then valuable information will be absent from the historic suspended sediment record as represented by a floodplain core. Comparison between particle size characteristics, including SSA and particle size distribution, of contemporary suspended sediment sampled during flood events and floodplain core sediment, could help to identify the influence of depositional selectivity on the composition of overbank sediment.

10.5.3 Floodplain cores

The use of single cores to represent the sediment histories of the respective case study floodplains raises questions regarding representativeness. However, in view of the resources required to collect, process and analyse each core, a pragmatic approach had to be adopted to balance the number of study catchments against the level of detail possible in the study of the individual catchments. Other concerns relating to the floodplain cores acknowledged that a proportion of the downcore variation in geochemical property concentrations might be reflect post-depositional transformation and migration rather than changes in source type contributions and this could compromise their efficacy as source fingerprints (Collins *et al*., 1997b; Foster *et al*., 1998; Hudson-Edwards *et al*., 1998; Owens *et al*., 1999; Owens and Walling, 2002) Work by Owens *et al*., (1999) reported that significant correlation existed between geochemical property concentration and depth for a selection of 13 properties within seven floodplain cores from different sites in the River Ouse basin. However, the behaviour of specific properties varied between cores, in that, an individual property might decrease, increase or remain constant with depth at different locations. The significant correlation with depth could reflect the progressive change in sediment source over time or gradual in situ property transformation over time. It has been considered unlikely that all of the geochemical properties used in this study would be subject to post-depositional transformations and, further, that by incorporating a wide range of heavy metals, trace metals lanthanides and actinides in composite fingerprints any problems associated with post-depositional transformations will be minimised (Owens *et al*., 1999). Given the resource limitations of this study, including time and the access to analytical facilities and materials, the use of single cores to represent the floodplain sediment record were considered reasonable and appropriate.

10.5.4 Geochronology

Assumptions used in producing the geochronology estimates based on the ^{137}Cs technique, excluded the potential influence of post-depositional downward migration on the 1963 and 1986 markers which may introduce additional uncertainty (Owens and Walling, 2002), particularly when post 1963 depositional rates were extrapolated retrospectively to estimate pre-1963 chronologies extending back ca.100 years. Due to their respective decay rates, chronologies based on ^{210}Pb$_{ex}$ should ideally be used for estimates going as far back as 100-150 years, with ^{137}Cs derived chronologies being used to validate the ^{210}Pb$_{ex}$ estimates over the initial ca. 45 years. However, the limitations of time and analytical equipment available to this project restricted the application of the ^{210}Pb$_{ex}$ technique to the River Torridge catchment case study, where good agreement was obtained for the chronologies estimated by the respective techniques. In addition, the assumption of constant sedimentation rates used to provide geochronology estimates excluded any potential influence on such rates by the progressive accretion of the floodplain surface relative to the channel bed which could lead to reduced flood frequency. However, any such influence would be negated by channel bed accretion occurring at a similar rate to that of the floodplain (Owens and Walling, 2002). Further, it was necessary to assume that post depositional mixing and remobilisation was strictly limited, both between respective 1963 and 1986 markers (e.g. when both are available) and also between the upper or single marker (e.g. where only a 1963 marker exists) and the current floodplain surface. However, this is may not always be the case (Walling and He, 1994). For example, saturated floodplain fields with high stocking densities are liable to considerable poaching during flood events. Notwithstanding the above observations, the ^{137}Cs technique afforded a simple and convenient method of providing chronological estimates for the floodplain cores. The technique appeared to provide broadly consistent estimates when considered against known dates of substantial land use changes as reflected by shifts of relative source contributions.

10.5.5 Related dependencies - meteorological and hydrological data

Changes in the relative sediment contributions from sources within a catchment through time may reflect not only the land use, but also the weather patterns and catchment hydrology. In this respect, retrospective investigation of the influence of land use changes on sediment sources, including any mitigation measures, might be more robust when considered together with meteorological and hydrological data covering the same time period. Seasonal and annual, rainfall patterns and high magnitude storm events could significantly influence sediment mobilisation and transport. Changes in the hydrological regime of the catchment, including data on flow rates and stage, would be particularly useful in assessing the patterns of overbank flooding. Identifying those reaches which have a documented record of regular overbank flooding would aid the selection of suitable floodplain sites for core sampling. Historical hydrological data would also provide a valuable context for the assessing temporal variability in the intensity of channel bank erosion.

This section has highlighted some of the inherent problems associated with attempting to identify the specific influences of land use change, often occurring in localised areas, on the source of floodplain sediment at a catchment scale. However, the continued development of sustainable catchment management is only likely to be achieved through increased awareness of the potential for integrated farm-scale land use management decisions to result in catchment-scale hydrological improvements. Notwithstanding the limitations identified above, the sediment source fingerprinting technique applied to floodplain cores collected in the study was able to relate recent historical land use change to relative changes in the sources of floodplain overbank sedimentation with reasonable success and chronological accuracy.

10.6 Future work and development

10.6.1 Extending coverage – Comparing the provenance and behaviour of suspended sediment at varying temporal and spatial scales

It has not been possible in this study to compare the information obtained on the sources of the overbank floodplain sediment in the study catchments with equivalent information on interstitial fine sediment or with the main sources of the contemporary suspended sediment loads. Including such comparisons in retrospective sediment source studies would be extremely useful to obtain a fuller understanding of the catchment sediment dynamics and the associated sediment problems across the case study catchments. For example, work on the River Torridge catchment reported by Nicholls (2000) demonstrated that the sources of interstitial fines and of suspended sediment may differ in some river basins, suggesting that interstitial fines accumulate during periods of more stable flow, rather than the main periods of suspended sediment flux. Understanding these and other sediment behaviours would aid in the wider interpretation of overbank floodplain sediment deposits and their ability to represent reliable records of historical suspended sediment sources.

10.6.2 Extending coverage – The nested sub-catchment approach

In order to address the problems, raised during this study, of using the sediment source fingerprinting technique to detect localised sediment-related impacts within a catchment- scale study, it would be of benefit to extend the coverage of the research design by adopting a nested approach which could permit assessment of the impact of localised land use change or mitigation measures progressively from reach-scale up to catchment-scale. Such an approach could compare the effects of a range of environmental changes occurring at differing temporal and spatial scales, including those which affect the entire catchment but might provoke differing responses in different sub-catchments or on different land uses in the catchment. Such a fingerprinting study, when combined with the use of meteorological and hydrological data might be of particular interest in helping to inform the modelling of land use change and climate change impacts on sources of sediment at varying scales.

10.6.3 Robustly representing the 'typical' value and statistical dispersion of concentration values - Use of the median and the MAD

The use of the mean concentration value to represent a particular source has been justified previously on the basis of being realistic physically as the sediment retrieved from the catchment outlet represents a mixture of material mobilised and delivered from various locations in the catchment (Collins *et al*., 2010a). Consequently, the use of representative source material samples collected from throughout the catchment to derive mean geochemical property concentrations has been assumed to be analogous to natural sediment mixing during the mobilisation and delivery process. However, given that the concentration values for many of the properties analysed during this study have been observed to be characterized by non-normal distributions, it is felt that a more representative value might be achieved by the use of median property values. Further, in consideration of the use of mean values as inputs for the generation of the Monte Carlo dataset, a more robust approach, which would minimise the skew created by the use of means derived from non-normal distributions, could be afforded by the use of median values. Similarly, the variation in dataset property concentrations within the Monte Carlo framework, which have been defined previously by the standard deviation from the mean values, might be more robustly represented by the use of the Median Absolute Deviation (MAD) to further reduce the influence of outliers (Chung *et al*., 2008).

10.6.4 Alternative methods of quantification and novel tracer properties

A particularly interesting contribution to the analysis of the relationship between particle size and property concentration might concern the relationship between actual particle size, shape and surface texture and geochemical property concentrations. A technique which has hitherto been little used in environmental water research, but could prove of particular use in this area is the use of Scanning Electron Microscopy combined with Energy Dispersive X-ray (SEM-EDX). This combines the quantitative determination of elemental concentrations with the opportunity to accurately measure and visually classify attributes such as particle size, shape and surface topography. This technique may also have potential to offer a novel set of tracer properties, which could augment the geochemical properties available for source fingerprinting in this study.

10.7 Perspective

In order to satisfy current and emerging legislative requirements and to meet current and future environmental challenges, it is important to understand the effects of previous land use change on the sources and delivery of sediment to the aquatic environment. The application of the sediment source fingerprinting technique to floodplain sediment cores can be useful in providing an informed view of the influence of past land-use on the relative importance of different sources. Greater understanding of the sources of sediment within a river system is an intrinsic component of any effective catchment management strategy. In order to establish the significance of any information on present sediment sources, it is useful to establish a context for such information, based on the variation of sediment source contributions in the past. It may then be possible to compare any temporal variations or trends in the sources of sediment against variations in other changing environmental factors, to thereby improve understanding of the processes involved, and also to target and monitor the success of any remedial strategies and mitigation measures. The efficacy of mitigation measures can be tested against evidence-based historic trends and those management approaches which provide identifiable improvements can be seen as best practice options for future land management targeted at reducing the negative impacts of excessive sediment ingress to river systems.

REFERENCES

Adachi, K. and Tainosho Y. (2005) Single particle characterization of size-fractionated road sediments. *Applied Geochemistry*, 20, 5, 849-859

Ahn, Y.S., Nakamura, Kizuka, T. and Nakamura, Y. (2009) Elevated sedimentation in lake records linked to agricultural activities in the Ishikari River floodplain, northern Japan. *Earth Surface Processes and Landforms*, 34, 1650–1660

Allen, S. (1986) Radiation: A guide to a contaminated countryside. The Guardian, July 25, 1986. Cited in: Walling, D.E., Rowan, J.S. and Bradley, S.B. (1989) Sediment-associated transport and redistribution of Chernobyl fallout radionuclides. *Sediment and the environment (Proceedings of the Baltimore Symposium, May 1989) IAHS Publication 184*, 37-45

Allen, S.E., (1989) *Chemical Analysis of Ecological Materials*. Blackwell, Oxford

ApSimon, H.M., Wilson, J.J.N., Guirguis, S. and Stott, P.A. (1987) Assessment of the Chernobyl release in the immediate aftermath of the accident. *Nuclear Energy*, 26, 5, 295-301

Appleby, P. G., Nolan, P. J., Gifford, D. W., Godfrey, M. J., Oldfield, F., Anderson, N. J. and Battarbee, R. W. (1986) ^{210}Pb dating by low background gamma counting. *Hydrobiologia*, 143, 1, 21-27

Appleby, P.G., Oldfield, F. (1978) The calculation of lead-210 dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. *Catena*, 5, 1, 1-8

Appleby, P.G. Richardson, N. Nolan, P.J. Oldfield, F. (1990) Radiometric Dating of the United Kingdom SWAP Sites. *Philosophical Transactions of the Royal Society of London Series B, Biological Sciences*, 327, 1240, Palaeolimnology and Lake Acidification, 233-238

Auerswald, K., Gerl, G. and Kainz, M. (2006) Influence of cropping system on harvest erosion under potato. *Soil and Tillage Research*, 89, 1, 22-34

Baka, J. and Roland-Holst, D. (2009) Food or fuel? What European farmers can contribute to Europe’s transport energy requirements and the Doha Round. *Energy Policy*, 37, 2505–2513

Bakker, M.M., Govers, G., Kosmas, C., Vanacker, V., van Oost, K., and Rounsevell, M. (2005) Soil erosion as a driver of land-use change. *Agriculture, Ecosystems & Environment*, 105, 3, 467-481

Balistrieri, L.S. and Murray, J.W. (1986) The surface chemistry of sediments from the Panama Basin: The influence of Mn oxides on metal adsorption. *Geochimica et Cosmochimica Acta*, 50, 2235-2244.

Barclay, C. (2010) [WWW] Agriculture – CAP Reforms. House of Commons Briefing Paper, SN/SC/3680
http://www.parliament.uk/briefingpapers/commons/lib/research/briefings/snsc-03680.pdf Accessed: 10.08.2010

Basnyat, P., Teeter, L.D., Lockaby, B. G. and Flynn, K. M. (2000) The use of remote sensing and GIS in watershed level analyses of non-point source pollution problems. *Forest Ecology and Management*, 128, 1-2, 65-73

BBC (2010a) [WWW] Devon Coast and County, Devon's rivers: The Torridge
http://www.bbc.co.uk/devon/discovering/rivers/torridge.shtml Accessed: 07.04.2010

BBC (2010b) [WWW] Foot and Mouth outbreak in Devon.
http://news.bbc.co.uk/local/devon/hi/people_and_places/history/newsid_8481000/8481545.stm Accessed: 08.04.2010

BBC (2010c) [WWW] News Europe - EU experts to tackle Hungary toxic sludge
http://www.bbc.co.uk/news/world-europe-11512199 Accessed: 11.10.2010

Benoit, G. and Rozan, T.F. (2001) ^{210}Pb and ^{137}Cs dating methods in lakes: a retrospective study. *Journal of Paliolimnology*, 25, 455-465

Benton, T.G., Vickery, J.A. and Wilson, J.D. (2003) Farmland biodiversity: is habitat heterogeneity the key? *Trends in Ecological Evolution*, 18, 182–188

Bevan, K. (1996) Equifinality and Uncertainty in Geomorphological Modelling In: Rhoads, B.L. and Thorn. C.E. (eds.) *The Scientific Nature of Geomorphology* (Proceedings of the 27th Binghamton Symposium in Geomorphology held 27-29 September 1996). John Wiley & Sons Ltd, 12, 289-313

Biggs, B., Corfield, A., Per Grøn, P., Hansen, H. O. Walker, D., Whitfield, M. and Williams, P. (1998) Restoration of the rivers Brede, Cole and Skerne: a joint Danish and British EU-LIFE demonstration project, V - short-term impacts on the conservation value of aquatic macroinvertebrate and macrophyte assemblages. *Aquatic Conservation: Marine and Freshwater Ecosystems*, 8, 1, 241 – 255

Bilotta, G.S., Brazier, R.E., Butler, P., Freer, J., Granger, S. and Haygarth, P., Krueger, T., Macleod, C.J.A. and Quinton, J.N. (2008) Rethinking the contribution of drained and undrained grasslands to sediment related water quality problems. *Journal of Environmental Quality*, 37, 3, 906-914

Bilotta, G.S., Brazier, R.E. and Haygarth, P. M. (2007) Processes affecting transfer of sediment and colloids, with associated phosphorus, from intensively farmed grasslands: erosion. *Hydrological Processes*, 21, 135–139

Boardman, J. (1995) Damage to Property by Runoff from Agricultural Land, South Downs Southern England, 1976-93. *The Geographical Journal*, 161, 177–191.

Boardman, J. (2002) The need for soil conservation in Britain - revisited. *Area*, 34, 419-427

Boardman, J., Shepheard, M.L., Walker, E. and Foster, I.D.L. (2009) Soil erosion and risk-assessment for on- and off-farm impacts: A test case using the Midhurst area, West Sussex, UK. *Journal of Environmental Management*, 90, 8, 2578-2588

Bohren, C.F., Huffman, D. (1983) *Absorption and scattering of light by small particles*. Wiley, New York.

Bottrill, L.J., Walling, D.E. and Leeks, G.J.L. (1999) Geochemical characteristics of overbank deposits and their potential for determining suspended sediment provenance: an example from the River Severn, UK. In: Marriott S.B. and Alexander, J. (eds) *Floodplains: interdisciplinary approaches, Special Publication-Geological Society of London*, 163, 241–257

Bottrill, L.J., Walling, D.E. and Leeks, G.J.L. (2000) Using recent overbank deposits to investigate contemporary sediment sources in larger river basins. In: I.D.L. Foster, (ed), *Tracers in Geomorphology*, Wiley, Chichester, 369–387.

Brierley, G., Hillman, M, and, Fryirs, K. (2006) Knowing Your Place: an Australasian perspective on catchment-framed approaches to river repair. *Australian Geographer*, 37, 2, 131-145

Brook, E.J. and Moore, J.N. (1988) Particle-size and chemical control of As, Cd, Cu, Fe, Mn, Ni, Pb and Zn in bed sediment from the Clark Fork river, Montana (USA). *Science of the Total Environment*, 76, 247-266

Brown, A.G., Carpenter, R.G. and Walling, D.E. (2007) Monitoring fluvial pollen transport, its relationship to catchment vegetation and implications for palaeoenvironmental studies, *Review of Palaeobotany and Palynology*, 147, 1-4, 60-76

Bruland, K., Bertine, K, Koide, M. and Goldberg, E. (1974) History of metal Pollution in the southern California coastal zone. *Environmental Science and Technology*, 8, 425-432

Bryan, G.W. and Langston, W.J. (1992) Bioavailability, accumulation and effects of heavy metals in sediments with special reference to United Kingdom estuaries: A review. *Environmental Pollution,* 76, 89–131.

Burch, G.J., Barnes, C.J., Moore, I.D., Mackenzie, D., Barling, R. and Ollev, I.M. (1988) Detection and prediction of sediment sources in catchments: use of Be and Cs. In: *Proceedings Hydrology and Water Resources Symposium (ANU, Canberra, February 1988)*, 146-151

Burgoa, B. and Wauchope, R.D. (1995) Pesticides in run-off and surface waters. In: Roberts, T.R., Kearney, P.C. (eds.), *Progress in Pesticide Biochemistry and Toxicology: Environmental Behaviour of Agrochemicals*. John Wiley and Sons, Chichester, pp. 221–255

Burrell, A. (2004) The 2003 CAP reform: Implications for the EU dairy sector. *Outlook on Agriculture*, 33, 1, 15-25

Burt, T.P., Donohoe, M.A. and Vann, A.R. (1984) A comparison of suspended sediment yields from two small upland catchments following open ditching for forestry drainage. *Zeitschrift Fur Geomorphologie*, N.S., 51-62

Cabezas, A., Angulo-Martinez, Gonzalez-Sanchis, M.M., Jimenez, J.J. and Comin, F.A. (2010) Spatial variability in floodplain sedimentation: the use of generalized linear mixed-effects models *Hydrology and Earth System Sciences Discussions*, **7**, 1589–1619

Caitcheon, G.G. (1993) Sediment source tracing using environmental magnetism: a new approach with examples from Australia, *Hydrological Processes*, **7**, 349-358

Callaway, J.C., R.D. Delaune, and Patrick, W.H.Jr. (1996) Chernobyl ^{137}Cs used to determine sediment accretion rates at selected northern European coastal wetlands. *Limnology and Oceanography* 41, 444–450

Cambray, R. S., Cawse, P.A., Garland, J. A., Gibson, J. A. B., Johnson, P., Lewis, G. N. J, Newton, D., Salmon, L. and Wade, B. 0. (1987) Observations of radioactivity from the Chernobyl accident. *Nuclear Energy*, 26, 77-101

Campbell, B.L., Loughran, R.J. and Elliott, G.L. (1988) A method for determining sediment budgets using caesium-137. In: *Sediment Budgets*, (eds. Bordas, M.P. and Walling, D.E.). IAHS Publication No.174, Wallingford, U.K., 171-179

Carter, J., Owens, P.N., Walling D.E. and Leeks, G.J.L. (2003) Fingerprinting suspended sediment sources in a large urban river system, *Science of the Total Environment*, 314–316, 513–534

Chapman, A.S., Foster, I.D.L.. Lees, J.A., Hodgkinson, R.J. and Jackson, R.H. (2003) Sediment and phosphorus delivery from field to river via land drains in England and Wales. A risk assessment using field and national databases. *Soil Use and Management*, 19, 4, 347–355.

Chapman, A.S., Foster, I.D.L., Lees, J.A. and Hodgkinson, R.A. (2005) Sediment delivery from agricultural land to rivers via subsurface drainage. *Hydrological Processes*, 19, 2875-2897

Charles, M.J. and Hites, R.A., (1987) Sediments as archives of environmental pollution trends. In: R.A. Hites and S.J. Eisenreich (eds), *Sources and Fates of Aquatic Pollutants. Advances in Chemistry Series,* 216, 365-389

Chen, J.H., Lion, L.W., Ghiorse, W. and Shuler, M. (1995) Mobilization of adsorbed cadmium and lead in aquifer material by bacterial extracellular polymers. *Water Research,* 29, 421-430

Chiang, P.N., Wang, M.K., Huang, P.M. and Wang, J.J. (2008) Kinetics of radiocesium released from contaminated soil by fertilizer solutions. *Journal of Environmental Radioactivity*, 99, 1, 159-166

Chung, N., Zhang, X.D., Kreamer, A., Locco, L., Kuan, P-F., Bartz, S., Linsley, P.S., Ferrer, M. and Strulovici, B. (2008) Median Absolute Deviation to Improve Hit Selection for Genome-Scale RNAi Screens. *Journal of Biomolecular Screening*, 13, 149-158

Ciszewskia, D. and Malik, I. (2007) The use of heavy metal concentrations and dendrochronology in the reconstruction of sediment accumulation, Mala Panew River Valley, southern Poland. *Geomorphology*, 58, 161–174

Clark, E.H. (1985) The off-site costs of soil erosion. *Journal of Soil and Water Conservation*, 40, 1, 19-22

Clark, J. (2009) [WWW] In: Leys, K and Kupiec, J. (eds.) Rivers and their catchments: potentially damaging physical impacts of commercial forestry. Information and Advisory Note Number 19. Scottish Natural Heratige.org.uk/
http://www.snh.org.uk/publications/on-line/advisorynotes/19/19.htm
Accessed: 19.7.2009

Collins, A.L. (1995) Unpublished PhD Thesis. University of Exeter, Exeter

Collins, A.L., Walling, D.E. (2002) Selecting fingerprint properties for discriminating potential suspended sediment sources in river basins. *Journal of Hydrology*, 261, 218–244

Collins, A.L. and Walling, D.E. (2004) Selecting fingerprint properties for discriminating potential suspended sediment sources in river basins, *Journal of Hydrology*, 261, 218–244

Collins, A.L. and Walling, D.E. (2007a) The storage and provenance of fine sediment on the channel bed of two contrasting lowland permeable catchments, UK. *River Research and Applications*, 23, 4, 429-450

Collins, A.L. and Walling, D.E. (2007b) Sources of fine sediment recovered from the channel bed of lowland groundwater-fed catchments in the UK. *Geomorphology*, 88, 120-138

Collins, A.L., Walling D.E. and Leeks, G.J.L. (1996) Composite fingerprinting of the spatial source of fluvial suspended sediment: a case study of the Exe and Severn river basins, United Kingdom. *Geomorphology: Relief, Process, Environment*, 2, 41–54

Collins, A.L., Walling, D.E. and Leeks, G.J.L. (1997a) Source type ascription for fluvial suspended sediment based on a quantitative composite fingerprint technique. *Catena*, 29, 1-27

Collins, A.L., Walling, D.E., and Leeks, G.J.L. (1997b). Use of the geochemical record preserved in floodplain deposits to reconstruct recent changes in river basin sediment sources. *Geomorphology*, 19, 151-167.

Collins, A.L., Walling, D.E. and Leeks, G.J.L. (1997c) Fingerprinting the Origin of Fluvial Suspended Sediment in Larger River Basins: Combining Assessment of Spatial Provenance and Source Type. *Geografiska Annaler: Series A, Physical Geography*, 79, 239–254

Collins, A.L., Walling, D.E., and Leeks, G.J.L. (1997d) Sediment sources in the Upper Seven catchment: a fingerprinting approach. *Hydrology and Earth System Sciences*, 1, 3, 509-521

Collins, A.L., Walling, D.E., Sichingabula, H.M. and Leeks G.J.L. (2001) Suspended sediment source fingerprinting in a small tropical catchment and some management implications. *Applied Geography,* 21, 4, 387-412

Collins, A.L., Walling, D.E., Webb, L. and King, P. (2010a) Apportioning catchment scale sediment sources using a modified composite fingerprinting technique incorporating property weightings and prior information. *Geoderma*, 155, 249–261

Collins, A.L., Walling, D.E., Stroud, R.W., Robson, M. and Peet, L.M. (2010b) Assessing damaged road verges as a suspended sediment source in the Hampshire Avon catchment, southern United Kingdom. *Hydrological Processes,* 24, 1106–1122

Collins, A.L., Walling, D.E., McMellin, G.K., Zhang, Y., Gray, J., McGonigle, D. and Cherrington, R. (2010c) A preliminary investigation of the efficacy of riparian fencing schemes for reducing contributions from eroding channel banks to the siltation of salmonid spawning gravels across the South West UK, *Journal of Environmental Management*, 91, 6, 1341-1349

Collins, A.L., Zhang, Y., Walling, D.E., Grenfell, S.E. and Smith, P. (2010d) Tracing sediment loss from eroding farm tracks using a geochemical fingerprinting procedure combining local and genetic algorithm optimisation, *Science of The Total Environment*, 408, 22, 15, 5461-5471

Collins, E. (2009) Sheep Farmer, Bearwood Farm, Pembridge, Leominster. Personal communication (28.8.2009)

Coquery, M. and Welbourn, P.M. (1995) The relationship between metal concentration and organic matter in sediments and metal concentration in the aquatic macrophyte *Eriocaulon septangulare. Water Research*, 29, 9, 2094-2102

Cordone, A.J. and Kelley, D.W. (1961) The influences of inorganic sediment on the aquatic of streams. *California Fish and Game*, 47, 2, 189-227

Cotton, F.A., Wilkinson, G., Murillo, C.A, and Bochmann, M. (1999) *Advanced inorganic chemistry. 6th ed*. Wiley, New York

Cox, R. (2008) (CSFO River Waver and Wampool, Environment Agency, Penrith) Personal Communication, 21.09.2008

Cremers, A., Elsen, A., De Preter, P. and Maes, A. (1988) Quantitative analysis of radio caesium retention in soils. *Nature*, 335, 9–247

Crown copyright (1934) *Soil map for Herefordshire*, HMSO, London

Crown copyright (2009) [WWW] EDINA Geology Digimap: Geology Maps http://edina.ac.uk/digimap/description/bgsoverview.shtml Accessed 4.7.2009

Crown copyright (2009) [WWW] EDINA Geology Digimap: Geology Maps http://digimap.edina.ac.uk/ Accessed 6.12.2009

Cycleau (2006) Nature of the Study Area – The Axe & Char catchments http://www.cycleau.com/index.asp?id=1003238 Accessed: 02.03.2010

D'Arcy, B. and Frost, A. (2001) The role of best management practices in alleviating water quality problems associated with diffuse pollution, *The Science of The Total Environment*, 265, 1-3, 359-367

Daelnet (2009) [WWW] Countryside news for the dales and beyond – Fifty years of flood defence neglect, 27th November, 2009 http://www.daelnet.co.uk/news/weekend/weekend_27112009.cfm Accessed 8.7.2010

Datta, D.K. and Subramanian, V. (1998) Distribution and fractionation of heavy metals in the surface sediments of the Ganges- Brahmaputra-Meghna river system in the Bengal basin. *Environmental Geology*, 36, (1-2), 93-101

Davidson, E.A. and Janssens, I.A. (2006) Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature*, 440, 165–173

Davis, J.J. (1963) Caesium and its relationship to potassium in ecology. In: Schultz V. & Klement, A. W. Jr. (eds.) *Radioecology*, Reinhold, New York, pp.539-56.

Dayan, F.E., Cantrell, C.L. and Duke, S.O. (2009) Natural products in crop protection, *Bioorganic & Medicinal Chemistry - Modern Trends in Agrochemistry*, 17, 12, 4022-4034

de Vente, J., Poesen, J., Arabkhedri, M. and Verstraeten, G. (2007) The sediment delivery problem revisited. *Progress in Physical Geography*, 31, 155-178

De Vos, W., Demetriades, K., Otteson, R., Reeder, S., Pirc, S., Salminen, R. and Tarvainen, T. (2006) Comparison of Elements in all Sample Media, General Comments and Conclusions. In: De Vos, W. and Tarvainen, T. (eds.) (2006) *Geochemical Atlas of Europe Part 2 – Interpretation of Geochemical Maps, Additional Tables, Figures, Maps and Related Publications*. EuroGeoSurveys, Brussels, Belgium

Dearing, J.A. and Foster, I.D.L. (1986) Limnic sediments used to reconstruct sediment yields and sources in the English Midlands since 1765. In: Gardiner, V. (ed) *International geomorphology*, Wiley, Chichester, 853–868

Defra (2006) [WWW] Rural Development Service, *Revised Calculation of Livestock Units for Higher Level Stewardship Agreements, Technical Advice Note 33 (Second edition).* http://www.defra.gov.uk/rds/publications/technical/tan_33.pdf. Accessed 23.4.08

Defra (2006) [WWW] Rural Development Service, Revised Calculation of Livestock Units for Higher Level Stewardship Agreements, Technical Advice Note 33 (Second edition). http://www.defra.gov.uk/rds/publications/technical/tan_33.pdf. Accessed 23.4.09

Defra (2007) [WWW] Process: Farm Business – Indicator B12: Livestock Numbers http://www.defra.gov.uk/evidence/statistics/foodfarm/enviro/observatory/indicators/b/b12_data.htm Accessed: 30.09.2010

Defra (2008) [WWW] Stocking Density: An Example Calculation (Revised) http://www.defra.gov.uk/corporate/regulat/forms/erdp/hfas/hfaannexaamend-2008.pdf Accessed 28.6.2009

Defra (2009a) [WWW] Catchment Sensitive Farming Initiative – Catchment Priorities http://www.defra.gov.uk/farm/environment/water/csf/pdf/catchment-priorities.pdf Accessed: 3.2.2009

Defra (2009b) [WWW] Information note – Evidence Base - Recapturing the environmental benefits of set-aside http://www.defra.gov.uk/corporate/consult/gaec/info-note.pdf Accessed: 07.06.2010

Defra (2010a) [WWW] Catchment Sensitive Farming – The 50 Priority Catchments http://www.defra.gov.uk/foodfarm/landmanage/water/csf/catchments/priority/index.htm Accessed: 23.4.2010

Defra (2010b) [WWW] River Basin Districts Typology, Standards and Groundwater threshold values (Water Framework Directive) (England and Wales) Direction 2009. http://www.defra.gov.uk/environment/quality/water/wfd/documents/river-basin-typology-standards.pdf Accessed: 03.05.2010.

Defra (2010c) [WWW] Farming Statistics http://farmstats.defra.gov.uk Accessed 22.1.2010

Defra (2010d) [WWW] Food and Farming - Catchment Sensitive Farming http://www.defra.gov.uk/foodfarm/landmanage/water/csf/index.htm Accessed: 30.09.2010.

Defra (2010e) [WWW] Environment – Environmental liability http://www.defra.gov.uk/environment/policy/liability/#existing Accessed: 30.09.2010.

Defra, (2010f) [WWW] Food and Farming - Further information: Cross Compliance http://www.defra.gov.uk/foodfarm/farmmanage/singlepay/furtherinfo/crosscomply/

Demars, B.O.L. and Harper, D.M. (2005) Water column and sediment phosphorus in a calcareous lowland river and their differential response to point source control measures. *Water, Air, and Soil Pollution*, 167, 273-293

Demetriades, A., Pirc, S., De Vos, W., Ottesen, R., Reeder, S., O'Connor, P., Bidovec, M and De Vivo, B. (2005) Distribution of Elements in Floodplain Sediment. In: De Vos, W. and Tarvainen, T. (eds.) (2005) *Geochemical Atlas of Europe Part 2 – Interpretation of Geochemical Maps, Additional Tables, Figures, Maps and Related Publications*. EuroGeoSurveys, Brussels, Belgium

Douglas, R.W., Menary, W. and Jordan, P. (2007) *Phosphorus and sediment transfers in a grassland river catchment.* Nutrient Cycling in Agroecosystems, 77, 3, 199-212

Droppo, I. G. (2001) Rethinking what constitutes suspended sediment. *Hydrological Processes*, 15, 1551–1564

Droppo, I.G. and Jaskot, C. (1995) Impact of river transport characteristics on contaminant sampling error and design. *Environmental Science and Technology*, 28, 161-170

Duck, R.W. (1985) The effect of road construction on sediment deposition in Loch Earn, Scotland. *Earth Surface Processes and Landforms*, 10, 401-406

Duck, R.W., Rowan, J.S., Jenkins, P.A. and Youngs, I. (2001) A multi-method study of bedload provenance and transport pathways in an estuarine channel. *Physics and Chemistry of the Earth (B),* 26, 747–752

EA (2006) *The Derwent Catchment Abstraction Management Strategy* http://publications.environment-agency.gov.uk/pdf/GENE0206BKFB-e-e.pdf. Accessed: 30.4.2010

EA (2007) [WWW] What's in your backyard–Risk of flooding. http://maps.environment-agency.gov.uk/wiyby/wiybyController?x=466500.0&y=479500.0&topic=floodmap&ep=map&scale=4&location=Nunnington,%20North%20Yorkshire&lang=_e&layerGroups=default&textonly=off Accessed: 3.6.2007

EA (2008) [WWW] Catchment Sensitive Farming - Priority Catchment http://www.environment-agency.gov.uk/static/documents/Business/csfmethodology_1247009.pdf Accessed: 23.4.2008

EA (2010) [WWW] Flooding http://maps.environment-agency.gov.uk/wiyby/wiybyController?x=339500.0&y=258500.0&topic=floodmap&ep=map&scale=3&location=Pembridge,%20Herefordshire&lang=_e&layerGroups=default&textonly=off#x=339500&y=258500&lg=1,&scale=5 Accessed: 20.3.2010

EA (2010) [WWW] Environment Agency - Identifying artificial and heavily modified water bodies http://www.environment-agency.gov.uk/research/planning/33352.aspx Accessed: 03.05.2010.

EC (2003) [WWW] Common Implementation Strategy for the Water Framework Directive (2000/60/EC) Guidance Document No 4 http://circa.europa.eu/Public/irc/env/wfd/library?l=/framework_directive/guidance_documents/guidancesnos4sheavilysmo/_EN_1.0_&a=d Accessed: 03.05.2010.

EDINA (2009) [WWW] Agcensus. http://edina.ac.uk/agcensus. Accessed: 24.2.2009

EDINA (2010) [WWW] Edina Geology Digimap: Geology Maps http://digimap.edina.ac.uk/bgsmapper/ Accessed: 17.6.2010

Edwards, A.C. and Withers, P.J.A. (1998) Soil phosphorus management and water quality: a UK perspective. *Soil Use and Management*, **14**, 124–130

Elliott, E.T., Palm, C.A., Reuss, D.E. and Monz, C.A. (1991) Organic matter contained in soil aggregates from a tropical chronosequence: correction for sand and light fraction. *Agriculture, Ecosystems and Environment,* 34, 443-451

Endsreport (2006) Tough challenges ahead to meet ecological standards for water. *Endsreport,* 373, 35

English Nature (2009) [WWW] Black Mountains and Golden Valley http://www.english-nature.net/science/natural/profiles%5CnaProfile60.pdf Accessed 6.8.2009

Entwistle, J.A., Flowers, A.G., Nageldinger, G., Greenwood, J.C. (2003). Identification and characterization of radioactive 'hot' particles in Chernobyl fallout-contaminated soils: the application of two novel approaches. *Mineralogical Magazine*, 67, 183-204

Erba, S., Buffagni, A., Holmes, N., O'Hare, M., Scarlett, P. and Stenico, A. (2006) Preliminary testing of River Habitat Survey features for the aims of the WFD hydro-morphological assessment: an overview from the STAR Project. *Hydrobiologica*, 566, 281-296

Eshel, G., Levy, G., Mingelgrin U. and Singer, M. (2004). Critical evaluation of the use of laser diffraction for particle-size distribution analysis. *Soil Science Society of America Journal*, 68, 736–743

Europa (2008) [WWW] Environment: Commission welcomes EP vote on water quality standardshttp://europa.eu/rapid/pressReleasesAction.do?reference=IP/08/958&format=HTML&aged=0&language=EN&guiLanguage=en#fn2 Accessed: 03.05.2010

European Commission (2000) Directive 2000/60/EC, Establishing a framework for community action in the field of water policy. *Official Journal of the European Communities.* 327, 1–71

Evans, R. (1990) Soil erosion: its impact on the English and Welsh landscape since woodland clearance. In: Boardman, J., Foster, I.D.L., Dearing, J.A. (eds.) *Soil erosion on agricultural land. Proceedings of a workshop sponsored by the British Geomorphological Research Group, Coventry, UK, January 1989.* John Wiley & Sons Ltd, Chichester, 231 -254

Evans, R. (2004) Outdoor pigs and flooding: an English case study. *Soil Use and Management*, 20 (2), 178-181

Evans, R. (2005) Land use, sediment delivery and sediment yield in England and Wales. In: Owens, P.N. and Collins, A.J. (eds) *Soil erosion and sediment redistribution in river catchments – Measurement, Modeling and Management*. CABI Publishing, Wallingford, 70-85

Fanning, P.C. (1994) Long-term contemporary erosion rates in an arid rangelands environment in western New South Wales, Australia. *Journal of Arid Environments*, 28, 173–187

FAWC (Farm Animal Welfare Council) (2009) [WWW] *Report on the Welfare of Pigs Kept Outdoors.* http://www.fawc.org.uk/reports/pigs/fawcptoc.htm. Accessed 20.5.2009

Fiedler, S., Vepraskas, M.J. and Richardson, J.L. (2007) Soil redox potential: importance, field measurements and observations. *Advances in Agronomy*, 94, 2–44

Fiener, P., Auerswald, K. (2007) Rotation Effects of Potato, Maize, and Winter Wheat on Soil Erosion by Water. *Soil Science Society of America Journal*, 71, 1919-1925

Finch, J.W., Hall, R.L., Rosier, P.T.W., Clark, D.B., Stratford, C., Davies, H.N., Marsh, T.J., Roberts, J.M., Riche, A.B. and Christian, D.G. (2004) *The Hydrological Impacts of Energy Crop Production in the UK*. B/CR/000783/00/00. Department of Trade and Industry, London

Fleischer, S., Gustafson, A., Joelsson, A., Pansar, J. and Stibe, L., (1994) Nitrogen removal in created ponds. *Ambio,* 23 6, 349–357

Flemming, H.C., Schmitt, J. and Marshall, K.C. (1996) Sorption properties of biofilms. In: Calmano, W. (Ed) *Sediments and Toxic Substances*, Springer, Berlin, 115-157

Forstner, U. (1990) Inorganic sediment chemistry and elemental speciation. In: Baudo, R., Giesy, J. and Muntau, H. (eds.) *Sediments: chemistry and toxicity of in-place pollutants.* CRC Press, Danvers, M.A., 61-106

Forstner, U. and Wittmann, G. (1981) *Metal Pollution in the Aquatic Environment, 2nd edition*. Springer-Verlag, Berlin

Foster, I.D.L. Chapman, A.S. Hodgkinson, R.M. Jones, A.R.. Lees J.A and. Turner S.E. (2003) Changing suspended sediment and particulate phosphorus loads and pathways in underdrained lowland agricultural catchments; Herefordshire and Worcestershire, UK, *Hydrobiologia*, 494, 119–126.

Foster, I.D.L. (1995) Lake and reservoir bottom sediments as a source of soil erosion and sediment transport data in the U.K. In: Foster, I.D.L.. Gurnell, A.M. and Webb, B.W. (eds.) *Sediment and Water Quality in River Catchments*. Wiley, Chichester, 265-283

Foster, I.D.L. (2006) Lakes in the sediment delivery system. In: Owens, P.N. and Collins, A.J. (eds) Soil Erosion and Sediment Redistribution in River Catchments. CAB International, Wallingford, 128-142

Foster, I.D.L. (2010) Lakes and Reservoirs in the Sediment Cascade, In: Burt T. P. and Allison R. J. (eds.) *Sediment Cascades: An Integrated Approach*. John Wiley & Sons, Ltd, Chichester, UK. 12, 309-322

Foster, I.D.L. and Charlesworth, S.M. (1996) Heavy metals in the hydrological cycle: trends and explanation. *Hydrological Processes*, 10, 227-261

Foster, I.D.L., Charlesworth, S.M., Dearing, J.A., Keen, D.H. and Dalgleish, H. (1991) *Lake sediments: a surrogate measure of sediment associated heavy metal transport in fluvial systems? IAHS Publication 203*, 321–328

Foster, I.D.L. and Dearing, J.A. (1987) Lake-Catchments and Environmental Chemistry: A Comparative Study of Contemporary and Historical: Catchment Processes in Midland England. *Geodoumal,* 14, 3, 285-297

Foster, I.D.L., Dearing, J.A., and Appleby, P.G. (1986) Historical trends in catchment sediment yields: a case study in reconstruction from lake sediment records in Warwickshire, U.K. *Hydrological Sciences Journal,* 31, 427-443

Foster, I.D.L., Dearing, J.A., Simpson, A., Carter, A.D., Appleby, P.G. (1985) Lake catchment studies of erosion and denudation in the Merevale catchment, Warwickshire, UK. *Earth Surface Processes and Landforms* 10, 45–68

Foster, I.D.L., Grew, R. and Dearing, J.A. (1990) Magnitude and frequency of sediment transport in agricultural catchments: A paired lake-catchment study in midland England. In: Boardman, J. Foster, I.D.L. and Dearing, J.A. (eds.) *Soil Erosion on Agricultural Land,* Wiley, Chichester, 153-171

Foster, I.D.L. and Lees, J.A. (1999) Changing headwater suspended sediment yields in the LOIS catchments over the last century: apalaeolimnolological approach. *Hydrological Processes*, 13, 1137-1153

Foster, I.D.L. and Lees, J.A. (2000) Tracers in Geomorphology: Theory and Applicaions in Tracing Fine Particulate Sediments. In: Foster, I.D.L. (ed.) *Tracers in Geomorphology*. John Wiley and Sons, Ltd. London, 2-19

Foster, I.D.L., Lees, J.A., Owen, P.N. and Walling, D.E. (1998) Mineral magnetic characterisation of sediment sources from an analysis of lake and floodplain sediments of the Old Mill reservoir and Slapton Ley, South Devon, UK. *Earth Surface Processes and Land Forms* 23, 685-703

Foster, I.D.L., Owens, P.N. and Walling, D.E., (1996) Sediment yields and sediment delivery in the catchments of Slapton Lower Ley, South Devon, UK. *Field Studies,* 8, 629–661

Foster, I.D.L. and Walling, D.E. (1994) Using reservoir deposits to reconstruct changing sediment yields and sources in the catchment of the Old Mill Reservoir, South Devon, UK, over the past 50 years. *Hydrological Sciences Journal*, 39, 4, 347 – 368

Fowler, J. and Cohen, L. (1990) *Practical statistics for field biology*. Wiley, Chichester

Franks, S.W. and. Rowan, J.S. (2000) Multi-parameter fingerprinting of sediment sources: uncertainty estimation and tracer selection: computational methods in water resources. In: *Proceedings of the XIII International Conference on Computational Methods in Water Resources, Calgary, June 2000, Balkema, Rotterdam.* 1067–1074

Furse, M., Hering, D., Moog, O., Verdonschot, P., Johnson,R. K., Brabec, K., Gritzalis, K., Buffagni, A., Pinto, P., Friberg, N., Murray-Bligh, J., Kokes, J., Alber, R., Usseglio-Polatera, P; Haase, P., Sweeting, R., Bis, B., Szoszkiewicz, K., Soszka, H., Springe, G., Sporka, F. and Krno, I. (2006) The STAR project: context, objectives and approaches. *Hydrobiologia,* 566, 3-29

Garnier, J-M., Ciffry, P. and Benyahya, L. (2006) Implications of short and long term (30 days) sorption on the desorption kinetic of trace metals (Cd, Zn, Co, Mn, Fe, Ag, Cs) associated with river suspended matter. *Science of the Total Environment*, 366, 350-360

Garrad, P.N. and Hay, R.D. (1989) Sources of suspended and deposited sediment in a Broadland river. *Earth Surface Processes and Landforms*, 14, 41-62

Ghosh, S. and LaPara, T.M. (2007) The effects of subtherapeutic antibiotic use in farm animals on the proliferation and persistence of antibiotic resistance among soil bacteria. *The ISME Journal*, 1, 191–203

Giménez, R., Marzolff, I., Campo, M. A., Seeger, M., Ries, J. B., Casalí, J. and Álvarez-Mozos, J. (2009), Accuracy of high-resolution photogrammetric measurements of gullies with contrasting morphology. *Earth Surface Processes and Landforms*, 34, 1915–1926

Goetz S.J., Gardiner, N. And Viers, J.H. (2008) Monitoring freshwater, estuarine and near-shore benthic ecosystems with multi-sensor remote sensing: An introduction to the special issue, *Remote Sensing of Environment. 112*, *11*, *Applications of Remote Sensing to Monitoring Freshwater and Estuarine Systems*, 3993-3995

Gohin, A. (2006) Assessing CAP Reform: Sensitivity of Modelling Decoupled Policies. Journal of Agricultural Economics, 57, 415–440

Goldberg, E.D. (1963) Geochronology with Pb-210. In: *Radioactive Dating*, International Atomic Energy Agency, Vienna, 121-131

Goodson, J. M.; Gurnell A. M.; Angold P. G. and Morrissey I. P. (2001) Riparian seed banks: structure, process and implications for riparian management. *Progress in Physical Geography*, 25, 3: 301-325

Google Earth (2010) [WWW] http://earth.google.com Accessed: 5..2.2010

Google Earth (2010) [WWW] http://earth.google.com Accessed: 16.03.2010

Gordev,V., Rachold, V., and Vlasova, I. (2004) Geochemical behaviour of major and trace elements in suspended particulate material of the Irtysh river, the main tributary of the Ob river, Siberia. *Applied Geochemistry*, 4, 593-610

Gore, J. A. (Ed.) (1985) *The Restoration of Rivers and Streams: Theories and Experience*. Butterworth Publishers: Stoneham, MA, USA

Granger, S.J., Hawkins, J.M.B., Bol, R., White, S.M., Naden, P., Old, G., Bilotta, G.S., Brazier, R.E., Macleod, C.J.A. and Haygarth, P.M. (2010)

Green, J. C. (2005) Modeling flow resistance in vegetated streams: review and development of new theory. *Hydrological Processes*, 19, 1245–1259

Greenwood, P., Walling, D.E. and Quine, T.A (2008) Assessing the remobilisation of recently deposited sediment from river flood plains during single overbank flood events, using caesium-134 and cobalt-60 as tracers. *Sediment Dynamics in Changing Environments, IAHS-AISH Publication* 325, 13-22

Grigg, D. (1965) The Logic of Regional Systems, *Annals of the Association of American Geographers*, 55, 3, 465 – 491

Grimshaw, D.L. and Lewin, J. (1980) Source identification for suspended sediments, *Journal of Hydrology*, 47,151–162

Gruszowski, K.E., Foster, I.D.L., Lees, J.A. and Charlesworth, S.M. (2003) Sediment sources and transport pathways in a rural catchment, Herefordshire, UK. *Hydrological Processes*, 17, 2665-2681

Gunstone, F.D. (2002) Production and trade of vegetable oils. In: Gunstone, F.D. (ed.) *Vegetable oils in food technology: composition, properties and uses*, Blackwell, Oxford, 1 -17

Gurnell, A. M., Van Oosterhout, M. P., De Vlieger, B. and Goodson, J. M. (2006) Reach-scale interactions between aquatic plants and physical habitat: River Frome, Dorset. *River Research and Applications*, 22, 667-680

Haines, A. Y., B. L. Finlayson, and T. A. McMahon. (1988) A global classification of river regimes. *Applied Geography*, 8, 255–272

Hartman, W.H., Richardson, C.J., Vilgalys, R., and Bruland, G.L. (2008) Environmental and anthropogenic controls over bacterial communities in wetland soils. *Proceedings of the National Academy of Sciences USA*, 105, 17842–17847

Hasholt, B (1988) On identification of sources of sediment transport in small basins with special reference to particulate phosphorus. In: Bordas, M.P. and Walling, D.E. (*eds*) *Sediment Budgets*. pp 241-250. IAHS Publication No. 174

Haughton, A.J., Bond, A.J., Lovett, A.A., Dockerty, T., Sünnenberg, G., Clark, S.J., Bohan, D.A., Sage, R.B., Mallott, M.D., Mallott, V.E., Cunningham, M.D., Riche, A.B., Shield, I.F., Finch, J.W., Turner, M.M. and Karp, A. (2009), A novel, integrated approach to assessing social, economic and environmental implications of changing rural land-use: a case study of perennial biomass crops. *Journal of Applied Ecology*, 46, 315–322

He, Q. and Owens, P. (1995) Determination of suspended sediment provenance using caesium-137, unsupported lead-210 and radium-226: a numerical mixing model approach In: Foster, I.D.L., Gurnell, A.M. and Webb, B.W. (eds) *Sediment and Water Quality in River Catchments*. Wiley, Chichester, 207-227

He, Q. and Walling, D.E. (1996) Interpreting particle size effects in the adsorption of ^{137}Cs and unsupported ^{210}Pb by mineral salts and sediments. *Journal of Environmental Radioactivity*, 30, 117-137

He, Q. and Walling, D.E. (1997) The distribution of fallout ^{137}Cs and ^{210}Pb in undisturbed and cultivated soils. *Applied Radiation and Isotopes*, 48, 5, 677-690

Heathwaite, A.L. (1994) Chemical fractionation of lake sediments to determine the effects of land-use change on nutrient loading. *Journal of Hydrology*, 159, 395–421

Herefordshire Nature Trust (2009) [WWW]
http://www.wildlifetrust.org.uk/hereford/reserves/wildherefordshire.htm
Accessed: 11.6.2009

Heberer, T., Schmidt-Baumler, K., Stan, H.J., (1998) Occurrence and distribution of organic contaminants in aquatic systems in Berlin. Part I: Drug residues and other polar contaminants in Berlin surface and groundwater. *Acta Hydrochimica et Hydrobiologica*, 26, 272–278

Herefordshire and Worcestershire Earth Heritage Trust (2009) [WWW] Designated RIGS in Herefordshire
http://www.earthheritagetrust.org/blog/LocalGAPs Accessed 25.5.2009

Herefordshire Rivers (2009) [WWW] The River Arrow.
http://www.herefordshirerivers.org. Accessed: 8.6.2009

Hickman, L. (2009) [WWW] Sheep farmers still stuck under a Chernobyl cloud, *The Gaurdian.* http://www.guardian.co.uk/uk/2009/dec/29/sheep-farmers-chernobyl-meat-restricted Accessed: 2.2.2010

High Temporal Resolution Monitoring of Multiple Pollutant Responses in Drainage from an Intensively Managed Grassland Catchment Caused by a Summer Storm Water, Air, & Soil Pollution,Volume 205, Numbers 1-4, 377-393

Hird, A.B., Rimmer, D.L. and Livens, F.R. (1996) Factors affecting the sorption and fixation of caesium in acid organic soil. *European Journal of Soil Science*, 47, 97-104

Hiscock, K.M., Lister, D.H., Boar, R.R. and Green, F.M.L. (2001) An integrated assessment of long-term changes in the hydrology of three lowland rivers in eastern England. *Journal of Environmental Quality*, 61, 195–214

HMSO (2009a) [WWW] The Environmental Damage (Prevention and Remediation) Regulations 2009 No.153.
http://www.legislation.gov.uk/uksi/2009/153/regulation/5/made Accessed 04.05.2010

HMSO (2009b) [WWW] The Water Resources Act 1991 (Amendment) (England and Wales) Regulations 2009 No.3104
http://www.legislation.gov.uk/uksi/2009/3104/regulation/3/made Accessed: 30.09.2010

Hodge, C. A., H. Burton, W. M., Corbett, W. M., Evans R. and Searle. R. S. (1984) *Soils and their use in Eastern England, Bulletin Number 13*, Soil Survey of England and Wales, Harpenden

Holden, J. Chapman P.J. and. Labadz, J.C. (2004) Artificial drainage of peatlands: hydrological and hydrochemical process and wetland restoration. *Progress in Physical Geography*, 28, 1, 95–123

Holman, I.P., Hollis, J.M., Bramley, M.E. and Thompson, T.R.E. (2003) The contribution of soil structural degradation to catchment flooding: a preliminary investigation of the 2000 floods in England and Wales. *Hydrology and Earth System Sciences*, 7, 5, 755-766

Holme St. Cuthbert History Group, (2009) [WWW] Solway Plain-Past and present – Farming
http://myweb.tiscali.co.uk/hstchg/livestock.htm Accessed: 17.9.2009

Hopkinson, C.S.J., Giblin, A.E., Tucker, J., and Garritt, R.H. (1999) Benthic metabolism and nutrient cycling along an estuarine salinity gradient. *Estuaries* 22, 863–881

Horowitz, A.J. (1984) *A primer on trace meta-sediment chemistry, 2nd edition*. Lewis Publishers, Michigan

Horowitz, A.J. (1991) *A primer on sediment-trace element chemistry*. Lewis Publishers, Chelsea, Michigan

Horowitz, A. J. and Elrick, K. A. (1987) The relation of stream sediment surface area, grain size and composition to trace element chemistry. *Applied Geochemistry*, 2, 437-451

Horowitz, A. and Elrick, K. (1988) Interpretation of bed sediment trace metal data: methods for dealing with the grain size effect. In: Litchenberg, J. (Ed) *Chemical and biological characterization of sludges, sediments, dredge spoils and drilling muds*. ASTM International, Philadephia, Penn, 114-128

Horowitz, A.J., Elrick, K.A., Robbins, J.A., and Cook, R.B. (1995) Effect of mining and related activities on the sediment trace element geochemistry of Lake Coeur d'Alene, Idaho, USA. II: Subsurface sediments. *Hydrological processes*, 9, 1, 35-54

Howard, D.C., Wadsworth, R.A., Whitaker, J.W., Hughes, N. and Bunce, R.G.H. (2009) The impact of sustainable energy production on land use in Britain through to 2050. *Land Use Policy,* 26, 1, 284-292

Hupp, C. R. (2000) Hydrology, geomorphology and vegetation of Coastal Plain rivers in the southeastern USA, *Hydrological Processes* 14, 2991–3010

Imeson, A.C. (1974) The origin of sediment in a moorland catchment with special reference to the role of vegetation. *Fluvial Processes in Instrumented Watersheds, Transactions of the Institute of British Geographers*, Special Publication No. 6, 69-72

Institute of Geological Sciences (IGS) (1976) *Lake District sheet 54H 04W, Solid Edition*, Crown copyright

Institute of Hydrology (1992) Low flow estimation in the United Kingdom. *Institute of Hydrology Report No 108*, Institute of Hydrology, Wallingford, 83

James, W. F., Eakin, H. L., Ruiz, C.E. and Barko, J.W. (2004) Variations in Field-Scale Nitrogen and Phosphorus Concentrations in Runoff as a Function of Land-Use Practice *SMART Technical Notes Collection*, ERDC/TN SMART-04-6, U.S. Army Engineer Research and Development Center, Vickburg, MS.

Jafaar, M. (2010) Soil erosion, diffuse source pollution and sediment problems associated with maize cultivation in England. Unpublished PhD thesis. School of Geography, University of Exeter, UK

Johnson, R.C. (1993) Effects of forestry on suspended solids and bedload yields in the Balquhidder catchments, *Journal of Hydrology*, 145, 3-4, 403-417

Johnson, A.C., White, C., Besien, T.J. and Jurgens, M.D., (1998) The sorption potential of octylphenol, a xenobiotic oestrogen, to suspended and bed-sediments collected from industrial and rural reaches of three English rivers. *Science of the Total Environment* 210/211, 271–282

Joint Nature Conservancy Council (JNCC) (2010) [WWW] *River Torridge-Special Area of Conservation-SAS-Habitats Directive* http://www.jncc.gov.uk/ProtectedSites/SACselection/sac.asp?EUCode=UK0012647 Accessed: 11.6.2010

Jones J.B. & Smock L.A. (1991) Transport and retention of particulate organic matter in two low-gradient headwater streams. *Journal of the North American Benthological Society*, 10, 115-126

Jowett, I. G., Richardson, J. and Bonnett, M. L. (2005) Relationship between flow regime and fish abundances in a gravel-bed river, New Zealand. *Journal of Fish Biology*, 66, 1419–1436

Jowit, J. (2009) [WWW] Wildlife fears prompt return of set-aside payments. The Guardian, February 16th, 2009. http://www.guardian.co.uk/environment/2009/feb/16/set-aside-payments-farming Accessed 26.05.2010

Jungwirth, M., Muhar, S. and Schmutz, S. (2002) Re-establishing and assessing ecological integrity in riverine landscapes. *Freshwater Biology*, 47, 867-887

Ketterer, M.E., Hafer, K.M. and Mietelski, J.W. (2004) Resolving Chernobyl vs. global fallout contributions in soils from Poland using Plutonium atom ratios measured by inductively coupled plasma mass spectrometry. *Journal of Environmental Radioactivity*, 73, 183-201

Ketterer, M.E. and Szechenyi, S.C. (2008) Determination of plutonium and other transuranic elements by inductively coupled plasma mass spectrometry: A historical perspective and new frontiers in the environmental sciences. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 63, 7, 719-737

Kim, B. A., Tomiyasu, B., Owari, M. and Nihei, Y. (2001) Individual particle analysis for source apportionment of suspended particulate matter using electron probe microanalysis. *Surface and Interface Analysis*, 31, 106–113

Kim, S.C. and Carlson, K. (2005) LC–MS^2 for quantifying trace amounts of pharmaceutical compounds in soil and sediment matrices. *Trends in Analytical Chemistry*, 24, 7, 635-644

Klages, M.G. and Hsieh, Y.P. (1975) Suspended solids carried by the Galatin River of Southwestern Montana: II. Using mineralogy for inferring sources. *Journal of Environmental Quality*, 4, 68–73

Klamer, J.C., Hegemain, W.J.M. and Smedes, F. (1990) Comparison of grain size correction procedures for organic micropollutants and heavy metals in marine sediments. *Hydrobiologia*, 208, 213-220

Klecka, W. R. (1980). *Discriminant Analysis*. Sage Publications. Beverly Hills, CA.

Kronvang, B., Hoffmann, C.C., Svendsen, L.M., Windolf, J., Jensen, J.P., Dørge, J. (1998). Retention of nutrients in river basins Aquatic Ecology 33(1): 29-40

Kronvang, B. Svendsen, L.M. Jensen J.P. and Dørge, J. (1999) Scenario analysis of nutrient management at the river basin scale. *Hydrobiologia*, **410**, 207–212.

Laloy, E. and Bielders, C.L (2010) Effect of Intercropping Period Management on Runoff and Erosion in a Maize Cropping System. *Journal of Environmental Quality*, 39, 3, 1001-1008

Landis (2010) [WWW] National Soil Research Institute Cranfield University Landis-soilscapes http://www.landis.org.uk/soilscapes/ Accessed: 8.6.2009

Lang, T. (2010) Crisis? What Crisis? The Normality of the Current Food Crisis. *Journal of Agrarian Change*, 10, 87–97

Lawler, D.M. Thorne, C.R. and Hooke, J.M. (1997) Bank erosion and instability. In: C.R. Thorne, R.D. Hey and M.D. Newson, (eds), Applied fluvial geomorphology for river engineering and management, John Wiley, London. pp 137–1

Lawler, D.M., Petts, G.E., Foster, I.D.L. and Harper, S. (2006) Turbidity dynamics during spring storm events in an urban headwater river system: The Upper Tame, West Midlands, UK, *Science of the Total Environment*, 360, 1-3, 109-126

Leeks, G.J.L. (1992) Impact of plantation forestry on sediment transport processes. In: Billi, P., Hey, R.D., Thorne, C.R., and Tacconi, P. (eds.) *Dynamics of Gravel Bed Rivers*. Wiley, Chichester, UK

Lees, J.A., Foster, I.D.L., Jones, E.D., Owens, P.N., Walling, D.E., and Leeks, G.J.L. (1997) Sediment yields in a changing environment: a historical reconstruction using reservoir bottom sediments in three contrasting small catchments, North York Moors, UK. *Human Impact on Erosion and Sedimentation (Proceedings of the Rabat Symposium). IAHS Publication*, 245, 169-179

Levin, G. and Rudbeck-Jepsen, M. (2010) Abolition of set-aside schemes, associated impacts on habitat structure and modelling of potential effects of cross-farm regulation, *Ecological Modelling*, 221, 22, 2728-2737

Lewin, J. and Wolfenden, P.J. (1978) The assessment of sediment sources: a field experiment. *Earth Surface Processes* 3, 171–178

Lewis, M. (2006) *Farm Business Survey 2005/6 – Pig Production in England*. Rural Business Research Unit, Askham Bryan College, Askham Bryan,York

Liu, W., Li, X., Shen, Z., Wang, D., Wai, O. and Li, Y. (2003) Multivariate statistical study of heavy metal enrichment in sediments of the Pearl River Estuary. *Environmental Pollution*, 121, 3, 377-388

Livingston, H.D. and Cambray R.S. (1978) Confirmation of ^{137}Cs dating by algal stratigraphy in Rostherne Mere. *Nature*, 276, 259-261

Longmore, M.E. (1982) The caesium-137 dating technique and associated applications in Australia-A review, pp. 310-321. *In*: Ambrose, W. and Duerden, P. (eds.) *Archaeometry: an Australasian perspective*, Australian National University Press, Canberra, Australia

Loughran, R.J. (1989) The measurement of soil erosion. Progress in Physical Geography, 13, 216-233

Loughran J. and Campbell, B.L. (1995) The identification of catchment sediment sources. In: I.D.L. Foster, A.M. Gurnell and B.W. Webb, (eds), *Sediment and Water Quality in River Catchments*, Wiley, Chichester pp. 189–205

Lovett, A.A., Sünnenberg, G.M., Richter, G.M., Dailey, A.G., Riche, A.B. and Karp, A. (2009) Land use implications of increased biomass production identified by GIS-based suitability and yield mapping for Miscanthus in England. *Bioenergy Research*, 2, 1–2, 17–28

Mackenzie, A.B., Farmer, J.G. and Sugden, C.L. (1997) Isotopic evidence of the relative retention and mobility of lead and radiocaesium in Scottish ombrotrophic peats. *The Science of the Total Environment*, 203, 115-127

MAFF (1970) 'Modern farming and the soil' *Report of the Agricultural Advisory Council on Soil Structure and Soil Fertility*, HMSO, London

Maguire, S., Pulford, I.D., Crooke G.T. and MacKenzie, A.B. (1992) Caesium sorption-desorption in clay-humic acid system. *Journal of Soil Science.* 43, 96–689

Mantei, E.J. and Sappington, E.J. (1994) Heavy metal concentrations in sediments of streams affected by sanitary landfill: A comparison of metal enrichment in two size sediment fractions. *Environmental Geology*, 24, 287-292

Martincic, D., Kwokal, Z. and Branica, M. (1990) Distribution of Zn, Pb, Cd, Cu between different size fractions of sediments. *Science of the Total Environment*, 95, 217-225

Martínez-Carreras, N., Gallart, F., Iffly, J.F., Pfister, L., Walling, D.E. and Krein, A. (2008) Uncertainty assessment in suspended sediment fingerprinting based on tracer mixing models: a case study from Luxembourg. *Proceedings of a symposium on 'sediment dynamics in changing environments'.* Christchurch, New Zealand. IAHS Publication No.325, 94–105

Martínez-Carreras, N., Krein, A., Gallart, F., Iffly, J., Pfister, L., Hoffmann, L. and Owens, P.N. (2010) Assessment of different colour parameters for discriminating potential suspended sediment sources and provenance: A multi-scale study in Luxembourg. *Geomorphology*, 118, 118–129

Mayer, L.M. (1994) Surface area control of organic carbon accumulation in continental shelf sediments, *Geochimica et Cosmochimica Acta* 58, 1271–1284

Micromeritics (2002) *Saturn DigiSizer 5200 Operator's Manual*, Micromeritics Instrument Corporation, Norcross, G.A

Micromeritics (2009) [WWW] Family of Products Brochure http://www.micromeritics.com/Repository/Files/Family_Brochure_2009.pdf Accessed: 2.4.2010

Middelkoop, H. and Van der Perk, M. (1998) Modelling spatial patterns of overbank sedimentation on embanked floodplains, *Geografiska Annaler Series A-Physical Geography*, 80A, 95–109

Miessler, G.L. and Tarr, D.A. (1999) *Inorganic chemistry. 2nd ed*. Prentice Hall, Upper Saddle River, New.Jersey

Milsom, T.P., Aegerter, J., Bishop, J.D., Allcock, J.A., Barker, D., Boatman, N.D., Hill, V., Jones, N., Marshall, J., McKay, H.V., Moore, N.P. & Robertson, P.A. (2003). *Review of hilledge habitats in the uplands of* England and Wales. Project No BD1235. Report to Defra.

Molinaroli, E., Blom, M. and Basu, A. (1991) Methods of provenance determination tested with Discriminant Function Analysis. *Journal of Sedimentary Petrology*, 61, 900-908

Morris, N.L. Miller, P.C.H. Orson, J.H. and Froud-Williams, R.J. (2010) The adoption of non-inversion tillage systems in the United Kingdom and the agronomic impact on soil, crops and the environment – A review, *Soil and Tillage Research*, 108, 1-2, 1-15

Motha, J.A., Wallbrink, P.J., Hairsine, P.B. and Grayson, R.B. (2002) Tracer properties of eroded sediment and source material. Htdrological Processes, 16, 1983-2000

Motha, J.A., Wallbrink, P.J., Hairsine, P.B. and Grayson, R.B. (2003) Determining the sources of suspended sediment in a forested catchment in southeastern Australia. *Water Resources Research*, 39, 1056-1070

Mundry, R. and Nunn, C.L. (2009) Stepwise Model Fitting and Statistical Inference: Turning Noise into Signal Pollution. *The American Naturalist*, 173, 1, 119-123

Murray, K. A. (1955) *History of the Second World War – Agriculture*. HMSO, Longmans, London

Nagle, G.N. and Ritchie, J.C. (2004) Wheat field erosion rates and channel bottom sediment sources in an intensively cropped northeastern Oregon drainage basin. *Land Degradation & Development*, 15, 1, 15-26

Naiman, R. J., Bunn, S. E., Nilsson, C., Petts, G. E., Pinay, G and Thompson, L. C. (2002) Legitimizing fluvial ecosystems as users of water: An overview. *Environmental Management*, 30, 4, 455-467

Natural England (2009) *River Wensum restoration strategy-Natural England Commissioned Report NECR010.* Natural England, Sheffield

Natural England (2010) [WWW] Sites of Special Scientific Interest – SSSI units for the River Axe http://www.english-nature.org.uk/Special/sssi/unitlist.cfm?sssi_id=2000139 Accessed: 06.08.2010

Natural England (2010) [WWW] Our work - England Catchment Sensitive Farming Delivery Initiative (ECSFDI)
http://www.naturalengland.org.uk/ourwork/farming/csf/default.aspx
Accessed: 18.10.2010

Naylor, R.L., Liska, A.J., Burke, M.B., Falcon, W.P., Gaskell, J.C., Rozelle, S.D. and Cassman, K.G. (2008) The ripple effect: biofuels, food security, and the environment *Environment*, 49, 9, 30-43

Newson, M.D. (1980) The erosion of drainage ditches and its effects on bedload yields in Mid-Wales. *Earth Surface Processes and Landforms*, 5, 275-290

Nicholls, D.J. (2000) *The source and behaviour of fine sediment deposits in the River Torridge, Devon and their implications for Salmon spawning*. Unpublished PhD thesis. University of Exeter, Exeter

Ning, S-K., Chang, N-B., Jeng, K-Y. and Tseng, Y-H. (2006) Soil erosion and non-point source pollution impacts assessment with the aid of multi-temporal remote sensing images, *Journal of Environmental Management*, 79, 1, 88-101

Nisbet, T.R. (2001) The role of forest management in controlling diffuse pollution in UK forestry. *Forest Ecology and Management*, 143, 1-3, 215-226

Nislow, K.H. (2005) Forest change and stream fish habitat: lessons from 'Olde' and New England. *Journal of Fish Biology*, 67, 186–204

Nixon, S.W. (1995). Coastal marine eutrophication: a definition, social causes, and future concerns. *Ophelia*, 41, 199 – 219

Noe, G.B. and Hupp, C.R. (2005) Carbon, nitrogen, and phosphorus accumulation in floodplains of Atlantic Coastal Plain rivers, USA, *Ecological Applications*, 15, 1178–1190

Norfolk Anglers Conservation Association (NACA) (2010) [WWW] *Sayers Meadow Restoration Project*
http://norfolkanglers.co.uk/fisheries/sayers-meadow/sayers-restoration.html
Accessed: 11.6.2010

Novotny, V, and Chesters, G. (1981) *Handbook of Nonpoint Pollution: Sources and Management*. Van Nostrand Reinhold Environmental Engineering Series. Van Nostrand Reinhold Co. New York

Novotny, V. and Olem, H. (1994) *Water Quality: Prevention, Identification, and Management of Diffuse Pollution*, Van Nostrand Reinhold, New York

Novotny, V., Tran, H., Simsiman, G.V. and Chesters, G. (1978) Mathematical Modeling of Land Runoff Contaminated by Phosphorus. *Journal (Water Pollution Control Federation),* 50, 1, 101-112

Nriagu, J.O. (ed) *The biochemistry of lead in the environment*. Elsevier, Amsterdam, 285-393

NSRI (2007) [WWW] National Soil Research Institute Cranfield University http://www.landis.org.uk/soilscapes/ Accessed: 8.6.2009

NSRI (2010) [WWW] National Soil Research Institute (NSRI) LandIS-Land Information System http://www.landis.org.uk/soilscapes/ Accessed: 06.01.2010

Ntekim, E.E.U., Ekwere, S.J. and Ukpong, E.E. (1993) Heavy metal distribution in sediments from Calabar River, southeastern Nigieria. *Environmental Geology*, 21, 237–241

Ogg, C.W. (2009) Avoiding more biofuel surprises: The fuel, food and forest trade-offs *Journal of Development and Agricultural Economics*, 1, 1, 012-017

O'Hara, S.L., Street-Perrott, F.A. and Burt, T.P. (1993) Accelerated soil erosion around a Mexican highland lake caused by prehispanic agriculture. Nature, 362, 48–51

O'Hare, M. T., Baattrup-Pedersen, A., Nijboer, R., Szoszkiewicz, K., & Ferreira, T. (2006) Macrophyte communities of European streams with altered physical habitat. *Hydorbiologia*, 566, 197-210

Ohyama, T., Jin, K., Katoh, Y., Chiba, Y. and Inoue, K. (1987) Fate and behavior of herbicides, butachlor, CNP, chlomethoxynil and simetryne in river water, shellfish, and sediments of the Ishikari River. *Bulletin of Environmental Contamination and Toxicology*, 39, 555-562

Oldfield, F. and Appleby, P.G., (1984) Empirical testing of 210Pb-dating models for lake sediments, In: Haworth, E.Y., and Lund, J.W.G. (eds.) *Lake Sediments and Environmental History*, 93-124, University of Minnesota, Minneapolis, Mn.

Oldfield, F., Rummery, T.A., Thompson, R. and Walling, D.E. (1979) Identification of suspended sediment sources by means of magnetic measurements: some preliminary results. *Water Resources Research*, 15, 211-218

Oldfield, F., Hunt, A., Jones, M.D.H., Chester, R., Dearing, J. A., Olsson, L., Prospero, J. M. (1985) Magnetic differentiation of atmospheric dusts. *Nature*, 317 (6037), 516-18

Oldfield, F and Clark, R.L. (1990) Lake sediment-based studies of soil erosion. In: Boardman, J., Foster, I.D.L. and Dearing, J.A. (eds.) *Soil Erosion on Agricultural Land*, Wiley, Chichester, 201-208

Ormerod, L.M. (1998) Estimating sedimentation rates and sources in a partially urbanised catchment using caesium-137. *Hydrological Processes*, 12, 1009-1020

Ormerod, S. L. (2004) A golden age of river restoration science? Aquatic Conservation: *Marine and Freshwater Ecosystems*, 14, 543-549

Ormerod, S.J. (2009) Climate change, river conservation and the adaptation challenge. *Aquatic Conservation: Marine and Freshwater Ecosystems*, 19, 609–613

Owens, P.N. (1994) *Towards improved interpretation of caesium-137 measurements in soil erosion studies*. Unpublished PhD Thesis. Department of Geography, University of Exeter, Exeter, UK

Owens, P.N., Batalla, R.J., Collins, A.J., Gomez, B., Hicks, D.M., Horowitz, A.J., Kondolf, G.M., Marden, M., Page, M.J., Peacock, D.H., Petticrew, E.L., Salomons, W. and Trustrum, N.A. (2005) Fine-grained sediment in river systems: Environmental significance and management issues. *River Research and Applications*, 21, 693-717

Owens, P.N. and Slaymaker, O. (1994) Post-glacial temporal variability of sediment accumulation in a small alpine lake. In: Olive, L.J., Loughran, R.J., Kesby, J.A. (Eds.) *Variability in Stream Erosion and Sediment Transport. IAHS Publication No. 224*, IAHS Press, Wallingford, UK, 187–195

Owens, P.N. and Walling, D.E. (1996) Spatial variability of caesium-137 inventories at reference sites: an example from two contrasting sites in England and Zimbabwe. *Applied Radiation and Isotopes,* 47, 7, 699–707

Owens, P. N. and Walling, D. E. (2002) Changes in sediment sources and floodplain deposition rates in catchment of the River Tweed, Scotland, over the last 100 years: The impact of climate change and land use change. *Earth Surface processes and Landforms* 27, 403-423

Owens, P.N. and Walling, D.E. (2003) Temporal changes in the metal and phosphorus content of suspended sediment transported by Yorkshire rivers, UK over the last 100 years, as recorded by overbank floodplain deposits. *Hydrobiologia*, 494, 185-91

Owens, P.N., Walling, D.E., Carton, J., Meharg, A.A., Wright, J. and Leeks, G.J.L. (2001) Downstream changes in the transport and storage of sediment-associated contaminants (P, Cr and PCBs) in agricultural and industrialized drainage basins, *The Science of The Total Environment*, 266, 1-3, 177-186

Owens, P.N., Walling, D.E. and Leeks G.J.L. (1999) Use of floodplain sediment cores to investigate recent historical changes in overbank sedimentation rates and sediment sources in the catchment of the River Ouse, Yorkshire, UK. *Catena*, 36, 21-47

Owens, P.N., Walling, D.E. and Leeks G.J.L. (2000) Tracing fluvial suspended sediment sources in the catchment of the River Tweed, Scotland, using composite fingerprints and a numerical mixing model. In: Foster, I.D.L. (ed.) *Tracers in Geomorphology*, Wiley, Chichester, 291–307

Page, M.J. and Trustrum, N.A. (1997) A late Holocene lake sediment record of the erosion response to land use change in a steepland catchment, New Zealand. *Zeitschrift fur Geomorphologie* 41, 369–392

Pagliai, M., Vignozzi, N. and Pellegrini, S. (2004) Soil structure and the effect of management practices, *Soil and Tillage Research*, 79, 2, 131-143

Palmer, M. A., Bernhardt, E. S. Allan, J. D., Lake, P. S., Alexander, G., Brooks, S., Carr, J., Clayton, S., Dahm, C. N., Follstad Shah, J., Galat, D. L., Loss, S. G., Goodwin, P., Hart, D. D., Hassett, B., Jenkinson, R., Kondolf, G. M., Lave, R., Meyer, J. L., O'Donnell, T. K., Pagano, L., and Sudduth, E. (2005) Standards for ecologically successful river restoration. *Journal of Applied Ecology*, 42, 208–217

Palmer, M.A., Liermann, C.A.R., Nilsson, C. Flörke, M. J., Alcamo, J., Lake, S. and Bond, N. (2008) Climate change and the world's river basins: anticipating management options *Frontiers in Ecology and the Environment,* 6, 81–89

Pant, H. K. and Reddy, K.R. (2001) Phosphorus sorption characteristics of estuarine sediments under different redox conditions. *Journal of Environmental Quality,* 30, 1474-1479

Passmore, D.G. and Macklin, M.G. (1994) Provenance of fine-grained alluvium and late Holocene land-use change in the Tyne basin, Northern England. *Geomorphology*, 9, 127–142

Peart, M.R. (1993) Fingerprinting suspended sediment sources: an example from Hong Kong. In: Foster, I.D.L., Gurnell, A.M. and Webb, B.W. (eds.) *Sediment and Water Quality in River Catchments*, 179-186. Wiley, Chichester

Peart, M.R. and Walling, D.E. (1986) Fingerprinting sediment source: the example of a drainage basin in Devon, UK. In: Hadley, R.F. (ed.) *Drainage Basin Sediment Delivery*. IAHS Publication No. 159, 41-55

Peart, M.R. and Walling, D.E. (1988) Techniques for establishing suspended sediment sources in two drainage basins in Devon, UK: a comparative assessment. In: Bordas, M.P. & Walling, D.E. (eds.) *Sediment Budgets, IAHS Publication 174*, 269-279

Pennington, W., Cambray, R.S. and Fisher, E.M. (1973) Observations on lake sediments using fallout ^{137}Cs as a tracer. *Nature*, 242, 324-326

Petersen, L.W., Moldrup, P., Jacobsen O.H. and Rolston, D.E. (1996) Relations between specific surface area and soil physical and chemical properties, *Soil Science*, 161, 9–21

Petrou, E.C. and Pappis, C.P. (2009) Biofuels: A Survey on Pros and Cons. *Energy Fuels*, 23 2, 1055–1066

Petts, G.E., Heathcote, J. and Martin, D. (2002) *Urban Rivers: Our Inheritance and Future*, IWA Publishing/Environment Agency

Piegay, H., Hupp, C. R., Citterio, A., Dufour, S., Moulin, B., and Walling, D. E. (2008) Spatial and temporal variability in sedimentation rates associated with cutoff channel infill deposits: Ain River, France, *Water Resources Research*., 44, 18

Pignatello, J. J. and Xing, B. (1996) Mechanisms of slow sorption of organic chemicals to natural particles. *Environmental Science and Technology*, 30, 1, 1-11

Pimentel, D., Harvey, C., Resosudarmo, P., Sinclair, K., Kurz, D., McNair, M., Crist, S., Shpritz, L., Fitton, L., Saffouri, R. and Blair, R. (1995) Environmental and Economic Costs of Soil Erosion and Conservation Benefits. *Science,* 267, (5201), 1117-1123

Pinnacle Consulting Engineers Ltd (2006) *Engineering site appraisal for Tesco at South End, Wigton,* unpublished report

Piper, D. (1973) Origin of metalliferous sediments from the East Pacific Rise. Earth and Planetary Science Letters, 19, 75-82

Phillips, M. (2007) Catchment Sensitive Farming Officer. *Catchment Sensitive Farming issues in the River Rye catchment area.* Personal communication 12.11.2007

Planer-Friedrich, B., Becker, J., Brimer, B. and Merkel, B. J. (2008) Low-cost aerial photography for high-resolution mapping of hydrothermal areas in Yellowstone National Park. *International Journal of Remote Sensing*, 29, 6

Poff, N. L., Allan, J. D., Palmer, M. A., Hart, D. D., Richter, B. D., Arthington, A. H., Rogers, K. H., Meyer, J. L.and Stanford J. A. (2003) River flows and water wars: emerging science for environmental decision making. *Frontiers in Ecology and the Environment,* 1, 6, 298-306

Potter, C. (1997) Europe’s changing farmed landscapes. In: Pain, D.J. and Pienkowski, M.W. (eds) *Farming and Birds in Europe: The Common Agriculture Policy and its Implications for Bird Conservation.* Academic Press, London, UK, 25–42

Pretty, J. L., Harrison, S. S. C., Shepherd, D. J., Smith, C., Hildrew, A. G. and Hey, R. D. (2003) River rehabilitation and fish populations: assessing the benefit of instream structures. *Journal of Applied Ecology,* 40, 251–265

Price, E. (2003). *Lowland Grassland and Heathland Habitats*, Routledge, London

Prodromou, K.P. Pavlatou-Ve, A.S. (1998) Changes in soil pH due to the storage of soils. *Soil Use and Management,* 14, 3, 182-183

Przybylski, R. and Mag, T. (2002) Canola/rapeseed oil. In: Gunstone, F.D. (ed.) *Vegetable oils in food technology: composition, properties and uses*, Blackwell, Oxford, 98 -124

Pywell, R.F., Bullock, J.M,, Hopkins, A., Walker, K.J., Sparks, T.H., Burke, M.J.W. and Peel, S. (2002) Restoration of species-rich grassland on arable land: assessing the limiting processes using a multi-site experiment, *Journal of Applied Ecology* 39, 294–309

Quinton, J.N., Catt, J.A., (2004). The effects of minimal tillage and contour cultivation on surface runoff, soil loss and crop yields in the long-term Woburn Erosion Reference Experiment on sandy soil at Woburn, England. *Soil Use and Management*, 20, 343–349

Ramchunder, S.J., Brown, L.E. and Holden, J. (2009) Environmental effects of drainage, drain-blocking and prescribed vegetation burning in UK upland peatlands. *Progress in Physical Geography*, 33, 1, 49-79

Richards, C., Host, C.E and Arthur, J.W. (1993) Identification of predominant environmental factors structuring stream macroinvertebrate communities within a large agricultural catchment. *Freshwater Biology,* 29, 285-29.

Richter, R. D., Baumgartner, J. V., Wigington, R and Braun, D. P. (1997) How much water does a river need? *Freshwater Biology (Special Applied Issues Section)* 37, 231-249

Ries, J.B. and Marzolff, I. (1997) Identification of sediment sources by large-scale aerial photography taken from a monitoring blimp, *Physics and Chemistry of The Earth*, 22, 3-4, 295-302

Riley, M. and Harvey, D. (2005) Landscape Archaeology, Heritage and the Community in Devon: An Oral History Approach. *International Journal of Heritage Studies*, 11, 4, 269-288

Riley, M. and Harvey, D. (2007) Oral histories, farm practice and uncovering meaning in the countryside. *Social and Cultural Geography*, 8, 3, 391-415

Ritchie, J.C., McHenry, J.R. and Gill, A.C. (1973) Dating recent reservoir sediments, *Limnology and Oceanography*, 18, 254-263

Rhoads, D.C. and Germano, J.D. (1986) Interpreting long-term changes in benthic community structure: a new protocol *Hydrobiologia*, 142, 291-308

Robbins, J.A. (1978) Geochemistry and Geophysical application of radioactive lead. In Nriagu, J.O. (ed) *The Biochemistry of Lead in the Environment*. Elsevier, Amsterdam, 285-393

Robbins, J.A. and Edgington, D.N. (1975) Determination of recent sedimentation rates in Lake Michigan using Pb-2l0 and Cs-137. *Geochimica et Cosmochimica Acta*, 39, 285-304

Robinson, G.M. (1991) EC agricultural policy and the environment – Land use implications in the UK, *Land Use Policy*, 8, 2, 95-107

Robinson, M. and Armstrong, A. C. (1987) The extent of agricultural field drainage in England and Wales, 1971-80. *Transactions of the Institute of British Geographers, New Series*, 13, 1, 19-28

Robinson, D.A. and Blackman, J.D. (1990) Soil erosion and flooding: consequences on land use policy and agricultural practice on the South Downs, East Sussex, UK. *Land Use Policy*, 7, 41–52

Robinson, M. and Blyth, K. (1982) The effect of forestry drainage operations on upland sediment yields: A case study. *Earth Surface Processes and Landforms,* 7, 1, 85-90

Robinson, M., Boardman, J., Evans, R., Heppell, K.. Packman, J. And Leeks, G. (2000) Land Use Change. In: Acreman, M.C. (ed.) *The Hydrology of the UK*, Routledge, London, 30-54

Robinson, R.A. and Sutherland, W.J. (2002) Post-war changes in arable farming and biodiversity in Great Britain. *Journal of Applied Ecology*, 39, 157-176

Roddy, B.P. (2010) *The use of the sediment fingerprinting technique to quantify the different sediment sources entering the Whangapoua Estuary, North Island, in New Zealand.* Unpublished PhD Thesis, University of Waikato, New Zealand

Rodwell, J.S. (1998) *British Plant Communities Volume 3 - Grasslands and Montane Communities*. Cambridge University Press, Cambridge

Rosenzweig, C., Karoly, D., Vicarelli, M., Neofotis, P., Wu, Q., Casassa, G., Menzel, A., Root, T.L., Estrella, N. and Seguin, B. (2008) Attributing physical and biological impacts to anthropogenic climate change. *Nature*, 453, 353-357

Rowan, J.S. Goodwill P. and Franks, S.W. (2000) Uncertainty estimation in fingerprinting suspended sediment sources. In: I.D.L. Foster, (ed.) *Tracers in Geomorphology*, Wiley, Chichester. 279–290

Rowe, R.L., Street, N.R. and Taylor, G. (2009) Identifying potential environmental impacts of large-scale deployment of dedicated bioenergy crops in the UK. *Renewable and Sustainable Energy Reviews*, 13, 1, 271-290

Rubio, B., Nombela, M. and Vilas, F. (2000) Geochemistry of Major and Trace Elements in Sediments of the Ria de Vigo (NW Spain): an Assessment of Metal Pollution, *Marine Pollution Bulletin*, 40 (11), 968-980

Rumsby, B.T. and Macklin, M.G. (1994). Floodplain and channel response to recent abrupt climate change: the Tyne basin, Northern England. *Earth Surface Processes and Landforms*, 19, 499–515

Russell, M.A., Walling, D.E. and Hodgkinson, R.A. (2001) Suspended sediment sources in two small lowland agricultural catchments in the UK. *Journal of Hydrology*, 252, 1–24

Sanderson, D.C.W. and Scott, E.M. (1989) *Aerial radiometric survey in West Cumbria 1988: Project N611*. Ministry of Agriculture and Fisheries and Foods (MAFF), London.

Sapozhnikova, Y., Bawardi, O. and Schlenk, D. (2004) Pesticides and PCBs in sediments and fish from the Salton Sea, California, USA. *Chemosphere*, 55, 797–809

Schleiger, S.L. (2000) Use of an index of biotic integrity to detect effects of land uses on stream fish communities in wet-central Georgia, Transactions of the American Fisheries Society, 129, 1118–1133

Schmidhuber, J. (2006) *Impact of an increased biomass use on agricultural markets, prices and food security: A longer-term perspective*. International symposium of Notre Europe, Paris

Schorer, M. and Eisele M. (1997) Accumulation of inorganic and organic pollutants by biofilms in the aquatic environment. *Water Air and Soil Pollution*, 99, 651-9

Schulp, C.J.A., Nabuurs, G.-J. and Verburg, P.H. (2008) Future carbon sequestration in Europe – effects of land use change. *Agriculture, Ecosystems and Environment*, 127, 251–326

Schutz, L. and Rahn, K. (1982) Trace-element concentrations in erodible soils. *Atmospheric Environment*, 16, 1, 171-176

Scoullos, M. J. & Pavlidou, A.S. (2001) Metal Speciation Studies In A Brackish / Marine Interface System. *Global Nest: The International Journal*, 2, 3: 255-264

Seaman, P. (2008) Mill owner. *Recent land use history around Bintree Mill, Norfolk*. [*Conversation*] Personal Communication, 24.5.2008

Self, P. and Storing, H.J. (1962) *The State and the Farmer.* London: Allen and Unwin

Shand, C.A., Cheshire, M.V., Smith, S., Vidal, M. and Rauret, G. (1994) Distribution of radiocaesium in organic soils, *Journal of Environmental Radioactivity*, 23, 3, 285-302

Sharma, K. D. and Singh, S. (1995) Satellite remote sensing for soil erosion modelling using the ANSWERS model, *Hydrological Sciences*, 40, 2, 259-272

Sheail, J. (1973) Changes in the Use and Management of Farmland in England and Wales, 1915-19. *Transactions of the Institute of British Geographers*, 60, 17-32

Sheail, J. (1976) Land improvement and reclamation: the experiences of the First World War in England and Wales. *Agricultural History Review,* 24, 110–125

Sherrington, C., Bartley, J. and Moran, D. (2008) Farm-level constraints on the domestic supply of perennial energy crops in the UK, *Energy Policy*, 36, 2504–2512

Short, B. (2007) War in the Fields and Villages: The County War Agricultural Committees in England, 1939-45. *Rural History*, 18, 2, 217-244

Silgram, M., Jackson, D., Bailey, A., Quinton, J. and Stevens, C. (2010) Hillslope scale surface runoff, sediment and nutrient losses associated with tramline wheelings. *Earth Surface Processes and Landforms*, 35, 699–706

Slattery, M.C., Burt, T.P. and Walden, J. (1995) The application of mineral magnetic measurements to quantify within-storm variations in suspended sediment sources. In: *Tracer Technologies for Hydrological Systems (Proceedings of a Boulder Symposium). IAHS Publication 229*, 143–151

Slob, A.F.L., Eenhoorn, J., Ellen, G.J., Gomez, C.M., Kind, J. and vander Vlies, J. (2008) Costs and Benefits of Sediment Management. In: Owens, P. (Ed) *Sustainable Management of Sediment Resources – Sediment Management at the River Basin Scale*. Elsevier, Amsterdam, 175-197

Small, I.F., Rowan, J.S., Franks, S.W., Wyatt, A. and Duck, R.W. (2004) Bayesian sediment fingerprinting provides a robust tool for environmental forensic geosciences applications. *Geological Society, London, Special Publications*, 232, 207-213

Small, I.F., Rowan, J.S. and Franks, S.W. (2002) Quantitative sediment fingerprinting using a Bayesian uncertainty estimation framework. In *The Structure, Function and Management Implications of Fluvial Sedimentary Systems*, Dyer, F.J., Thoms, M.C. and Olley, J.M. (eds). *Publication No.* 276, International Association of Hydrological Sciences: Wallingford, 443-450

Smith, V.H. (2009) Eutrophication In: Likens, G.E. (ed) *Encyclopaedia of Inland Waters,* Academic Press, Oxford, 61-73

Smith, J.T., Appleby, P.G., Hilton, J. and Richardson, N. (1997) Inventories and Fluxes of ^{210}Pb and ^{241}Am determined from the soils of three small catchments in Cumbria, UK. *Journal of Environmental Radioactivity*, 37, 2, 127-142

Smol, J. P. (2002) *Pollution of Lakes and Rivers: A Paleoenvironmental Perspective*, Arnold, London

Solway Coast AONB (2009) [WWW] Solway Coast Area of Outstanding Natural Beauty http://solwaycoastaonb.org.uk/ Accessed: 17.9.2009

South West Observatory (2010) [WWW] Environment – Fresh water fish http://www.swenvo.org.uk/themes/biodiversity/freshwater-fish/ Accessed: 22.08.2010

Sparks, D. L. (2003) *Environmental Soil Chemistry (Second Edition)* Academic Press, London

Speirs, R.B. and Frost, C.A. (1985). The increasing incidence of accelerated erosion on arable land in the east of Scotland. *Research and Development in Agriculture*, 2, 161–167

Stamp, L.D. (1940) Fertility, Productivity and Classification of Land in Britain. *The Geographical Journal*, 96, 6, 389-406

Staniszewski, R., Szoszkiewicz, K., Zbierska, J., Lesny, J., Jusik, S. and Clarke, R. T. (2006) Assessment of sources of uncertainty in macrophyte surveys and the consequences for river classification. *Hydrobiologia*, 566, 235-246

Steiger, J., Gurnell, A. M., and Goodson, J. M. (2003) Quantifying and characterizing contemporary riparian sedimentation, *River Research and Applications*, 19, 335–352

Stevenson, M.J., Ward, L.K. and Pywell, R,F, (1997) Recreating semi-natural communities: vacuum harvesting and hand collection of seed on calcareous grassland. *Restoration Ecology*, 5, 66 – 76

Steyerberg, E.W., Eijkemans, M.J.C. and Habbema, J.D.F. (1999) Stepwise Selection in Small Data Sets: A Simulation Study of Bias in Logistic Regression Analysis. *Journal of Clinical Epidemiology*, 52, 10, 935-942

Stone, M. and Droppo, I.G. (1996) Distribution of lead, copper, and zinc in size-fractionated river bed sediment in two agricultural catchments of Southern Ontario, Canada. *Environmental Pollution*, 93, 3, 353-362

Stone, P.M. and Walling, D.E., (1996) The particle size selectivity of sediment mobilization from Devon hillslopes. In: Anderson, M.G. and Brooks, S.M., (eds) (1996) *Advances in Hillslope Hydrology*, Wiley, Chichester, 507–527

Stott, A.P. (1986) Sediment tracing in a reservoir catchment system using a magnetic mixing model. *Physics of the Earth and Planetary Interiors*, 42, 105-112

Stott, T. (1989) Upland afforestation, does it increase erosion and sedimentation. *Geography Review*, March 1989, 30-32

Stott T. (1999) Stream bank and forest ditch erosion: preliminary response to timber harvesting in Mid-Wales. In: *Fluvial Processes and Environmental Change*. Brown, G.A. and Quine, T.A. (eds). Wiley: Chichester; 47–70

Stott, T. and Mount, N. (2004) Plantation forestry impacts on sediment yields and downstream channel dynamics in the UK: a review, *Progress in Physical Geography*, 28, 2, 197–240

Stutter, M.I., Langan, S.J., Lumsdon, D.G. and Clark, L.M. (2009) Multi-element signatures of stream sediments and sources under moderate to low flow conditions. *Applied Geochemistry*, 24, 800-809

Sullivan, A., Ternan, J.L. and Williams, A.G. (2004) Land use change and hydrological response in the Camel catchment, Cornwall. *Applied Geography*, 24, 119–137

Szoszkiewicz, K., Buffagni, A., Davy-Bowker, J., Lesny, J., Chojnicki, B. H., Zbierska, J., Staniszewski, R. and Zgola, T. (2006) Occurance and variability of River Habiat Survey features across Europe and the consequences for data collection and evaluation. *Hydrobiologia*, 566, 267-280

Tanizaki, Y., Shimokawa, T and Yamazaki, M (1992) Physico-chemical speciation of trace elements in urban streams by size fractionation. *Water Research*, 26, 55-63

Ter Laak, T. L., Agbo, S. O., Barendregt, A. and Hermens, J. L. M. (2006) Freely dissolved concentrations of PAHs in soil pore water: Measurements via solid-phase extraction and consequences for soil tests. *Environmental Science and Technology, 40*, 1307–1313

Tessier, A., Campbell, P.G.C. and Bisson, M. (1982) Particulate trace metal speciation in stream sediments and relationships with grain size: implications for geochemical exploration. *Journal of Geochemical Exploration*, 16, 77-104

The Countryside Museum (2010) [WWW] The Countryside Museum: Crop Rotation. http://www.fellpony.f9.co.uk/country/seedtime/stitch.htm Accessed: 2.2.2010

The Wye and Usk Foundation (2006) [WWW] The Wye and Usk Foundation - Problems on our rivers http://www.wyeuskfoundation.org/problems/index.php Accessed: 07.06.2010

Thorpe T. & Lloyd B. (1999) The macroinvertebrate fauna of St. Lucia elucidated by canonical correspondence analysis. *Hydrobiologia*, 400, 195–203

Tricker, P.J., Peccgiari, M., Bunn, S.M., Vaccari, F.P., Peresotti, A., Miglietta, F. and Taylor, G. (2009) Water use of a bioenergy plantation increases in a future high CO2 world. *Biomass and Bioenergy*, 33, 2, 200-208

Trimble, S and Mendal, A.C. (1995) The cow as a geomorphic agent — A critical review. *Geomorphology*, 13, 1-4, 233-253

Troeh, F.R. and Thompson, L.M. (2005) *Soils and soil fertility (6th Edition)*. Blackwell Publishing, Oxford

Tscharntke, T., Klein, A. M., Kruess, A., Steffan-Dewenter, I. and Thies, C. (2005) Landscape perspectives on agricultural intensification and biodiversity – ecosystem service management. *Ecology Letters*, 8, 857–874

Tucker, G., Hart, K., Baldock, D. Farmer, M. and Hegarty, J. (2010) Recent and possible EU agricultural policy developments and their potential implications for farmland birds. Agricultural policy developments. *BOU Proceedings – Lowland Farmland Birds III*. 1-21

UKTAG (2006) [WWW] United Kingdom Technical Advisory Group (UKTAG) Water Framework Directive Site
http://www.wfduk.org/tag_guidance/Article%20_11/POMEnvStds/WP11a-19-10-05
Accessed: 03.05.2010

UKTAG (2008) UK Environmental Standards and Conditions (Phase 1) Final Report
http://www.wfduk.org/UK_Environmental_Standards/ES_Phase1_final_report/
Accessed: 03.05.2010

Vaithiyanthan, P., Ramathan, A.L. and Subramanian, V. (1993) Transport and distribution of heavy metals in Cauvery River. *Air and Soil Pollution*, 71, 13-28

Vandaele, K. Poesen, J. Govers, G. and van Wesemael B. (1996) Geomorphic threshold conditions for ephemeral gully incision. *Geomorphology*, 16, 2, 161–173

Vickery, J.A., Tallowin, J.R., Feber, R.E., Asteraki, E. J., Atkinson, P.W., Fuller, R.J. and Brown, V.K. (2001) The management of lowland neutral grasslands in Britain: effects of agricultural practices on birds and their food resources. *Journal of Applied Ecology*, 38, 3, 647-664

Vollmer, S. and Goelz, E. (2006) Sediment monitoring and sediment management in the Rhine River. *Sediment Dynamics and the Hydmmorphology of Fluvial Systems. (Proceedings of a symposium held in Dundee, UK, July 2006).* IAHS Publication No. 306.

Von Braun, J. (2009) The food crisis isn't over. *Nature*, 456, 701

Vought, L.B.M., Pinay, G., Fugslang, A. and Ruffinoni, C. (1995) Structure and function of buffer strips from a water quality perspective in agricultural landscapes. *Landscape and Urban Planning*, 31, 323-331

Wagner, K., Neuwirth, J. and Janetschek, H. (2009) [WWW] Flood risk – Prevention and Impact on Agricultural Lands. The 83rd Annual Conference of the Agricultural Economics Society Dublin 30th March to 1st April 2009 http://www.aesi.ie/aes2009/s3d.pdf Accessed: 10.06.2010

Walden, J., Slattery, M.C. and Burt, T.P. (1997) Use of mineral magnetic measurements to fingerprint suspended sediment sources: approaches and techniques for data analysis. *Journal of Hydrology*, 202, 353-372

Wall, G.J. and Wilding L.P. (1976) Mineralogy and related parameters of fluvial suspended sediments in northwestern Ohio. *Journal of Environmental Quality,* 5, 168–173

Wallbrink, P.J. and Murray, A.S. (1990) The use of fallout radionuclides as indicators of surface and subsoils. Paper presented at the Workshop on Environmental Radioactivity and Radionuclide Measurement, Adelaide

Wallbrink, P.J., Murray, A.S. and Olley, J.M. (1998) Determining sources and transit times of suspended sediment in the Murrumbidgee River, New South Wales, Australia, using fallout ^{137}Cs and ^{210}Pb. *Water Resources Research*, 34, 879-887

Walling, D.E. (1988) Erosion and sediment yield research - Some recent perspectives, *Journal of Hydrology*, 100, 1-3, 113-141

Walling, D.E. (1999) Linking land use erosion and sediment loads in river basins. *Hydrobiologia*, 410, 223-240

Walling, D.E. (1983) The sediment delivery problem. *Journal of Hydrology*, 65, 209–237

Walling, D.E. (2004) Using environmental radionuclides to trace sediment mobilization and delivery in river basins as an aid to catchment management. *Proceedings of the Ninth International Symposium on River Sedimentation, 21, Yichang, China*, 121-135

Walling, D.E. (2005) Tracing suspended sediment sources in catchment and river systems. *Science of the Total Environment,* 344, 1-3, 159-184

Walling, D.E. and Amos, C.M. (1999) Source, storage and mobilization of fine sediment in a chalk stream system. *Hydrological Processes,* 13, 323–340

Walling, D.E. and Collins, A.L. (2000) *An Integrated Assessment of Catchment Sediment Budgets: A Technical Manual* – Produced within the framework of UK Department for International Development Research Project R6868. School of Geography and Archaeology, University of Exeter, Exeter

Walling, D.E. and Collins, A. L. (2008). Tracing suspended sediment and particulate phosphorus sources in catchments. *Journal of Hydrol*ogy, 350, 3-4, 274-289

Walling, D.E., Collins, A.L. and McMellin, G.K. (2003) A reconnaissance survey of the source of interstitial fine sediment recovered from salmonid spawning gravels in England and Wales. *Hydrobiologia*, 497, 91-108

Walling, D.E., Collins, A.L. and Stroud, R. (2008) Tracing suspended sediments and particulate phosphorus sources in catchments. *Journal of Hydrology*, 350, 274–289

Walling, D.E., Fang, D., Nicholas, A.P. and Sweet, R.J. (2006) River flood plains as carbon sinks. *Sediment Dynamics and the Hydromorphology of Fluvial Systems (Proceedings of a symposium held in Dundee, UK, July 2006*) IAHS Publication 306, 460-470

Walling, D.E. and He. Q. (1992) Interpretation of cesium-137 profile in lacustrine and other sediments - The role of catchment derived inputs. *Hydrobiologia*, 235/236, 219-230

Walling, D.E. and He. Q (1993) Use of Cesium-137 as a tracer in the study of rates and patterns of floodplain sedimentation. *Tracers in Hydrology (Proceedings of the Yokohama Symposium, July 1993) IAHS Publication No. 215*, 174-187

Walling, D.E. and He. Q (1994) Rates of overbank sedimentation on the flood plains of several British rivers during the past 100 years. *Variability in Stream Erosion and Sediment* Transport *(Proceedings of the Canberra Symposium IAHS Publication No. 224*, 203-212

Walling, D.E. and He, Q. (1997) Use of fallout 137Cs in investigations of overbank sediment deposition on river floodplains. *Catena,* 29, 263–282

Walling, D. E. and He, Q. (1998) The spatial variability of overbank sedimentation on river floodplains, *Geomorphology*, 24, 209–223

Walling, D.E., He, Q. and Quine, T.A. (1995) Use of caesium-137 and lead-210 as tracers in soil erosion investigations. *IAHS Publication No. 229*, 163-172

Walling, D.E. and Morehead, P.W. (1989) The particle size characteristics of fluvial suspended sediments: an overview. *Hydrobiologia*, 176/177, 125-149

Walling, D.E., Owens, P.N and Leeks, G.J.L. (1998) The characteristics of overbank deposits associated with a major flood event in the catchment of the River Ouse, Yorkshire, UK. *Catena,* 32, 309-331

Walling, D.E., Owens, P.N., Leeks, G.J.L. (1999) Fingerprinting suspended sediment sources in the catchment of the River Ouse, Yorkshire, UK. *Hydrological Processes*, 12, 955–975

Walling, D.E., Peart, M.R., Oldfield, F. and Thompson, R. (1979) Suspended sediment sources identified by magnetic measurements. *Nature,* 281, 110–113

Walling, D.E. and Quine, T.A. (1993) *Use of Caesium-137 as a Tracer of Erosion and Sedimentation: Handbook for the Application of the Caesium-137 technique.* UK Overseas Development Administration Research Scheme R4579. Department of Geography, University of Exeter, Exeter, UK

Walling, D.E., Rowan, J.S. and Bradley, S.B. (1989) Sediment-associated transport and redistribution of Chernobyl fallout radionuclides. *Sediment and the environment (Proceedings of the Baltimore Symposium, May, 1989) IAHS publication number 184*, 37-45

Walling, D.E. and Webb, B. (1987) Suspended Load in Gravel-bed Rivers: UK experience In: Walling, D.E. and Webb, B. (eds.) *Sediment Transfer in Gravel-Bed Rivers*. John Wiley & Sons New York. 691-723,

Walling, D.E. and Woodward, J.C. (1992) Use of radiometric fingerprints to derive information on suspended sediment sources. In: Bogen, J., Walling, D.E. and Day, T. (eds.) *Erosion and Sediment Transport Monitoring Programmes in River Basins*. IAHS Publication No. 210, 153-164

Walling, D.E., Woodward, J.C. and Nicholas, A.P. (1993) A multi-parameter approach to fingerprinting suspended sediment sources. In: Peters, N.E. Hoehn, E. Leibundgut, Ch., Tase, N. and Walling, D.E. (eds) *Tracers in Hydrology*, IAHS Publication No. 215, 329–337

Walling, D.E. and Woodward, J.C. (1995) Tracing sources of suspended sediment in river basins: A case study of the River Culm, Devon, UK. *Marine and Freshwater Research* 46, 327–336

Walters, D.M., Leigh, D.S. and Bearden, A.B. (2003) Urbanization, sedimentation and the homogenization of fish assemblages in the Etyowah River Basin, USA, *Hydrobiologia*, 494, 5–10

Wang, F and Chen, J. (2000) Relation of sediment characteristics to trace metal concentrations: a statistical study. *Water Research*, 34, 2, 694-698

Warren, N., Allan, I.J., Carter, J.E., House, W.A. and Parker, A. (2003) Pesticides and other micro-organic contaminants in freshwater sedimentary environments – a review, *Applied Geochemistry*, 18, 159–194

Wasson, R. (1987) Detection and measurment of land degradation processess. In: Chisholm, A.and.Dumsday, R. (eds.) *Land Degradation: Problems and Policies*. 49–69. Cambridge University Press. London

Weber, C.I. and Fradkin, L. (eds.) *Chemical and Biological Characterization of Sludges, Sediments, Dredged Spoils and Drilling Muds, ASTM STP 976.* American Society for Testing and Materials, Philadelphia, PA, 114-128

Weber, W.J. Jr., McGinley, P. M. and Katd, L. E. (1992) A Distributed Reactivity Model for Sorption by Soils and Sediments. 1. Conceptual Basis and Equilibrium Assessments. *Environmental Science and Technology*, 26, 1955-1962

Wentzal, K. (2002) Determination of the overall soil erosion potential in the Nsikazi District (Mpumalanga Province, South Africa) using remote sensing and GIS. *Canadian Journal of Remote Sensing*, 28, 2, 322–327

Wheaton, J. M., Darby, S. E., Sear, D. A. and Milne, J. A. (2006) Does scientific conjecture accurately describe restoration practise? Insight from an international river restoration survey. *Area*, 38**,** 2, 128-142

Whitehead, P.G., Wilby, R.L., Battarbee, R.W., Kernan, M., and Wade, A.J. (2009) A review of the potential impacts of climate change on surface water quality. *Hydrological Sciences Journal*, 54, 101-123

Whiting, P.J., Matisoff, G., Fornes, W. and Soster, F.M. (2005) Suspended sediment sources and transport distances in the Yellowstone River basin. *Geological Society of America Bulletin*, 117, 3/4, 515-529

Whitney, P.R. (1975) Relationship of manganese iron oxides and associated heavy metals to grain size in stream sediments. *Journal of Geochemical Exploration*, 4, 251-263

Whittingham, M. J., Stephens, P. A., Bradbury, R. B. and Freckleton, R. P. (2006), Why do we still use stepwise modelling in ecology and behaviour*?. Journal of Animal Ecology*, 75, 1182–1189

Wilby, R.L. and Dessai, S. (2010) Robust adaptation to climate change. *Weather*, 65, 180–185

Williams, A.G., Audsley, E. & Sandars, D. L. (2006). *Determining the environmental burdens and resource use in the production of agricultural and horticultural commodities.* Main Report for Defra Research Project IS0205

Williams, J.R. (1975) Sediment routing from agricultural watersheds. *Water Resources Bulletin*, 11, 965-974

Winter, M. and Gaskell, P. (1998) The Agenda 2000 debate and CAP reform in Great Britain: is the environment being sidelined? *Land Use Policy*, 15, 217–231

Winter, M., Gaskell, P. and Short, C. (1998) Upland landscapes in Britain and the 1992 CAP reforms. *Landscape Research*, *23*, 3, 273-288

Winter, M. and Lobley, M., (Eds), (2009) *What is Land for? The Food, Fuel and Climate Change Debate*. Earthscan, London

Withers, P.J.A., Hodgkinson, R. A., Bates, A. and Withers, C. M. (2006) Some effects of tramlines on surface runoff, sediment and phosphorus mobilization on an erosion-prone soil. *Soil Use and Management*, 22, 245-255

Wolman, M.G. (1977) Changing needs and opportunities in the sediment field. *Water Resources Research*, 13, 50-54

Wynne, B. (1989) Sheep farming after Chernobyl, a case study in communicating scientific information. *Environment*, 31, 2, 10-15

Yaru, B.T. and Buckney, R. T. (2000) Metal interactions in contaminated freshwater sediments from the fly river floodplain, Papua New Guinea. *International Journal of Environmental Studies*, 57, 3, 305-331

Young, R.A., Onstad, C.A., Bosch, D.D. and Anderson, W.P. (1989) AGMPS: A nonpoint-source pollution model for evaluating agricultural watersheds. *Journal of Soil and Water Conservation*, 44, 2, 168-173

Yu, L. And Oldfield, F. (1989) A multi-variate mixing model for identifying sediment source from magnetic measurements. *Quaternary Research*, 32, 168-181

Zapata, F. (Ed.) (2002) *Handbook for the Assessment of Soil Erosion and Sedimentation Using Environmental Radionuclides.* Kluwer, Dordrecht.

Zheltonozhsky, V., Mück, K. and Bondarkov, M (2001) Classification of hot particles from the Chernobyl accident and nuclear weapons detonations by non-destructive methods. *Journal of Environmental Radioactivity* 57, 151-166

Zolitschka, B. (1998) A 14,000 year sediment yield record from western Germany based on annually laminated lake sediments. *Geomorphology,* 22, 1–17