EXPLORING FINE SEDIMENT DYNAMICS AND THE UNCERTAINTIES ASSOCIATED WITH SEDIMENT FINGERPRINTING IN THE NENE RIVER BASIN, UK

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Abstract

To comply with the European Union Water Framework Directive (2000), National Governments are required to achieve good chemical and ecological status of freshwater bodies. Fine sediment has been shown to be a major cause of the degradation of lakes and rivers, and as a result research in geomorphology has been directed towards the understanding of fine sediment dynamics. It was identified by a review of published literature that at present a paucity of information on sediment dynamics existed for the East Midlands, UK.

The use of tracers within a sediment fingerprinting framework has recently become a heavily used technique to investigate the sources of fine sediment pressures. However, uncertainties associated with tracer behaviour have been cited as major potential limitations to sediment fingerprinting methodologies. At present few studies have quantified the uncertainties associated with tracer use, or the exact reasons why different tracers are producing different sediment provenance results.

This thesis had two aims based on these gaps in published literature. First, to assess the impact of sediment sampling methodology, tracer selection, particle size corrections and organic enrichment corrections on a fine sediment fingerprinting study. Secondly, to develop a partial sediment budget for the Upper Nene river basin and its major tributaries. The results of this thesis were presented in two parts. The first part investigated Aim 1 when fingerprinting; historically deposited sediment, suspended sediment and recently deposited sediment. The second part investigated Aim 2 by constructing a fine sediment budget for the Nene river basin, consisting of; sediment yield, sediment provenance, floodplain sediment accumulation and channel bed sediment storage.

A mean difference of 24.1% between the predicted contributions of sediment originating from channel banks was found when using nine different tracer groups to fingerprint the river sediment samples. When fingerprinting contributions from urban street dusts mean differences between tracer group predictions were lower, at between 8% and 11%. There was little indication that organic matter content and / or particle size caused differences between tracer group predictions. Within-source variability in tracer concentrations, and small contrasts between the tracer concentrations of the sediment source groups, were identified as probable causes of inherent uncertainty present in the fingerprinting analysis. It was determined that the ratio of the percentage difference between median tracer

concentrations in the source groups and the average within-source tracer concentration coefficient of variation could indicate the likely uncertainty in model predictions prior to tracer use.

When fingerprinting historically deposited sediment, a reservoir core was fingerprinted with the least uncertainty, with tracer group provenance predictions ~28% apart and with consistent down-core trends. When fingerprinting an on-line lake core and four floodplain cores, differences between tracer group predictions were as large as 100%; the down-core trends in changing sediment provenance were also different. The differences between tracer group predictions could be attributed to the organic matter content and particle size of the sediment. There was also evidence of the in-growth of bacterially derived magnetite and chemical dissolution affecting the preservation of tracer signatures.

Despite the prior indications that organic matter and particle size were causing tracer non-conservatism in historical sediment cores, data corrections were found to often be ineffective at reducing the differences between tracer group predictions. The corrections were found to either have no effect on, or increase the mean differences between, tracer group predictions when fingerprinting river sediment.

The sediment budget identified that the annual sediment yield of 13 - 19 t km^{-2} yr^{-1} for the Nene is low in comparison to other UK catchments. Channel banks were found to be the dominant sediment source in the Nene, typically contributing between 60% and 100% of the sediment. Rates of sediment accumulation on the Nene's floodplain was found to be highly variable (920– 7,200 t km^{-2} yr^{-1}); the presence of flood defences were likely to be a cause of this variability, and have caused a reduction in the accumulation rate since 1963. It was found that large quantities of sediment accumulated on channel beds during periods of low flows (~ 28% of the annual sediment yield), which was flushed from the bed by a series of flood events (leaving <1% of the annual sediment yield in temporary storage).

An original contribution to research was made by quantifying the uncertainties associated with tracer use in a fine sediment fingerprinting investigation, as well as identifying the probable causes of the observed uncertainty. The fine sediment dynamics of the Nene basin were also investigated for the first time, and it was identified that the high contributions from channel banks in the Nene were highly a-typical for UK catchments.

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Table of Contents

1. STUDY CONTEXT ... 16

1.1. INTRODUCTION ... 16
1.2. RESEARCH RATIONALE ... 16
1.2.1. A need for information on fine sediment dynamics in the UK ... 16
1.2.2. Sediment fingerprinting ... 18
1.3. AIMS AND OBJECTIVES ... 20
1.4. FORMAT OF THE PROJECT ... 21

2. SEDIMENT FINGERPRINTING ... 24

2.1. INTRODUCTION ... 24
2.2. THE DEVELOPMENT OF SEDIMENT FINGERPRINTING ... 24
2.3. TRACERS ... 27
2.3.1. Mineral magnetic signatures ... 28
2.3.2. Radionuclide activities ... 31
2.3.3. Geochemical tracers ... 33
2.4. TRACER CONSERVATISM ... 33
2.4.1. Changes in particle size distribution ... 34
2.4.2. Enrichment or depletion of organic material ... 36
2.4.3. Chemical transformations ... 37
2.4.4. Post-depositional alterations ... 39
2.5. CORRECTIONS TO ACCOUNT FOR DIFFERENCES IN PARTICLE SIZE AND ORGANIC ENRICHMENT ... 40
2.5.1. Organic enrichment corrections ... 40
2.5.2. Particle size corrections ... 40

3. FINE SEDIMENT DYNAMICS IN RIVER CATCHMENTS ... 42

3.1. THE NEED TO INVESTIGATE FINE SEDIMENT ... 42
3.2. SEDIMENT BUDGETS ... 42
3.3. INPUTS FROM SEDIMENT SOURCES ... 43
3.3.1. Connectivity and sediment delivery ... 45
3.3.2. Cultivated Land ... 47
3.3.3. Pasture ... 49
3.3.4. Channel banks ... 50
3.3.5. Urban street dusts ... 51
3.4. SEDIMENT IN THE FLUVIAL SYSTEM ... 53
3.4.1. Suspended sediment yield ... 53
3.4.2. Floodplain sedimentation ... 54
3.4.3. Channel beds ... 57

4. FIELD SAMPLING METHODOLOGY ... 59

4.1. INTRODUCTION ... 59
4.2. STUDY CATCHMENT ... 61
4.2.1. Catchment description ... 61
4.2.2. Observed erosion and sediment delivery ... 65
4.3. PALAEOLIMNOLOGICAL RECONSTRUCTION ... 68
4.3.1. Sediment Yield ... 68
4.3.2. Historical sediment in a semi-cut off floodplain lake ... 71
4.3.3. Historical floodplain deposition ... 71
4.4. CONTEMPORARY MONITORING ... 72
4.4.1. Stage and turbidity derived estimates of sediment yield ... 74
4.4.2. Contemporary suspended sediment sampling ... 77
4.4.3. Contemporary overbank sediment deposition ... 79
4.4.4. Channel bed sediment storage ... 79
4.5. SEDIMENT SOURCE SAMPLING ... 81
4.6. SUMMARY ... 83

5. LABORATORY AND SEDIMENT FINGERPRINTING METHODOLOGY ... 84

5.1. INTRODUCTION 84
5.2. SAMPLE PREPARATION....84
5.3. PARTICLE SIZE DISTRIBUTION AND ORGANIC MATTER CONTENT 84
5.3.1. Particle size distribution....84
5.3.2. Organic matter 86
5.4. ANALYSIS OF TRACERS 87
5.4.1. Mineral magnetic signatures....87
5.4.2. Radionuclides....89
5.4.3. Geochemistry 91
5.5. SEDIMENT FINGERPRINTING METHODOLOGY 96
5.5.1. Allocation of source samples 99
5.5.2. Mass conservation test and statistical procedure 100
5.5.3. Un-mixing modelling....102

6. SEDIMENT FINGERPRINTING HISTORICALLY DEPOSITED SEDIMENT 104

6.1. INTRODUCTION 104
6.2. SEDIMENT TRACER CONCENTRATIONS CHRONOLOGY, ORGANIC MATTER CONTENT AND PARTICLE SIZE DISTRIBUTION. ..105
6.3. STATISTICAL DETERMINATION OF COMPOSITE FINGERPRINTS 107
6.4. QUANTIFYING DIFFERENCES BETWEEN THE SEDIMENT PROVENANCE PREDICTIONS OF DIFFERENT TRACER GROUPS 114
6.5. THE EFFECTS OF CHANGES TO THE SEDIMENT ORGANIC CONTENT, PARTICLE SIZE DISTRIBUTION AND CHEMICAL ALTERATIONS OF SEDIMENT ON THE TRACER GROUP PROVENANCE PREDICTIONS. 121
6.5.1. The organic enrichment of sediment 122
6.5.2. Changes to sediment particle size 123
6.5.3. Alterations to mineral magnetic signatures 125
6.6. THE EFFECTIVENESS OF SIMPLE ORGANIC ENRICHMENT AND PARTICLE SIZE CORRECTIONS 133

7. FINGERPRINTING SUSPENDED AND RECENTLY DEPOSITED OVERBANK AND CHANNEL BED SEDIMENT.143

7.1. INTRODUCTION 143
7.2. THE DIFFERENCES BETWEEN TRACER GROUP PROVENANCE PREDICTIONS 144
7.2.1. Mass conservation test 144
7.2.2. Kruskal-Wallace H test....146
7.2.3. Discriminant analysis 148
7.2.4. Goodness of fit....150
7.2.5. Sediment provenance predictions....153
Percentage differences between tracer group provenance predictions....154
7.2.6. Trends in monthly sediment provenance....157
7.3. THE EFFECTS OF CHANGES TO THE SEDIMENT ORGANIC MATTER CONTENT, PARTICLE SIZE DISTRIBUTION AND WITHIN-SOURCE VARIABILITY ON THE DIFFERENCES BETWEEN TRACER GROUP FINGERPRINTING PREDICTIONS. 165
7.3.1. Changes to the organic content and particle size of the sediment....165
7.3.2. The potential uncertainties associated with catchment and tracer concentration heterogeneity169
7.4. CORRECTIONS FOR ORGANIC CONTENT AND PARTICLE SIZE DISTRIBUTION 188
7.4.1. Statisitcal composite fingerprint determination....189
7.4.2. The differences between corrected and uncorrected tracer group provenance predictions 197

8. FINE SEDIMENT DYNAMICS IN THE NENE RIVER BASIN. 201

8.1. INTRODUCTION 201
8.2. SEDIMENT YIELD 201
8.2.1. Palaeolimnological reconstruction 201
8.2.2. Sediment yield determined from turbidity and stage measurements 204
8.3. FLOODPLAIN SEDIMENT ACCUMULATION 208
8.4. CHANNEL BED SEDIMENT STORAGE....210
8.5. SEDIMENT PROVENANCE 215
8.5.1. A sediment budget for the Nene river basin 225

9. CONCLUSIONS AND EVALUATION 227

9.1. CHAPTER OUTLINE 227
9.2. KEY FINDINGS 227
9.2.1. Aim 1: Fingerprinting the sources of fine sediment 227
9.4.2. Aim 2: Fine sediment dynamics in the Nene river basin 236
9.3. STUDY EVALUATION 240
9.3.1. Research design 240
9.3.2. Scaling and representativeness 243

9.3.3. The importance of independent validation of field based results......246
9.4. REMAINING GAPS IN RESEARCH AND THE NEED FOR FUTURE RESEARCH......247
9.4.1. Aim 1: Fingerprinting the sources of fine sediment......247
9.4.2. Aim 2: Fine sediment dynamics......251
9.5. CLOSING STATEMENT......253
10. REFERENCES......256

List of Figures

Figure 1-1: The locations of published UK Sediment yield data derived from high and medium quality data (reproduced from, Walling *et al*., 2007). 17

Figure 1-2: Catchments where information about sediment provenance has been obtained via sediment fingerprinting (reproduced from, Walling *et al*., 2007). 17

Figure 1-3: The structure of this thesis. 21

Figure 1-4: The Partial sediment budget outline, sediment sources are highlighted in brown and sinks are in green. 22

Figure 2-1: The frequency of tracer groups use at varying temporal and spatial scales (reproduced from D'Haen *et al*., (2012)). 28

Figure 2-2: The vertical distribution of ^{137}Cs and unsupported ^{210}Pb in soil profiles in the Dart catchment UK (Reproduced from Walling and Woodward, 1992). 32

Figure 2-3: A simplified diagram of the processes potentially affecting tracer conservatism on the journey of sediment from source to sink, summarising the major sources of tracer non-conservatism highlighted in a review by Koiter et al., (2013). 34

Figure 2-4: Distribution of total pools of potentially toxic elements in soils — the size of the different fractions and the most relevant soil processes vary according to the element of interest and environmental conditions (reproduced from Rodrigues *et al*., (2010)). 37

Figure 3-1: Frequency distributions of the percentage contributions from surface sources and subsurface sources in UK catchments, reproduced from Walling *et al.,* (2007). 45

Figure 3-2: Rill erosion originating from a spring at the ironstone – mudstone lithology boundary in the Nene basin close to Moulton, Northamptonshire, UK. 48

Figure 3-3: Poaching along the river Nene close to Cogenhoe, Northamptonshire, UK (photograph taken 19/07/2012). 50

Figure 4-1: Elevation and slope of the terrain in the Nene basin. 62

Figure 4-2: The Lithology of the Nene basin (British Geological Survey, 2011). 63

Figure 4-3: Land Cover in the Nene basin in 1930s and 2007 (Stamp, 1932; Morton *et al*, 2011). 64

Figure 4-4: Total annual rainfall 1871 – 2010 recorded at Althorp. 64

Figure 4-5: The locations of raised flood defenses in the upper Nene river basin (Data courtesy of the Environment Agency Anglian Region). 64

Figure 4-6: Photographs of the Nene basin, highlighting potential sediment sources and connectivity. 67

Figure 4-7: The locations of historical sediment sampling sites in the Nene basin (Surface water and town locations derived from Ordnance Survey (2009). 68

Figure 4-8: Coring locations in Sywell reservoir and the locations of the bathymetric survey measurements (Base map from Ordnance Survey (2013). 71

Figure 4-9: Locations of the contemporary fine sediment sampling sites (Surface water and town locations derived from Ordnance Survey (2009). 73

Figure 4-10: The locations and of the turbidity meters and stage gauging sites (Surface water and town locations derived from Ordnance Survey (2009). 75

Figure 4-11: The effect of EMD correction on an example period of turbidity data affected by algal fouling......76

Figure 4-12: Polynomial calibration curves for the Dodford and Northampton turbidity meters. 77

Figure 4-13: A time integrated sediment trap, as described by Phillips *et al*., (2000). 78

Figure 4-14: The locations of sediment source sampling (Surface water and town locations derived from Ordnance Survey (2009). 82

Figure 5-1: A Flow diagram of the sediment fingerprinting procedure. 98

Figure 5-2: The division of the study area into surface source (A) and channel bank (B) regions for the separation of source samples. 99

Figure 6-1: Down-core profiles of the loss on ignition (LOI, A) and Specific surface area (SSA, B) of the sediment cores. 106

Figure 6-2: Down core plots of the median predicted contributions from channel banks derived using the different uncorrected tracer fingerprints and historically deposited sediment. 118

Figure 6-3: The relationships between Xlf and SIRM (A), and Xarm and SIRM (B) in sediment source samples. 127

Figure 6-4: The effects of the organic and particle size corrections on the median predicted contributions from channel banks in the sediment cores. 141

Figure 7-1: The percentage of river sediment samples passing the mass conservation test for each tracer......145

Figure 7-2: The relationship between the largest inter-source contrasts in median tracer concentrations and the proportion of river sediment samples passing the mass conservation test. 146

Figure 7-3: The average discriminatory efficiency of tracers used in this study when discriminating between channel banks, surface agricultural sources and urban street dusts (note Y axis starts at 33%). 148

Figure 7-4: The average discriminatory efficiency of tracers used in this study when discriminating between channel banks and surface agricultural sources. 149

Figure 7-5: The ability of tracer groups to form a composite fingerprint able to correctly classify >80% of source samples and produce a goodness of fit in excess of 80% in an un-mixing model (when the Mag geochem group is highlighted blue its fingerprint is identical to the 'All' group). 152

Figure 7-6: Composite probability density function of sediment source contributions to all contemporary sediment samples, produced with all tracer group combinations. 153

Figure 7-7: The mean absolute difference between tracer group predictions of contributions from channel banks to overbank sediment. 155

Figure 7-8: Mean differences between the predicted contribution of sediment from channel banks made by each tracer group in comparison all other tracer groups in overbank, suspended and channel bed sediment samples. 157

Figure 7-9: The monthly median predicted contributions from channel banks to suspended sediment, derived using different tracer groups..162

Figure 7-10: The SSA and LOI of suspended, channel bed and overbank sediment and sediment source samples. 166

Figure 7-11: Average differences between the predictions of each tracer group and all other tracer groups, when predicting contributions of from channel banks and urban street dusts to overbank deposited sediment..173

Figure 7-12: Probability density functions (PDF) of the first 12 randomly generated source tracer distributions, displayed alongside the original median and MAD distribution PDF and a composite PDF of all 25 random source tracer distributions. Results are for the "All" tracer group and predicted contribution from channel banks. 175

Figure 7-13: Composite PDFs of 25 randomly generated source tracer distributions in comparison to the PDFs generated using the median and MAD source groups. 176

Figure 7-14: Composite probability density function of 25 randomly generated source tracer distributions of the nine tracer groups. 177

Figure 7-15: The ratio of the percentage difference between the median tracer concentrations of source groups / average tracer coefficient of variation in source groups compared to the difference between 5th - 95th percentile Monte Carlo predictions (%). 180

Figure 7-16: The ratio of the percentage difference between the median tracer concentrations of source groups / average tracer coefficient of variation in source groups for the tracers in all source samples in the Nene basin. 182

Figure 7-17: A comparison of composite PDFs of predicted contributions from channel banks derived using the different tracer groups when large composite fingerprints and the shorter original composite fingerprints are used. 187
Figure 7-18: The percentage of river sediment samples where tracers pass the mass conservation test with and without data corrections. 190
Figure 7-19: The percentage point change in the discriminatory efficiency of mineral magnetic signatures after the application of corrections. 191
Figure 7-20: The percentage point change in the discriminatory efficiency of lithogenic and fallout radionuclides after the application of corrections. 192
Figure 7-21: The percentage point change in the discriminatory efficiency of geochemical tracers after the application of corrections. 194
Figure 7-22: The results of the GA-DFA analysis for uncorrected and corrected tracer signatures in contemporary sediment sampling sites, where the "Mag geochem" group is blue this indicates that it is identical to the 'All' group. 196
Figure 7-23: The mean differences between the sediment provenance prediction of each tracer group and all other tracer groups, with and without corrections, with standard deviation error bars. 199
Figure 7-24: The effect of organic matter and particle size corrections on the tracer variability ratio. 200
Figure 8-1: Depth-age curve calculated from the 'c-crs' model, and down-core variations in ^{137}Cs activity in Sywell reservoir. 202
Figure 8-2: The down-core trend in sediment accumulation rate in Sywell reservoir. 202
Figure 8-3: Bathymetric map, coring locations and depth of sediment in collected cores in Sywell reservoir. 203
Figure 8-4: Daily flow and daily suspended sediment yield at the Northampton and Dodford sampling sites. 206
Figure 8-5: Down-core plot of floodplain core ^{137}Cs activity. 208
Figure 8-6: Quantities of sediment stored on the channel beds at the sediment sampling locations (tonnes per kilometer square of channel bed)(see Figure 4-9 for sampling locations). 211
Figure 8-7: The estimated percentage of the annual suspended sediment yield stored on the channel beds of the Dodford and Northampton tributaries (Error bars were calculated using the mean + 1 standard deviation and the mean – 1 standard deviation). 213
Figure 8-8: Down-core trends in the predicted contributions from channel banks, surface agriculture and urban street dusts in Sywell reservoir. Error bars are the average 25th and 75th Monte Carlo results for each tracer group used to fingerprint the sediment. 216

Figure 8-9: Predicted provenance of suspended sediment in eight major tributaries of the River Nene (Sampling locations are given in Figure 4-9) 220

Figure 8-10: A partial sediment budget for the Nene river basin. 225

List of Tables

Table 2-1: The properties of commonly utilised mineral magnetic measurements (Walden, 1999; Wang *et al*., 2012; Yang *et al*., 2010; Walden, 1999). 30

Table 2-2: Down-core mobility of radionuclide elements in undisturbed soil profiles (Reproduced from Balonov *et al*., (2010)) 38

Table 2-3: Bioavailability of trace metals under different soil conditions (reproduced from Kabata-Pendias (2004)) 39

Table 3-1: Percentage contributions from sediment sources derived from sediment fingerprinting in UK catchments (reproduced from Walling *et al*., 2007). 44

Table 3-2 : Soil erosion rates in natural and undisturbed land in 7 countries (Reproduced from Slaymaker, 2003). 47

Table 3-3: The origin of urban sediments (Taylor and Owens, 2009). 52

Table 3-4: Ranges of medium – high quality sediment yield estimates in UK catchments (reproduced from Walling *et al*., 2007). 54

Table 3-5: Historical rates of floodplain sedimentation in selected river catchments in the UK using ^{137}Cs (over the previous 30-40 years) and $^{210}Pb_{un}$ (over the previous 100 years) chronologies (reproduced from Gruszowski, 2003). 56

Table 3-6: Storage of fine sediment on channel beds in UK rivers derived using the re-suspension technique developed by (Lambert and Walling, 1988) (Reproduced from Gruszowski, 2003). 57

Table 4-1: A summary of the methods used in the thesis and their relevance to the projects objectives. 59

Table 4-2: The periods of operation of the two turbidity meters. 75

Table 4-3: Number and timing of suspended sediment samples collected during the study period. 79

Table 4-4: Periods of bed disturbance sampling. 80

Table 4-5: The lithological and land cover distribution of source sampling. 82

Table 4-6: A summary of the sediment sampling methodology. 83

Table 5-1: Particle size sorting characteristics as used by Foster *et al.* (2008). 86

Table 5-2: Magnetic measurements used as by Foster *et al*., (2008), measurements highlighted in bold were used as fingerprinting tracers. 88

Table 5-3: Established measurement errors for magnetic susceptibility and remanence measurements. 89

Table 5-4: A summary of radionuclides used as environmental tracers in this thesis (after Foster *et al*., 2007). 90

Table 5-5: Error associated with radionuclide activity measurements. 91

Table 5-6: Breakdown of the microwave digestion temperature, power and heating time. 92

Table 5-7: The elements and wavelengths used for ICP-OES geochemical tracer analysis. 93

Table 5-8: Average contamination associated with geochemical element measurement determined by blank samples. 94

Table 5-9: The amount of sediment element concentration recovered by the microwave digestion and ICP analysis procedure, determined using a certified reference material (mg kg^{-1}). 95

Table 5-10: Errors associated with the measurement of geochemical tracers. 96

Table 5-11: Tracer groups used and their abbreviations. 97

Table 6-1: Median tracer concentrations in sediment source groups reported with median absolute deviations. 107

Table 6-2: The tracer groups used to fingerprint historically deposited sediment and their abbreviations. 108

Table 6-3: Tracers failing the mass conservation test for each core and each correction. 109

Table 6-4: Tracers failing the Kruskal–Wallis *H* test (p=0.05) for each core and each correction. 110

Table 6-5: The composite fingerprints, fingerprint discriminatory power and average goodness of fit of un-mixing model outcomes. 112

Table 6-6: The median and the 75^{th} and 25^{th} percentile Monte Carlo predicted contributions from channel banks of the results shown in Figure 6-2. 120

Table 6-7: Pearson correlation coefficients (r) and associated p values for correlations between differences between tracer group predictions and loss on ignition (LOI), specific surface area (SSA), and the Xarm/Sirm and Sirm/Xlf ratios. Statistically significant (p<0.05) values are highlighted in green. 131

Table 7-1: Median and median absolute deviation tracer concentrations in source groups. Colours correspond to the results of a Kruskal Wallace H-test, green = significantly different (p<0.05), from both other source groups, yellow = significantly different from one other source group, red = not significantly different from either other source. 147

Table 7-2: The mean percentage point distance of the 25^{th} and 75^{th} percentile Monte Carlo predictions from the median prediction, for each tracer group fingerprint at each suspended sediment sampling location. ...164

Table 7-3: Pearson correlation analysis between percentage point difference between tracer groups and sample SSA and LOI in the monthly sampling period for all suspended sediment samples. Only statistically significant (p<0.05) results are displayed. 168

Table 7-4: Coefficients of variation of tracer concentrations in source groups, calculated as (median absolute deviation/median)*100). 171

Table 7-5: The un-mixing models run to determine the impact of source tracer concentrations on the variability inherent in un-mixing model predictions. 178

Table 8-1: Floodplain sediment accumulation rates in the Nene basin from 1958 to 1963 and post 1963. 209

Table 8-2: The timescales for which each component of the sediment budget are valid. 226

1.Study context

1.1. Introduction

Under natural conditions fine sediment (usually defined as the fraction of less than 63µm in diameter (McCave *et al*., 1995)) is a key part of freshwater ecosystems and a major part of global geochemical cycling. Fine sediment is usually present in rivers in low concentrations, and is partly responsible for the delivery of essential nutrients to aquatic ecosystems (Walling, 2006). Anthropogenic activities such as modern agricultural practices, river modification and urbanisation have all been shown to significantly increase the supply of fine sediment to water bodies above background levels (Walling and Amos, 1999); often resulting in ecological damage such as a reduction in biodiversity (Newlon and Rabe, 1977), a reduction in fish reproductive success (Marks and Rutt, 1997) and harm to benthic invertebrates and macrophytes (Wood and Armitage, 1997). Fine sediment has also been shown to act as a vector for a variety of harmful contaminants such as toxic metals, nutrients and pesticides (Drouillard *et al.*, 2006; Langston *et al.*, 2010), further increasing the potential for ecological damage. As a result research in geomorphology has focused on investigating fine sediment dynamics, with the intention that targeted mitigation measures can be applied most efficiently. This thesis contributes to the knowledge of sediment dynamics in an under-investigated region of the UK, as well as enhancing the tools available to geomorphologists undertaking fine sediment investigations.

1.2. Research rationale

1.2.1. A need for information on fine sediment dynamics in the UK

The Water Framework Directive (WFD) (2000/60/EC) requires governments to achieve a ‘good’ chemical and ecological status for water bodies. While not explicitly addressed in the WFD the key role of sediments in overall water quality and compliance with the WFD has been highlighted (White, 2008; Tueros *et al*., 2009). The European Union (EU) Freshwater Fish Directive (2006/44/EC) also recognises the detrimental effect of sediment on the environment and specifies a maximum mean annual suspended sediment concentration (SSC) of 25mg l^{-1} (European Union, 2006). Given these requirements there is a clear need to assess sediment pressures in Europe, both for the purpose of water quality assessment and for the targeted application of appropriate mitigation strategies, to move towards the goal of achieving "good chemical and ecological status" of water bodies.

At present sediment dynamics have been widely investigated in river catchments in the northern and western regions of the UK. However there is a paucity of information for much of the remaining parts of the country (Figure 1-1 and Figure 1-2).

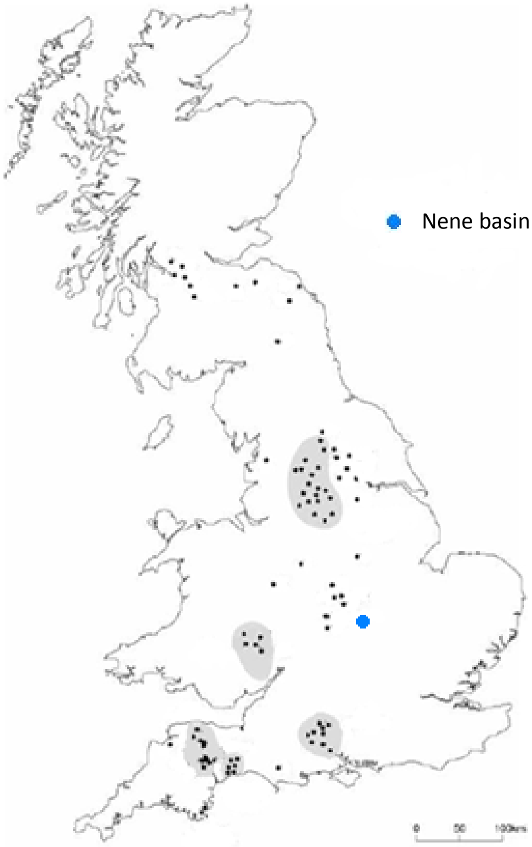

Figure 1-1: The locations of published UK Sediment yield data derived from high and medium quality data (reproduced from, Walling *et al*., 2007).

Figure 1-2: Catchments where information about sediment provenance has been obtained via sediment fingerprinting (reproduced from, Walling *et al*., 2007).

The Nene river basin is located in the East Midlands UK, has a total area of 1,634 km^2 and is considered by the NRA (1994) to be a typical river of the East Midlands and also a typical heavily regulated river. It also represents a river basin in a region where a paucity of information has been identified. As this region of the UK is experiencing the second highest rate of urban growth, on-going changes to the area are applying increasing pressures to the aquatic ecosystem, which may increase in the foreseeable future (Natural England, 2012). The Anglian region catchment management plan (Environment Agency, 2009) reports that only 47% of surface waters in the Nene catchment achieve good ecological and chemical status; of the reasons stated for these failures, fine sediment is suggested to be prominent, however insufficient standards and data are available to determine where fine sediment is excessive. Ammonia and phosphate are highlighted as the most common chemical reasons for the failure to achieve good ecological status and are commonly associated with fine sediment (Meybek, 1982). This project aims to address this paucity of data in the Nene basin and contribute to knowledge of the sediment dynamics in rivers typical of the East Midlands region.

1.2.2. Sediment fingerprinting

Having identified the need for fine sediment investigations, the methodologies available for fine sediment assessment must also be considered. Fine sediment is considered as a diffuse pollutant, which has been shown to be highly spatially and temporally variable within even small geographical areas (Chon *et al.,* 2012). It has also been recognised that the optimal means of mitigating the effects of fine sediment are at its source (Walling and Collins, 2008). As a result the information needed for suitable targeted mitigation requires the investigation of contributions from a wide variety of sediment sources within a large proportion of a catchment, with consideration given to the complex interconnectivity of environments (Collins and Walling, 2004). Because of this highly time consuming requirement, sediment fingerprinting methodologies have gained widespread adoption in geomorphological research. The principle of sediment fingerprinting is based upon comparing the properties of fine sediment deposited in a lake, deposited on a floodplain or transported by a river to those of the potential sediment sources present in a catchment. It relies on the ability of sources to be differentiated on the basis of their measured properties and on the assumption that properties of the sources reflect those of the sediment after delivery to a river, floodplain or lake (Collins *et al.*, 1997a). Using this method a suitably representative database of source and sediment samples provides sufficient information from which to quantify the relative importance of sediment sources in a catchment. This approach represents a far more practical methodology than the difficult and time consuming alternatives such as the direct measurement of a large number of erosion rates and sediment delivery ratios (Peart and Walling, 1988).

Although researchers have recognised the significant potential of sediment fingerprinting in a range of environments e.g. lakes (Miller *et al.*, 2005) floodplains (Collins *et al.*, 1997b) sediment stored on channel beds (Walling *et al.*, 2006) and suspended sediment (Gruszowski *et al.*, 2003); uncertainties exist regarding its correct application. For example, a wide variety of different tracers have been employed in the published literature which include magnetic minerals (e.g. Caitcheon, 1993), lithogenic radionuclides (e.g.Gruszowski *et al.*, 2003), fallout radionuclides (e.g. Walling *et al.*, 1999a), geochemistry (e.g. Collins *et al.*, 1997a), particle size, shape and colour (e.g. Krein *et al.*, 2003) and organic tracers (e.g. Collins *et al.*, 2010). At present very little research has explored the effects of tracer selection on fingerprinting results. In addition to an uncertainty associated with tracer selection, tracers have been shown to be affected by particle size distribution (e.g. Thompson and Morton, 1979) and organic enrichment of sediment (Motha *et al.*, 2003) so the need for data corrections has long been known. However these corrections often attempt to represent a complex and little understood relationship with a simple one, and are therefore only applied in a situational basis if at all (Koiter *et al.*, 2013). Specific sediment sampling locations have been shown to have their own inherent sources of error when fingerprinting, for example preservation of signatures in lake sediment cores are often affected by post depositional changes to tracer properties (D'Haen *et al.*, 2012). As of present, the above summary suggests that little systematic research has been done into the effect of sampling location, tracer selection and correction for particle size and organic content on the outcome of fingerprinting studies. It is therefore not possible to determine the extent to which experimental design affects the accuracy of fingerprinting results. Given these uncertainties, which have been highlighted in a number of recent publications (e.g. Koiter *et al.*, (2013); D'Haen *et al.*, (2012)); Smith and Blake, (2014), there is clearly scope for a comparison of different experimental designs to assist in future provenance investigations and test the validity of existing research. This project aims to contribute towards filling this research gap.

1.3. Aims and Objectives

From the research gaps highlighted above, two aims and four objectives of this project were identified:

Aim 1: To assess the impact of sediment sampling methodology, tracer selection, particle size correction and organic enrichment correction on a fine sediment fingerprinting study.

Objective 1: To conduct a fine sediment fingerprinting investigation, using multiple combinations of different tracer groups and different fine sediment sampling methods and quantify the differences between the fingerprinting results.

Objective 2: To investigate the factors affecting the consistency of fingerprinting results derived using different tracer groups.

Objective 3: To repeat the fine sediment fingerprinting investigation while utilising simple corrections for organic enrichment and particle size distribution.

Aim 2: To develop a partial sediment budget for the Upper Nene river basin and its major tributaries.

Objective 4: To develop a partial sediment budget for the Nene river basin, incorporating measurements of: sediment yield, floodplain sediment accumulation, channel bed sediment storage and sediment provenance.

1.4. Format of the project

Following this introduction and research rationale the aims of this thesis are addressed in nine chapters, the structure of these are shown in Figure 1-3.

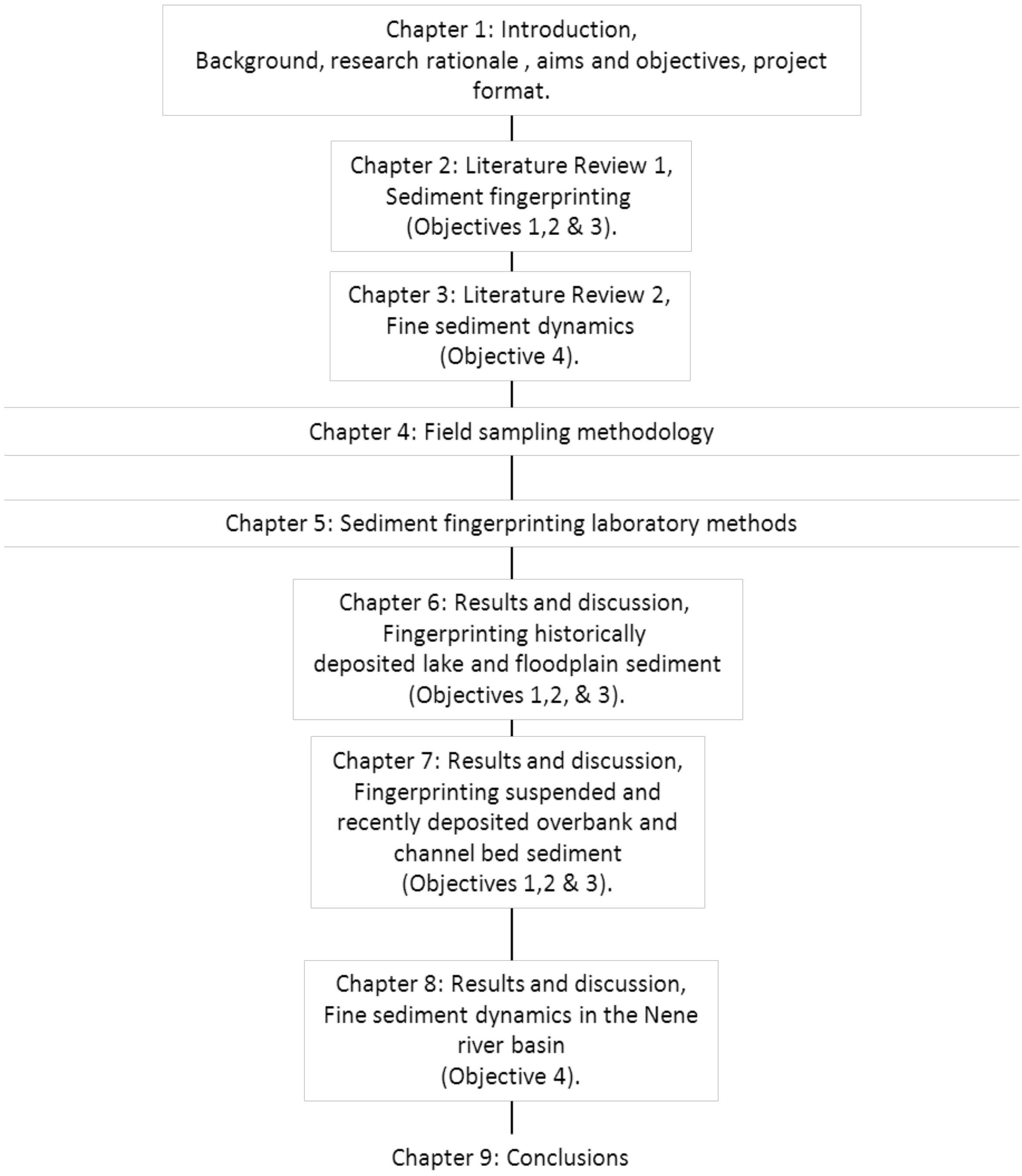

Figure 1-3: The structure of this thesis.

Chapter 2 addresses Objectives 1, 2 and 3 by providing an introduction to sediment fingerprinting. It begins with a literature review charting the developments in sediment fingerprinting methods, and an exploration of the experimental designs used in published literature. This chapter further highlights potential sources of error and common assumptions associated with performing sediment fingerprinting based research. Chapter 3 begins with a discussion of sediment dynamics in UK catchments. Particular emphasis is given to sediment budgets as in Objective 4, to provide a basis for comparison of the results obtained for the upper Nene.

Chapter 4 provides a description of the methods used in this thesis. It begins by describing the methods and calculations relevant to the development of a partial sediment budget for the Nene basin (Figure 1-4). These methods include those used to obtain the fine sediment samples used in the sediment fingerprinting investigation. The methods used to measure the tracers used in the sediment fingerprinting section of this thesis are then outlined along with the methods used to measure the organic content and particle size distribution of samples (Chapter 5). This is followed by a description of the statistical procedure and un-mixing model used in this study.

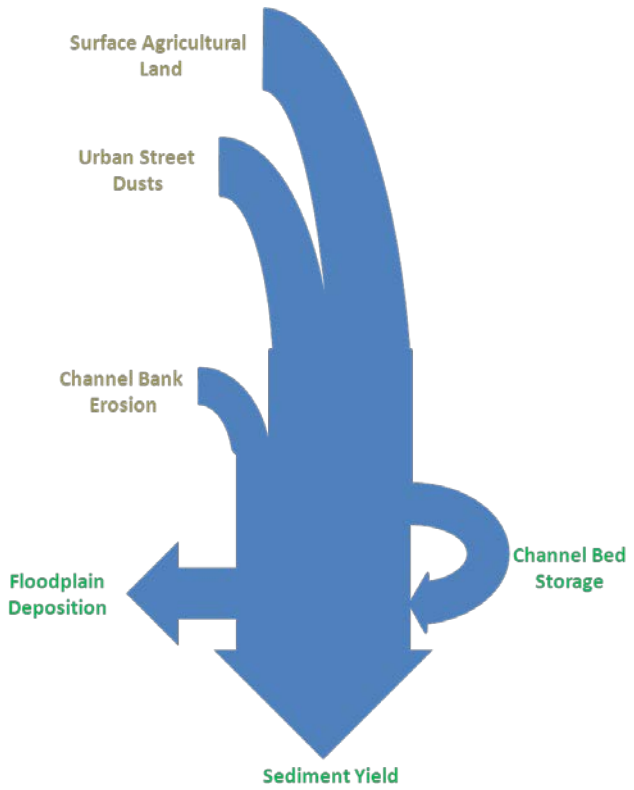

Figure 1-4: The Partial sediment budget outline, sediment sources are highlighted in brown and sinks are in green.

The results of this study are presented and discussed in Chapters 6, 7 and 8. Chapters 6 and 7 address Objectives 1,2 and 3 based on sediment fingerprinting. Chapter 6 investigates the fingerprinting of historically deposited sediment and Chapter 7 investigates the fingerprinting of suspended and recently deposited channel bed and overbank sediment. Chapter 8 addresses Objective 4, by investigating the components of a fine sediment budget for the Nene river basin. Chapter 9, the final chapter, summarises the major findings of this work in relation to published research, and by forming recommendations for future research. It also evaluates whether the aims have been successfully fulfilled.

2. Sediment Fingerprinting

2.1. Introduction

This chapter explores sediment fingerprinting methodologies and the use of tracers to determine sediment provenance. Its aim is to explore the potential impacts of tracer selection and tracer behaviour on a sediment fingerprinting study using a review of published literature, to aid in the fulfilment of Objectives 1, 2 and 3.

2.2. The development of sediment fingerprinting

Initial investigations into sediment provenance focused on the direct monitoring and measurement of potential sediment sources, using methods such as erosion pins (Davis and Gregory, 1994), profilometers (Sirvent *et al.*, 1997) and surveys of erosion features (Werrity and Ferguson, 1980). The time and resource costs of these sampling methods were quickly identified as a major limitation to conducting sediment provenance investigations (Peart and Walling, 1988). As a result the use of tracers to infer sediment provenance gained increasing popularity (e.g. Klages and Hsieh, 1975). However, it was quickly recognised that no single tracer could accurately differentiate between potential sediment sources (Walling *et al.,* 2003). As a result, the use of a mathematical un-mixing model, composite fingerprints consisting of multiple tracers, as well as statistical procedures to identify the fingerprint of tracers able to differentiate between sediment sources were developed.

The first methodology to be widely adopted as a framework for fingerprinting studies was that of Collins *et al.,* (1997), which can be viewed as the basis of many present day methodologies. Even in the early stages of tracer use it was recognised that there were multiple potential sources of error associated with their utilisation. In the methodology developed by Collins *et al.*, (1997) a test for tracer conservatism was used to minimise the possibility of tracers being used which were altered during transport. It was also recognised that organic matter and particle size distribution (especial specific surface area) exerted a strong influence on the conservatism of many tracers (Gibbs, 1973; Foster *et al.*, 1998), so corrections were included on the basis of the percentage organic matter content and sediment specific surface area of the sediment and the source samples. Other than recognising these potential sources of error, results from this methodology and comparable methodologies of the time were provided only as a mean contribution from each sediment source. Goodness of fit, a measure of how well the measured data for sediment and its sources fits the un-mixing model, provided the only indication of the accuracy and precision of the results.

Arguably the most significant development after the Collins *et al*. (1997) methodology was the addition of error analysis in the form of Monte Carlo uncertainty estimation by Rowan *et al.*, (2000). This removed the requirement of judging the robustness of model outcomes solely using goodness of fit, which as demonstrated, could be potentially near-equivalent for widely different model outcomes (Beven, 1993) and is misleadingly improved by the inclusion of highly correlated tracers (Beven, 1996). The Monte Carlo uncertainty analysis repeats the un-mixing model through a range of values representative of the within source variation in tracer measurement for each sediment source, and often also incorporates the analytical error associated with the measurement of the tracer properties (Collins *et al*., 2010). The selection of an average value and scaling indicator to represent the range of values used in the Monte Carlo simulation initially focused on means and standard deviations, however robust alternatives (i.e. median and median absolute deviation) have gained popularity due to the common presence of outliers and non-normally distributed nature of tracer properties (Collins *et al.*, 2012). Further modifications to fingerprinting methodologies have been introduced to account for tracer behaviour, for example Collins *et al.,* (2010) introduced weightings to prioritise the tracers with the smallest within-source variability. A weighting was also applied to account for the discriminatory efficiency of each tracer used in the model. In addition contributions from channel banks were constrained at a maximum contribution of 50%, as a review by (Walling and Collins, 2005) indicated that only two catchments studied in the UK showed contributions to suspended sediment load of over 50% from channel banks and subsurface sources.

Given that the outlined developments in sediment fingerprinting methodologies have commonly focused on the exploration of error, a major drawback remains that almost no studies attempt to validate fingerprinting results against independently derived data. A study by Minella *et al.*, (2008) combined sediment fingerprinting with the monitoring of storm runoff and suspended sediment concentration. Sediment fingerprinting and direct monitoring both indicated a reduction in sediment inputs from agricultural fields and unpaved roads after the implementation of improved land management practices. However this cannot be considered a validation of fingerprinting results, just a logical link between two means of measurement. In the absence of this independent source of data validation, consistency in results obtained in different parts of a catchment has been interpreted as improving the robustness of model results (Collins *et al.*, 2010).

An example of the potential errors which can occur when sediment fingerprinting is used without independent validation is given by Fu *et al.,* (2006). This study showed that the use of different combinations of geochemical tracers could produce significantly different model outcomes. The authors suggest that unless multiple combinations of tracers are selected the results may be biased by tracer selection and the sensitivity of the model is not fully explored. In an investigation by Nosrati (2011) an average difference in predictions of between 1.1% and 7.4% was found between geochemical tracers, and tracing using soil enzyme activity. For individual samples, however, the tracer predictions differed by up to 48%. Evrard *et al*., (2013) used a conventional fingerprinting approach based on fallout radionuclide activity and geochemical concentrations and an alternative diffuse reflectance infrared Fourier transform spectroscopy tracer analysis. Differences between the predicted contributions made by these methods were generally below 10%, but differences in many samples were as large as 20% to 30% and in one study catchment differences in predicted contributions were as high as 70%.

In addition to these uncertainties, Smith and Blake (2014) showed that tracers can fail to identify major source groups in river sediment despite there being a statistically sound theoretical basis for the fingerprint used. Lees (1997) used laboratory based mixing of known proportions of sediment source materials and showed that the assumption of linear additivity, which is required for successful un-mixing of sediment sources was not fulfilled when remanence carrying magnetic minerals were used. Additional uncertainties have been shown to be associated with the different mathematical un-mixing models used to apportion contributions from sediment sources. An example of this was shown in a study by Haddadchi *et al.* (2013), who demonstrated that differently programmed un-mixing models could produce provenance predictions up to 33% differently when models used local optimisation, and 95% differently with global optimisation. Similarly, Smith and Blake (2014) showed that using the mean and median absolute deviation to represent sediment source tracer concentrations, as opposed to the mean and standard deviation, could produce different sediment provenance results.

From these research studies it is therefore apparent that the lack of understanding regarding errors in the sediment fingerprinting process is a major limitation to its reliable application.

The impact of tracer selection has been somewhat reduced in recent work by Collins *et al.*, (2013), which has focused on the use of different statistical procedures to identify multiple composite signatures so that un-mixing models can be run using a range of tracers, reducing the potential impacts of tracer selection and increasing the robustness of the final output.

A range of potential errors, which most commonly relate to tracer behaviour and conservatism in the environment are highlighted in detail in two recent review papers written by Koiter *et al.*, (2013) and D'Haen *et al.*, (2012). The remainder of this chapter explores the potential causes of error relating to tracer behaviour identified in these reviews, beginning with a discussion of the tracer groups used in published fingerprinting studies.

2.3. Tracers

A number of guidelines for tracer selection exist in the literature. It has been shown that using the minimum number of tracers is advantageous, to reduce problems of solution equifinality (Rowan *et al*., 2000), and tracer selection should avoid a high level of co-linearity to minimise the likelihood of an artificially high goodness of fit (Devereux *et al.*, 2010). The major requirements for tracers are that they are conservative, measurable and able to differentiate between at least two sediment sources (D'Haen *et al.*, 2012). Collins and Walling, (2002) showed that the ability of tracers to differentiate between sediment sources varied significantly between catchments, so a ‘generic’ fingerprint which can be applied to a wide range of catchments is a near impossibility. Therefore the choice of appropriate tracers to be used in a fingerprinting study will be highly dependent upon the characteristics of the catchment investigated and the time scale over which tracers are being used e.g. in tracing in process studies or for palaeo-environmental reconstruction. A summary of the frequency of use of different tracer groups in the published literature, used on different spatial and temporal scales is shown in Figure 2-1.

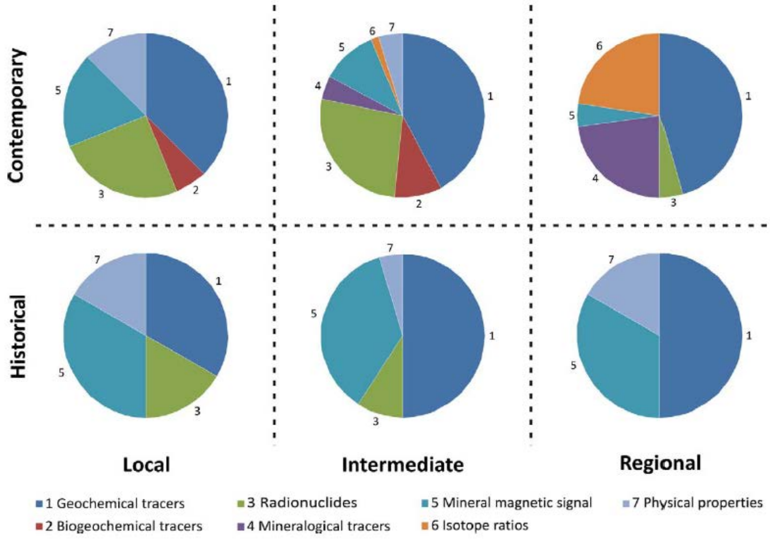

Figure 2-1: The frequency of tracer groups use at varying temporal and spatial scales (reproduced from D'Haen *et al.*, (2012)).

Figure 2-1 shows that geochemical tracers, mineral magnetic signatures, radionuclides and the physical properties of the sediment represent the most commonly utilised tracers, especially at local (< 10 km²) and intermediate (10 – 10 000 km²) scales which are most relevant to the majority of published fine sediment fingerprinting studies.

The tracers used in this study are geochemical tracers, mineral magnetic signatures and radionuclides. They were selected because they are the most commonly utilised tracer groups in the published literature and all could be measured at the University of Northampton. Each tracer type is discussed in detail below.

2.3.1. Mineral magnetic signatures

A suite of magnetic measurements has the advantage over most tracers in that they are quick to measure, require relatively inexpensive equipment and are non-destructive. For these reasons magnetic tracers have a well-established background of use both alone (Oldfield, 1977; Blake *et al.*, 2006; Foster *et al.*, 2008) and in combination with other tracers (Gruszowski *et al.*, 2003).

Magnetic measurements are controlled not only by various types of iron bearing minerals but also by mineral grain size (Walden, 1999). Minerals are formed and destroyed in different environments, as well as being related to the mineralogy of the bedrock parent material. This provides their potential to differentiate between sediment sources. For example, during soil formation, ferrimagnetic minerals are typically formed at small particle sizes (<0.02µm) that are close to the super paramagnetic and stable single domain boundary (Dearing *et al.*, 1996), at which size they exhibit frequency dependent susceptibility, providing the potential to differentiate between surface and subsurface sediment sources (Dearing, 1999). Combustion commonly results in the formation of large canted anti-ferromagnetic haematites allowing for the identification of urban sediments on the basis of the measurement of hard IRM (HIRM) (Blake *et al.*, 2006; Wang *et al.*, 2012). In addition magnetic tracers have also been shown to successfully differentiate on the basis of lithology (Owens *et al.*, 1999b). The interpretation and application of magnetic measurements is therefore approached from the standpoint of targeting specific mineral types and grain size fractions which may be characteristic of different land utilisations or geographic regions where sediment may originate.

Mineral magnetic measurements benefit from simple organic corrections due to magnetic minerals not being part of the organic fraction of sediments, they are often however highly affected by the particle size distribution of the sample (Thompson and Morton, 1979). Common magnetic tracers used in this study and their associated mineral assemblages are described below (Table 2-1).

Table 2-1: The properties of commonly utilised mineral magnetic measurements (Walden, 1999; Wang *et al*., 2012; Yang *et al*., 2010).

Measurement	Minerals measured	Interpretation
Susceptibility measurements		
Low Frequency Susceptibility (χlf)	All minerals: Diamagnetic, paramagnetic, canted anti-ferromagnetic, ferrimagnetic	Primarily determined by magnetic mineral type. Where present ferrimagnetic minerals will dominate even in small quantities. In the case of a low concentration of ferrimagnetic minerals canted anti-ferromagnetic grains will dominate.
Frequency Dependant Susceptibility (χfd)	Ultrafine super paramagnetic grains	Represents the concentration of ultrafine super paramagnetic minerals at the super paramagnetic - stable single domain border (<0.02um diameter). Ultrafine magnetite commonly formed in topsoils is the most significant contributor to χfd making it highly indicative of sediment derived from top soils.
Percentage Frequency Dependant Susceptibility (χfd %)	Ultrafine super paramagnetic grains	The Frequency Dependant Susceptibility (χfd) expressed as a percentage of (χlf) removes the influence of overall mineral concentration. Values range from 0-14% with measurements below 5% being indicative of very low concentrations and those above 10% indicating a sample dominated by ultrafine super paramagnetic grains. As this measurement is a ratio it is not suitable for use in un-mixing models but represents a useful qualitative indicator.
Remanence		
ARM (40µT)	Highly sensitive to stable single domain ferrimagnetic minerals.	Samples are exposed to an alternating field which decreases linearly from the initial field size. This removes any of the samples natural remanence. A 0.04T biasing field is then applied inducing artificial remanence. This measurement is selective of true stable single domain ferrimagnetic grains in the 0.02 to 0.4µm range (Maher, 1988).
Susceptibility of ARM (χarm)	Highly sensitive to stable single domain ferrimagnetic minerals.	ARM normalised to field strength (χarm) is more commonly expressed than ARM to ensure the results obtained are comparable to existing literature as different laboratories often use different field strengths.
Saturation isothermal remnant magnetization (SIRM)	Close to all minerals capable of carrying a remanence	A magnetic field of +1T magnetises nearly all remanence carrying minerals and is representative of both mineral assemblage and grain size.
Isothermal remnant magnetisation in a -100mT backfield (IRM^{-100}) (SOFT IRM)	'Soft' ferrimagnetic minerals	A -0.1T backfield has been shown to be sufficient to reverse the polarity of the majority of single domain magnetite in a sample while being incapable of reversing the field of larger multi-domain high coercively minerals.
Hard Isothermal remnant magnetisation (HIRM)	high-coactivity antiferromagnetic minerals	A representation of the SIRM incapable of being reversed in a backfield of -0.1T. This measurement is indicative of high coercivity canted antiferromagnetic minerals or coarse multi-domain magnetite which commonly occurs in high concentrations in un-weathered or mildly weathered bedrock and as a product of combustion.

2.3.2. Radionuclide activities

Radionuclides can be classified into two groups: (1) fallout radionuclides, which are produced in the atmosphere and deposited onto the ground and the surface of any water body, or (2) lithogenic nuclides, occurring as a product of natural decay series in a rock or soil or in a primordial form (Unscear, 2000). The fallout nuclides most commonly used as tracers are ^{137}Cs and unsupported ^{210}Pb ($^{210}Pb_{un}$). ^{7}Be, which is produced by cosmic ray bombardment, is also a commonly used fallout radionuclide (Blake *et al*., 2002). However due to its short half-life (53.44 days) it is less frequently utilised as a tracer. Fallout radionuclides have the advantage that they are independent of lithology and soil type, providing an increased chance of differentiating between sediment sources on the basis of land utilisation (Collins and Walling, 2004). ^{137}Cs is the most commonly used fallout radionuclide. It was created during thermonuclear weapons tests, and in nuclear accidents, with the peak weapons fallout occurring in 1963 in the northern hemisphere (Cambray *et al.*, 1989). Unsupported or excess ^{210}Pb ($^{210}Pb_{un}$) is the proportion of ^{210}Pb in a sediment or soil sample that is not in equilibrium with its parent isotope (^{226}Ra). It originates from the natural atmospheric decay of ^{226}Ra as part of the ^{238}U decay series (Appleby, 2001). $^{210}Pb_{un}$ transport to the ground occurs predominantly with rainfall, and along with ^{137}Cs, it has been shown to rapidly sorb to soil particles (Taylor *et al.*, 2012). The activities of fallout radionuclides are expected to vary due to their distribution through soil profiles, presenting the possibility to differentiate between land utilizations as demonstrated in Figure 2-2. In the case of channel banks which, are not exposed to fallout, greatly reduced activities or activities below the limits of detection are expected (Walling, 2004).

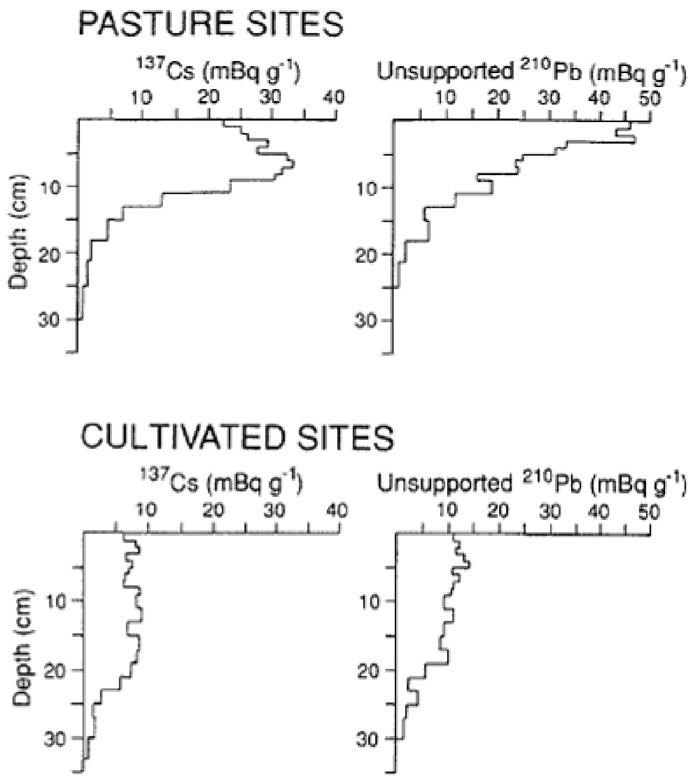

Figure 2-2: The vertical distribution of ^{137}Cs and unsupported ^{210}Pb in soil profiles in the Dart catchment UK (Reproduced from Walling and Woodward, 1992).

Fallout radionuclides experiencing both variable fallout history and having a short half-life have the disadvantage over other tracers in that they cannot be used in a palaeoenvironmental context (Walling, 2004).

Lithogenic radionuclides have received less attention than fallout radionuclides, with very few studies making use of them. As the technique of gamma spectrometry provides measurements of these as a by-product of fallout radionuclide measurement, there is therefore potential for a significant increase in their application. A review of radionuclides by Walling (2004) omits to mention them as tracers and a search of available literature reveals very few occurrences of the use of these radionuclides in fingerprinting studies despite the call by Murray *et al.* (1987) to evaluate their potential as the only direct cost in collecting the data is the time taken to interrogate the gamma spectrum and derive calibrations. In published literature their use is more common as qualitative indicators of sediment provenance. Of the fingerprinting studies they have been used in, they have been shown to be able to successfully differentiate between sediment sources (Foster *et al.*, 2007; Foster *et al.*, 2002). They have also been shown to associate with different minerals in the environment, for example ^{238}U and ^{232}Th are commonly associated with heavy minerals, whereas ^{40}K is concentrated within small clay minerals (Tsabaris *et al.*, 2007). An attempt to differentiate between geologies in the French Alps showed that ^{226}Ra could successfully differentiate between the different sedimentary geologies for 70% of source samples (Evrard *et al.*, 2011).

2.3.3. Geochemical tracers

Of the different types of tracers used, geochemical tracers are the most commonly utilised at all scales and in both a contemporary and historical context (D'Haen *et al.*, 2012). The most common form of geochemical tracer is concentrations of major and trace elements; which is likely due to the ability of ICP-OES or ICP-MS to rapidly measure multiple elements and their proven track record in provenance studies (Collins *et al.*, 1997a; Carter *et al.*, 2003). Stable isotopes form a second type of geochemical tracer which have been successfully used, especially vegetative-derived carbon and nitrogen, and have shown promise at differentiating between differing land uses (Fox, 2005); and lead isotopes, which have been used for historical reconstruction (Farmer *et al*., 1996). An example of the potential of trace element concentrations to differentiate between sediment sources is rare earth elements, which are generally not subject to anthropogenic inputs, and have been shown to be effective petrogenetic indicators (Wilson, 1989). For this reason, they have been used to trace the provenance of stream sediments (Chung *et al.*, 2009). In the urban environment, pollutants have been used to indicate sediments originating from urban street dusts and sewage treatment (de Miguel *et al.*, 2005; Neal *et al.*, 2005). Geochemical tracers can exhibit widely different behaviours in the environment and can be classified into three fractions, the available fraction which is readily added or dissociated from the soil or sediment, the reactive fraction which can be altered by chemical processes and the inert fraction trapped within the mineral matrix (Rodrigues *et al*., 2010). It is therefore important to consider the potential mobility of the tracers utilised.

2.4. Tracer conservatism

As previously highlighted, the behaviour of tracers during their journey with sediment from the point of initial erosion to the point of its collection or deposition is a major potential source of error in sediment fingerprinting studies. Two recent review papers address the conservatism of tracers in fingerprinting studies (Koiter *et al.* (2013) D'Haen *et al.* (2012)).

Figure 2-3 shows the major processes affecting tracer conservatism from source to sink, which these reviews highlight.

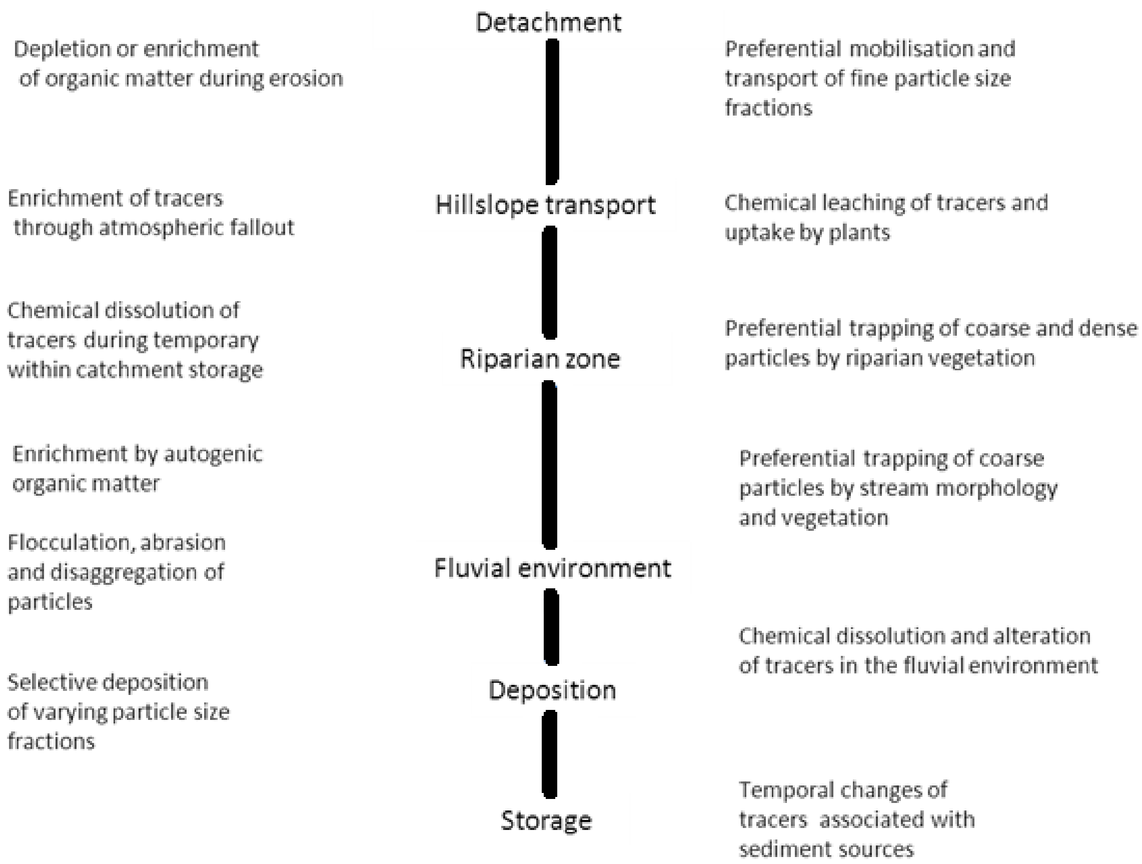

Figure 2-3: A simplified diagram of the processes potentially affecting tracer conservatism on the journey of sediment from source to sink, summarising the major sources of tracer non-conservatism highlighted in a review by Koiter et al., (2013).

The following sections address the processes affecting tracer conservatism highlighted in published research.

2.4.1. Changes in particle size distribution

Processes resulting in changes to sediment particle size distribution are the most commonly highlighted in published reviews and have been shown to occur constantly throughout each part of a river catchment. It has been shown that the largest and most dense particles would be most difficult to transport and the most readily deposited (Mclaren, 1981). However floccs composed of many smaller particles loosely bound together as aggregates are also likely to be impacted in this way (Droppo et al., 1997).

The impacts of selective transport and deposition of particle size fractions may vary with differing tracers. Mineral magnetic measurements have been shown to be highly dependent on grain size, for example individual haematite minerals can be larger than the <63µm particle size fraction, which is commonly selected for analysis in fingerprinting investigations (Walden, 1999). Alternatively smaller minerals can often exhibit a disproportionate effect on overall susceptibility and remanence (Walden, 1999). As a result in field studies investigating the relationship between particle size distribution and mineral magnetic measurements, the relationship has often been shown to be complex (Foster *et al.*, 1998; Oldfield *et al.*, 2009).

Fallout radionuclides have also been shown to have an affinity with finer particles, particularly clay minerals, due to their larger surface area and greater potential for sorption. Ab Razak *et al.*, (1996) showed ^{137}Cs was predominantly associated with clays and $^{210}Pb_{un}$ co-varied to some extent with clay. Livens and Baxter (1988) found that none of the total fixed ^{137}Cs was attached to sand-sized particles. However aggregates of clay minerals or clay coatings on the surface of coarser particles can result in increased ^{137}Cs association with coarse floccs composed of large and small individual particles (D'Haen *et al.*, 2012). Lithogenic radionuclides have also been shown to have trends of increasing activity with increasing particle size, in some studies. ^{40}K, for example, has been shown to be associated with fine clay particles whereas ^{235}Th was associated more with heavier minerals in the coarser particle size fractions (Bihari and Dezső, 2008).

Geochemical element concentrations have also been shown to often be related to sediment particle size. For example, a study of sedimentary Jurassic and Cretaceous soils in the UK showed most elements in a <63µm fractionated sample of soil are concentrated in the <20µm fraction (Pye *et al.*, 2007). Similarly Lanthanides have been shown to easily adsorb to clay minerals (Mahler *et al.*, 1998). The exceptions are elements associated with anthropogenic pollution such as lead and zinc which are often associated more with larger particles within the <63µm fraction (Horowitz and Elrick 1987; Pye *et al.*, 2007).

Particle size impacts are likely made more severe by the preferential abrasion of soft sediment particles into smaller particles (Schumm and Stevens, 1973), causing a change in the relationship between tracers and particle size and also a change in measured particle size distribution of the sediment which is unrelated to its selective transport or deposition. This potentially invalidates any correction for particle size based on the original sediment source material. For example Ohta (2008) reported an increase of between 21-59% of the material in the <40um size fraction of a fine sediment sample after abrasion for a 48h period in a tumbling mill. However in the case of ^{137}Cs activity in abraded material, little difference in activity has been observed when comparing it to naturally occurring <40µm material (Dyer and Olley, 1999).

2.4.2. Enrichment or depletion of organic material

Organic matter can be classified as either allochthonous (derived from sediment sources external to the fluvial or limnic environment) or autochthonous (produced within the fluvial or limnic environment). During erosion and transport of sediment to a river numerous processes have been shown to change the proportion of allochthonous organic matter associated with the sediment. For example Nadeu *et al.* (2011) showed that eroded sediment can be depleted in organic matter when compared to its source materials. Alternatively the organic fraction of sediments has been shown to be carried further through a catchment, by being carried in suspension longer, primarily due to its association with small particles and its lower density (Nadeu *et al*., 2011). Likewise any preferential erosion and hillslope transport of finer particle size fractions can result in a greater delivery of organic material to a lake or river. This was shown by Wang *et al*. (2010) in a catchment based study which showed that exported sediments were significantly enriched in organic carbon, with enrichment ratios varying between 1.2 and 3.0.

The accumulation of fallen leaves, aquatic vegetation, biofilms and aquatic life represent the primary inputs of autochthonous organic matter. Evidence for the organic enrichment of lake, river and wetland sediment by both allochthonous and autochthonous organic matter has been reported in numerous studies (Carr *et al.*, 2010). Kanassanen and Jaakkola (1985) identified an increase in algal-derived organic matter in lake sediments. Alternatively Kaushal and Binford (1999) showed increased allochthonous organic inputs to lake sediments resulting from deforestation.

The impacts of organic enrichment or depletion have been shown to vary between different tracers. For example ~30% of $^{210}Pb_{un}$ activity was shown to be associated with organic matter in soils in a forested catchment (Wallbrink *et al.*, 1997). Hirner *et al.* (1990) showed the elements B, V, Mn, Co, Ni, Cu, Zn, As, Mo, Ag, Cd, Sb, Hg and Pb were all enriched by up to three orders of magnitude within the organic fraction of sediments. In urban street dusts, pollutants such as Zn, Cu and Pb have been shown to be associated with the organic fraction (Robertson *et al.*, 2003). For example, Gibson and Farmer (1986) showed that 41% of copper and 29% of zinc was associated with the organic fraction of urban street dusts.

An examination of the published literature particularly highlights the paucity of research performed on the processes affecting organic material within the fluvial system.

2.4.3. Chemical transformations

The review by Koiter *et al.* (2013) highlights numerous chemical processes which can alter tracers during transport and, in particular, when sediment is in long term storage. A change of pH or redox potential occurring when sediment enters a river, or through the anoxic reducing conditions which are often present in long term sediment stores, represent the primary situations in which transformations can occur. Figure 2-4 shows a summary of the chemical transformations which may affect tracers.

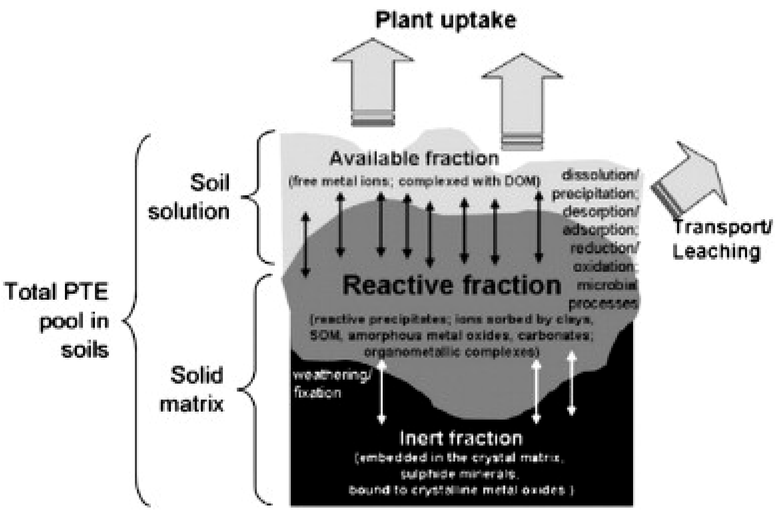

Figure 2-4: Distribution of total pools of potentially toxic elements in soils — the size of the different fractions and the most relevant soil processes vary according to the element of interest and environmental conditions (reproduced from Rodrigues *et al.*, (2010)).

In the case of magnetic minerals, chemical transformations have been shown to occur, both depleting the tracers and enriching them. For example oxidation and reduction reactions associated with groundwater table variations have been shown to result in the dissolution of minerals, beginning with the smaller grain sizes (Dearing, 2000). Alternatively, Oldfield and Wu (2000) and Maher and Thompson (1999) demonstrated the presence of autochthonous bacterially produced iron oxides in lake sediment.

Geochemical elements exhibit varying mobility within the environment. For example Ca^{2+}, Na^{+}, K^{+}, $Fe^{2+}$and Mg^{2+} are selectively leached relative to the relatively immobile hydrolysate constituents Al^{3+} and Ti^{4+} (Roy *et al.*, 2006). As a result indices of alteration such as Al/Na, Al/K, K/Na, Ti/Na and Rb/K ratios have been used to indicate dissolution of the mobile phases (Roy *et al.*, 2008). ^{137}Cs has been demonstrated to be very stable in regards to chemical dissolution (Walling and Quine, 1992). However Foster *et al.*, (2006) showed the mobilisation of ^{137}Cs in sediment contained in coastal lagoons affected by saline pore waters. The lithogenic radionuclides ^{40}K and ^{235}U have been shown to have a high mobility in the environment when compared to the largely immobile elements such as Cs, Th, Ac, Ra and Pb (Table 2-2). Relatively immobile radionuclides have however been observed to be mobile in some situations, especially when ground water or salt water come into prolonged contact with soil or sediment. For example ^{226}Ra, which is the parent isotope of $^{210}Pb_{un}$ and a lithogenic radionuclide tracer, has been shown to be mobilised by groundwater resulting in an enrichment in lake and wetland sediment (Brenner *et al.*, 2004).

Table 2-2: Down-core mobility of radionuclide elements in undisturbed soil profiles (Reproduced from Balonov *et al.*, (2010))

Element	Number of reported measurements	Kd (activity concentration in soil solid phase / activity concentration in the liquid phase)
Cs	469	1200
U	178	200
Th	46	1900
Ac	4	1700
K	237	13
Ra	51	2500
Pb	23	2000

Plant uptake and the biogeochemical cycling of chemical elements is also a key process which can alter tracers, especially when utilising tracers in sediment on a floodplain where vegetation grows on deposited sediment. For example Papastefanou *et al*., (2005) showed that half of the ^{137}Cs Chernobyl fallout was being cycled through plants 40 months after its fallout. This represents a large concentration which could potentially be removed or redistributed by grazing animals, or the cutting of vegetation, changing the sediment provenance results obtained with this tracers use. Geochemical tracers also can be highly bioavailable for plant uptake depending on the redox conditions found in the deposited sediment (Table 2-3), highlighting a potential source of error with the use of these tracers.

Table 2-3: Bioavailability of trace metals under different soil conditions (reproduced from Kabata-Pendias (2004))

Soil condition		Bioavailability	
Redox	pH	Easy	Moderate
Oxidizing	<3	Cd, Zn, Co, Cu, Ni	Mn, Hg, V
Oxidizing	>5	Cd, Zn	Mo, Se, Sr, Te, V
Oxidizing Fe-rich	>5	None	Cd, Zn
Reducing	>5	Se, Mo	Cd, Zn, Cu, Mn, Pb, Sr
Reducing, with H_2S	>5	None	Mn, Sr

2.4.4. Post-depositional alterations

The use of tracers with deposited sediment brings additional assumptions and requirements. The most apparent is that sediment must remain conservative during transport, deposition and post-deposition storage, in contrast to only transport for suspended sediment (Foster and Lees, 2000). Over long timescales the properties of the source materials must also remain conservative. For a number of tracers it is immediately apparent that this requirement is not fulfilled, such as ^{137}Cs, which was not present in the environment until the atomic era, so they are not suitable for tracing studies in an historical context. Similarly, heavy metals should not be used quantitatively in an historical context as the atmospheric flux of many metals onto soil surfaces means that soil concentrations today are likely much higher than they were in the past (Foster and Charlesworth, 1996).

It is far less often considered that anthropogenic activities have resulted in temporal changes in source properties; an example of which are roads and road verges used in tracing studies by Miller *et al*., (2005) and Collins *et al*., (2010). Such papers commonly include elements such as Cu, Ni and Cr as tracers which are likely present as a result of vehicle emissions which will have changed in magnitude over the previous 100 years. This raises the question whether an increase in a tracer concentration in an historical sediment sample (e.g. lake or floodplain sediment) represents an increased contribution from road sources, or an increase in tracer concentration in the source road dusts as a result of increased traffic density. It is therefore unclear whether omitting these source groups and their associated tracers is best practice or whether it is more desirable to include them and acknowledge the uncertainty of the results.

2.5. Corrections to account for differences in particle size and organic enrichment

The potential changes to tracers have been shown to often focus around changes to the particle size distribution and organic content of sediment. Published literature contains many examples of the use of simple corrections to account for these changes. Including corrections for particle size only (Walling *et al.*, 1999a; Collins *et al.*, 2010; Zhang *et al.*, 2012), corrections for both particle size and organic enrichment (Collins *et al.*, 1997a; Zhang *et al.*, 2012; Kim *et al.*, 2013) and no corrections (Hatfield and Maher, 2009; Devereux *et al.*, 2010). It is, however, uncommon for only an organic correction to be applied.

2.5.1. Organic enrichment corrections

Simple organic enrichment corrections rely on tracers not being associated with the organic fraction. With the use of mineral magnetism this type of organic enrichment correction is a common procedure as organic matter is only weakly diamagnetic (Dearing, 1999). In the case of radionuclides and geochemistry, tracers have often been shown to be associated with the organic fraction (Motha *et al.*, 2003) meaning a correction accounting for dilution by organic matter would be detrimental to model accuracy. A number of more complex approaches have been used to account for organic matter - tracer relationships. For example the removal of the organic fraction using hydrogen peroxide (Fu *et al.*, 2006); although in the case of many tracers such as mineral magnetic signatures, this method itself could potentially alter the tracers in the minerogenic fraction (Sandgren and Snowball, 2002). Motha *et al.*, (2003) investigated specific relationships between organic matter and tracers. It was shown that ^{137}Cs enrichment ratios of between 1.29 and 2.16 occur in the organic fraction of source materials. These methods, however, do not account for autochthonous organic material, and greatly increases the analysis time and resource requirements.

It is widely accepted that little is known about the relationships between tracers and organic enrichment (Koiter *et al.*, 2013), which is often cited as the reason why organic corrections are omitted from published fingerprinting studies.

2.5.2. Particle size corrections

Particle size corrections feature more frequently than organic corrections in published sediment fingerprinting studies. Limiting analysis to the <63um particle size fraction of source samples and sediment is the most common method of mitigating the impacts of differences in particle size distribution (Collins *et al*., 1997). Further corrections are commonly applied to account for variations in the <63μm fraction by normalising tracer measurements to the specific surface area (SSA) of source and sediment samples.

SSA corrections assume a linear relationship between particle size and tracer quantity. As has been discussed in previous sections, chemical and physical processes during erosion transport and deposition result in the selective erosion and chemical weathering of mineral fractions, meaning that in the environment a linear relationship is often not encountered. For example Foster *et al*. (1998), Blake *et al*. (2006) and Oldfield *et al*. (2009), showed relationships between particle size and magnetic mineral tracers were complex. Russell *et al.*, (2001) used individual corrections for particle size effects on tracers and found that the fingerprint properties had particle size correction values ranging from 0.12 and 4.55 indicating a wide range of different relationships between different tracers and SSA which can occur in a single catchment. Research by Motha (2003) shows varying relationships between tracers and sediment specific surface area, $^{210}Pb_{un}$ activity increased in the 2–20μm fraction compared to the <2μm fraction, activity then gradually decreased with increasing particle size. However, the study concluded that there was often a simple relationship between particle size and tracer properties for the geochemical and radiometric properties, but no simple relationships between particle size and mineral magnetic properties.

At present published research has shown relationships between specific surface area and tracers to be highly variable. However, unlike relationships with organic material specific surface area often follows linear trends with tracer concentrations.

3.Fine sediment dynamics in river catchments

3.1. The need to investigate fine sediment

The detrimental effect of anthropogenic pollutants on water quality has long been recognised. As a result various regulations have been introduced requiring both reduced pollutant inputs from anthropogenic activities and the application of mitigation measures by National Governments. Water quality in Europe is primarily legislated through the Water Framework Directive (Directive 2000/60/EC). The Directive requires governments to achieve a ‘good’ chemical and ecological status of water bodies. The assessment of sediment is not directly required by the WFD resulting in much criticism, which specifically highlights the key impact of sediment on overall water quality (e.g. White, 2008; Tueros *et al.*, 2009). The EU freshwater fish directive does recognise the detrimental effect of sediment on the environment and specifies a maximum mean annual suspended sediment concentration (SSC) of 25mg l^{-1} (European Union, 2006). The suitability of a single figure being applicable to all catchment types in England and Wales has been questioned (Foster *et al.*, 2011). Instead it is often seen that fine sediment investigation and mitigation must take into account the catchment as a whole unit recognising the diffuse nature of sediment inputs and the complex interconnectivity of environments within a basin (Chon *et al, 2012*).

3.2. Sediment budgets

Having identified a need to mitigate sediment pressures, attention must be given to the investigation of sediment inputs, movement and storage in the river system so that mitigation measures can be targeted in the most efficient manner. Sediment budgets provide a conceptual framework for quantifying inputs, outputs and storage of sediment within a catchment, and have been constructed at scales ranging from small lake catchments (Charlesworth and Foster, 1999) to large river basins (Walling *et al.*, 2006). From a practical standpoint they provide a useful means of understanding catchment processes and potentially predicting the effectiveness of future mitigation measures (Walling and Collins, 2008; Collins *et al.*, 2010).

A sediment budget attempts to consider the sediment dynamics of a catchment in its entirety. They are not limited to a single aspect of dynamics such as the sediment yield at the outflow of a catchment or in a reservoir, or rates of erosion in a specific field plot. The under-exploited potential for sediment budgets to act as a management tool is highlighted by Walling and Collins (2008) and Hinderer (2012). The reason for this under-exploitation is that use of a sediment budget approach requires measurements that are difficult of obtain of the sediment inputs from various sediment sources, in addition to the quantification of sediment storage and sediment yield (Hinderer, 2012). Quantification of sediment budgets is also hindered by uncertainties in parts of various methodologies used; for example the potential error in ^{137}Cs based soil erosion estimates highlighted by Parsons and Foster (2011). A further example is in the uncertainties regarding the suitability of plot-based soil erosion estimates when extended to larger scales, such as those used, for example in the formation of the Revised Universal Soil Loss Equation (Parsons, 2004). Values being reported for the sediment delivery ratios based only upon the un-measured difference between estimates of soil erosion and sediment yield (Parsons, 2012) are also a source of uncertainty. However, despite these potential limitations the quantification of a sediment budget represents a useful framework to investigate fine sediment dynamics.

The following sections address the components of a sediment budget describing their importance and a summary of their measurement in UK catchments.

3.3. Inputs from sediment sources

Sediment sources in the UK are typically classified by land utilisation. Table 3-1 shows a review of measured contributions from different land utilisation classes in UK catchments. Overall pasture and cultivated land are most commonly the dominant sediment sources, although the table does not account for the percentage coverage of each land use in the investigated catchments.

Table 3-1: Percentage contributions from sediment sources derived from sediment fingerprinting in UK catchments (reproduced from Walling *et al*., 2007).

River / Catchment	Area km2	Woodland	Pasture / Moorland	Cultivated	Channel Banks
Ettrick Water	500	3	49		48
Teviot	1110	15	21	24	39
Tweed	4390	7	20	35	39
Swale	1350		42	30	28
Ure	914	0.7	45	17	37
Nidd	484	6.9	75	2.8	15
Ouse	3315		25	38	37
Wharfe	814	4.4	70	3.6	23
Aire	282		45		55
Aire			57		43
Aire	1932		7	20	33
New Cliftonthorpe	0.96		30	33	6
Lower Smisby	2.6		26	37	6.2
Upper Hore	1.6	11	63		26
Hafren		78	28		4
Upper Severn	8.7	22	68		12
Upper Severn	580	48	29		23
Rhiw	140	2	89	2	7
Vymwy	778	2	83	4	11
Perry	181	2	71	22	5
Severn	4325	2	65	25	8
Tem	852	1	40	53	5
Jubilee	0.31		3.1	37	12
Belmont	1.5		3.9	30	11
Frome	77		14	38	48
Stretford Brook	55		9	48	43
Dore	42		2	56	42
Worm	69		25	20	55
Garron Brook	93		14	46	40
E.Avon	89		19	64	17
W.Avon	85		25	71	4
Till	55	1	46	33	20
Chiltern	16		30	69	1
Sem	21		10	78	12
Ebble	109		37	52	11
Nadder	221		4	54	32
Nadder	221	1.3	16	69	14
Upper Avon	324	1.8	12	78	8.2
Wylye	446	1.7	14	73	11
Lower Avon	1477	1.4	16	64	19
Waldon	78	4	48	27	21
Upper Torridge	115	2	48	29	21
Torridge	258	2	47	28	23
Barle	128	6	85	1	8
Bathem	64	1	87	3	9
Lowman	54	2	54	40	4
Dart	46	3	82	11	5
Exe	601	3	72	20	5
Culm	276		30	60	10
Culm	276		35	53	12

Figure 3-1 indicates that channel banks, as a sediment source in the UK, rarely exceeds a 50% contribution to total sediment yield. A general range of contributions shown is 85-95% from surface sources and 5-15% from channel/subsurface sources but emphasis is given to the wide range of values encountered.

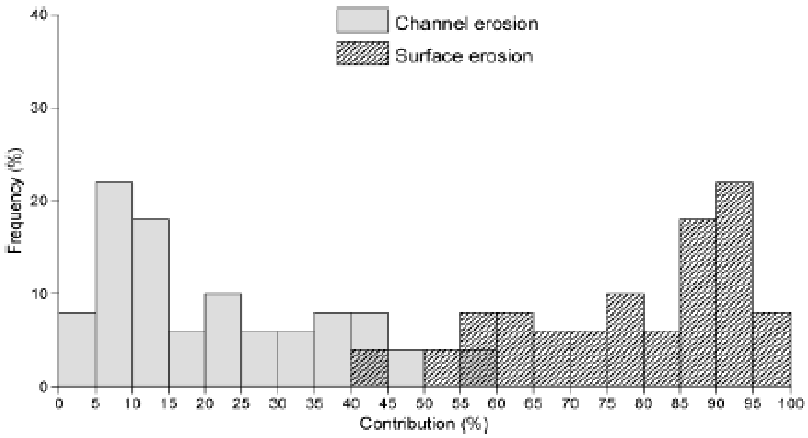

Figure 3-1: Frequency distributions of the percentage contributions from surface sources and subsurface sources in UK catchments, reproduced from Walling *et al.,* (2007).

3.3.1. Connectivity and sediment delivery

The proportion of gross erosion which reaches a lake or river in a given time interval is known as the sediment delivery ratio (SDR) (Walling, 1983). On geological timescales the ratio of eroded sediment to the amount of sediment delivered to a stream system will be 1; as material deposited within a catchment cannot accumulate indefinitely (Parsons, 2012). This is not the case over years to millennia. For example, in the case of the Pang and Lambourn catchments, Berkshire UK, 51% and 31% of sediment mobilised from cultivated land was sequestered before reaching the river channel (Walling *et al.*, 2006) and in the case of the Rosemaund catchment in Herefordshire and the Smisby catchment in Derbyshire between 14.2% and 25.7% of eroded sediment was sequestered before reaching the river channel (Walling *et al.*, 2002).

Due to the practical constraints of its measurement SDR is often not directly measured in field-based studies. Modelling approaches are more frequently used, where SDR is estimated using drainage basin area, gradient and rainfall, amongst other factors (de Vente *et al.*, 2007). In field based studies an estimate is often derived from differences between measured values in a sediment budget (i.e. erosion rates and sediment yield), an approach much criticised by Parsons (2012). Therefore these multiple complex factors affecting the SDR and lack of field based measurements have resulted in a large margin of error associated with its prediction (Walling, 1983). Trends in field based and modelling work have become apparent however with the SDR often being inversely related to catchment area (Walling, 1983). This is usually explained by the greater opportunities for sediment to become trapped in sinks, such as foot slopes, which give rise to longer sediment transit times through a catchment (de Vente *et al.*, 2007). Floodplains represent an important example of a sediment sink as they are scale dependent emergent features. They occupy a larger percentage of the total catchment area with increasing catchment size and effectively isolate adjacent hill slopes from the main river channel unless rivers run across them.

The primary route of overland sediment movement varies in catchments with different topographies. In hilly catchments the energy available in overland flows is able to form gullies which act as direct conduits for sediment to reach a river. In low gradient catchments bank erosion and overbank flows are more effective means of sediment delivery given the common absence of consolidated overland flows (Salant *et al.*, 2008). In UK catchments the role of roads and sunken lanes has been emphasised as increasing connectivity between agricultural fields and rivers (Gruszowski, 2003; Boardman, 2013) and sub-surface drainage has also been shown to contribute a high proportion of sediment in drained lowland agricultural catchments (Russell *et al*., 2001)

From a management standpoint an understanding of the sediment delivery ratio (SDR) is important as a large amount of temporary sequestration is likely to result in delayed catchment responses to changing erosion processes, such as might occur before or after mitigation measures or have occurred in the past (Walling and Collins, 2008). This is especially relevant as Parsons (2012) raises a criticism of sediment fingerprinting in that temporary sequestration of sediment is not addressed in its application. SDR returns to the classic idea in fluvial geomorphology of reaction and relaxation times in catchment response to changing sediment pressures or fluvial energy, many aspects of which are little understood, such as how landscapes respond to cumulative changes through time (Owens *et al*., 2010).

3.3.2. Cultivated Land

Conventional agricultural practices have been shown to cause erosion rates to greatly exceed pre-agricultural levels. In comparison to international catchments the UK generally exhibits low rates of erosion (Table 3-2).

Table 3-2 : Soil erosion rates in natural and undisturbed land in 7 countries (Reproduced from Slaymaker, 2003).

Country	Natural t km^{-2} $year^{-1}$	Cultivated t km^{-2} $year^{-1}$
China	<200	15000-20000
U.S.A.	3-300	0-17000
Ivory Coast	3-20	10-9000
Nigeria	50-100	10-3500
India	50-100	30-2000
Belgium	10-50	300-3000
U.K.	10-50	10-300

The erosion of cultivated land occurs by three processes; rill erosion, inter-rill erosion and gully erosion. Inter-rill erosion represents the breaking up of soil particles by the energy contained in rainfall, as well as unconsolidated runoff in the form of sheetwash. It is rarely of importance as a mechanism for soil redistribution, only for an increase in erosion rate, due to the low concentration of energy available for sediment transport (Evans, 2002). Gully and rill erosion are the primary means of sediment entrainment and transport in cultivated land. Gully erosion has been found to comprise between 10% and 94% of catchment soil erosion where it occurs (Poesen *et al.*, 2003). Gully erosion involves the formation of deep gullies in the land surface, eroding both surface and subsurface material. Rill erosion involves the formation of a series of shallow channels across a field surface as shown in Figure 3-2.

Figure 3-2: Rill erosion originating from a spring at the ironstone – mudstone lithology boundary in the Nene basin close to Moulton, Northamptonshire, UK.

Four main factors have been shown to affect the rates of these erosion processes; these are soil texture, poor crop cover, valley morphology and the presence of tramlines which concentrate flow and heavy rainfall, generally exceeding 15mm a day (Chambers *et al.*, 2000; Cerdan *et al.*, 2010).

Soil texture can reduce or increase rates of erosion depending upon local topography and land use. Clayey soils are more cohesive than their coarser counterparts and are therefore less susceptible to inter-rill erosion by raindrops. However the particles are also easier to transport due to their low mass and the greater runoff to be expected on less permeable clay soils (Evans, 1990). Data presented by Evans (1993) showed that in sandy soils in the UK, gully erosion in valley bottoms was an important process whereas in soils composed of clays and silts rill erosion on hillslopes became the dominant process. An effective generalisation is that as clay content increases, erosion by water decreases and therefore sandy soils erode most frequently, but soils rich in both silt and fine sand erode most severely (Evans, 1990; Evans, 2002).

Management practices can further increase or reduce soil erosion. For example, poor cropping practices can break up soil structure and remove organic matter making soils more susceptible to compaction, thereby increasing runoff. Bare cultivated earth has in turn been shown to be subject to the highest rates of erosion of any land use across Europe (Cerdan *et* *al.*, 2010). In a study of 12 catchments in the UK, 80% of the recorded erosion events occurred on land cropped with winter cereals (Chambers *et al.*, 2000). Numerous mitigation measures aimed at reducing soil erosion have been shown to be effective. Buffer zones and wetlands provide a commonly used mitigation measure, however their effectiveness has proved highly variable (Kay *et al.*, 2009). The high variability is attributed to the combination of low plant cover, a high water table and increased runoff reducing their effects in winter months. The presence of tile drains also provides a bypass to buffer zones (Gelbrecht *et al.*, 2005).

3.3.3. Pasture

In many studies pasture has been shown to be a relatively small contributor to the total sediment load of a river e.g. the river Wye and its sub catchments (Walling *et al.*, 2008). Likewise sediment concentrations in runoff from pasture have often been shown to be insignificant (Fullen, 1998). This is commonly attributed to continuous vegetation cover and relatively undisturbed soils presenting a barrier to rill and gully erosion common on cultivated land, and is highlighted in a review by James and Alexander (1998). This review indicated that erosion by animals and by surface wash in un-concentrated overland flows were instead the predominant erosion mechanisms present on upland pasture. As a result of these mechanisms, in catchments such as the Old Mill Reservoir, South Devon, UK, pasture has been shown to be the dominant sediment source. This was attributed to increased animal stocking densities (Foster and Walling, 1994). Collins *et al*., (2010) also showed a significant contribution of fine sediment from pasture due to the congregation of animals and poaching of riparian zones.

Bare soil on pasture can often be found where animals congregate such as along farm tracks, close to gates and fences (Figure 3-3). Sheep and deer have been shown to create scarring by rubbing against vegetation (Evans, 1997). These bare soils are subject to erosion by wind and rain until they are re-colonised by vegetation.

Figure 3-3: Poaching along the river Nene close to Cogenhoe, Northamptonshire, UK (photograph taken 19/07/2012).

3.3.4. Channel banks

Channel banks have been recognised as a major source of sediment in the UK and worldwide. Estimates for the contribution of channel banks to sediment yield in UK catchments typically range from between ~10 and 40% (Figure 3-1). There are three primary mechanisms which affect rates of channel banks erosion:

1. Sub-aerial processes, which include processes such as wetting and drying of the banks and freeze–thaw activity (Couper and Maddock, 2001).
2. Fluvial entrainment; the action of the water entraining material from channel banks.
3. Mass failures become the dominant process at points where the channel banks become too high to structurally support themselves. Such mass failures have been documented in the Swale - Ouse catchments, UK (Lawler *et al.*, 1999).

Lawler (1995) indicated that in small catchments sub-aerial mechanisms are the dominant erosion process. In middle-order basins fluvial entrainment becomes the more important process, and in larger catchments bank retreat due to mass failure mechanisms becomes an important process. It has also been pointed out that this is likely to be equally the case when moving downstream through reaches of an individual catchment in so called 'process domains' (Abernethy and Rutherfurd, 1998; Couper and Maddock, 2001).

The weakening of channel banks by sub-aerial erosion has been shown to be a contributing factor when considering fluvial entrainment and mass failures. For example Couper and Maddock (2001) showed that rates of erosion were greatest in high flows with a short lag time between sub-aerial preparation such as desiccation or freeze thawing and the high flow event. Different sub-aerial processes affecting river banks have been shown to vary in intensity. For example freeze–thaw in the River Arrow caused noticeably more bank retreat than was caused by desiccation; therefore a seasonal pattern of channel bank erosion occurred, with maximum rates occurring in the winter (Couper, 2003). Another factor influencing bank erosion is the moisture content of the bank material which acts to decrease cohesion between particles. This can result in the highest rates of erosion occurring after sustained wet periods (Simon *et al.*, 2000). Dry periods which lead to the drying of channel banks can likewise disrupt their structure, increasing rates of erosion (Dietrich and Gallinatti, 1991). Aquatic organisms such as invasive signal crayfish have been shown to be a potential cause of increased channel bank erosion. By digging holes of 10-20 m^{-2} in channel banks (Harvey *et al*., 2011) they have been observed to accelerate bank erosion (Guan, 1994). In contrast riparian vegetation has been shown to strengthen channel banks particularly reducing fluvial entrainment of bank material and mass failures. However in upper reaches of rivers collapse of tree roots may result in increased rates of bank erosion (Abernethy and Rutherfurd, 1998). Therefore numerous complex processes have been shown to affect rates of channel bank erosion. Unlike other sources, channel banks are in direct contact with the river channel therefore high levels of connectivity are of relevance to this source. The complex nature of bank erosion can be seen in studies such as presented by Bull (1996), where the location and presence of bank erosion and sediment mobilisation were highly variable between flood events.

3.3.5. Urban street dusts

The process of urbanisation rapidly changes the nature of the environment. Permeable soils are replaced with impermeable surfaces and river channels are heavily engineered and constrained (Taylor *et al.*, 2012). Vegetation is often removed resulting in temporary or permanent areas of bare earth; the weathering of soils is replaced with the weathering of structures and vehicles. These changes fundamentally alter the hydrology and composition of sediment and its movement, creating a very different environment to rural areas (Barbosa *et al., 2012*).

Annual sediment yields for urban areas are typically cited in the region of 0.4 to 5 t km^2 yr^{-1} (Taylor and Owens, 2009) representing a small quantity when compared to cultivated land or many areas of pasture. Sediment in urban areas does however benefit from the increased connectivity provided by roads and engineered waterways (Carter *et al.*, 2003). Urban sediment discharges have been attributed to two major transport pathways, the first being separate or combined sewer overflows (CSOs) and the second as surface runoff or snow melts transporting street dusts (Burton and Pitt, 2001). A greater quantity of sediment is also expected to originate from urban areas during the initial stages of development and construction, due to the increased areas of bare earth and availability of construction materials (Wolman 1967).

CSOs represent a combination of sewage treatment solids as well as street runoff. This gives them a far higher concentration of phosphate and nitrate and a higher Biological oxygen demand (BOD) than storm runoff (Gasperi *et al.*, 2010), which is characterised by its primary composition of street dusts (Table 3-3).

Table 3-3: The origin of urban sediments (Taylor and Owens, 2009).

	Street dusts	CSOs
Soil Erosion	✓	✓
Atmospheric dusts	✓	✓
Sewage treatment solids		✓
Road sediment	✓	✓
Construction sediments	✓	✓
Winter gritting of roads	✓	✓

Sediment provenance studies are infrequently performed in urbanised catchments. As a result the review shown in Figure 3-1 does not include any estimates of contributions from urban street dusts. Studies by Charlesworth *et al.* (2000) and Charlesworth and Lees (2001) show that the rapidly changing nature of sources can make high resolution urban source tracing impractical in a historical context. A study examining contemporary sediment in the highly urbanised River Aire catchment during high flow events showed 19–22% of inputs were from street dusts and 14–18% was solids derived from sewage treatment (Carter *et al.*, 2003).

Like other sediment sources inputs from urban areas and their impacts are dependant primarily on rainfall and the nature of the preceding time period. Storm events provide the energy necessary to transport sediment from distal sources such as the above-mentioned street dusts as well as in more extreme events exceeding the capacity of CSOs allowing for a discharge of sewage into water courses (Lee *et al.*, 2002). Numerous investigations have identified what is known as "first flush" where the majority of pollutants move in the initial storm of the season or initial period of an individual storm event and especially in the case of pollutant discharges is highly affected by an antecedent dry period (Lee *et al.*, 2002). This effect has not been shown to be a constant for all environments and all pollutants however, with some research showing increasing inputs through a series of storm events or in the later stages of a storm (Lee *et al.*, 2004). Urban street dusts are typically a more finite sediment source so it may be expected that a depletion of material available for transport may occur in some urban catchments during closely spaced storm runoff events.

3.4. Sediment in the fluvial system

3.4.1. Suspended sediment yield

Sediment yield is defined as the amount of material per unit area per unit time eroded and delivered to a stream system (Vanmaercke *et al.*, 2011). As a consequence sediment yield is dependent on the rate of erosion and the sediment delivery ratio. A major benefit is that it provides a useful figure to quantify overall sediment movement in a catchment which can be easily compared to other catchments (Walling *et al*., 2007). Sediment yield has been shown to be catchment specific and to vary largely between different catchments (Collins and Walling, 2004). Its controlling factors have been shown to include the amount of runoff, catchment size, lithology, topography, soil type, land management practices and connectivity; although land use has often been viewed as the primary factor affecting sediment dynamics and controlling impacts of the other environmental factors (Lexartza-Artza and Wainwright, 2011). UK catchments generally exhibit low sediment yields when compared to their southern European counterparts (Vanmaercke *et al.*, 2011). A review of UK sediment yields (Table 3-4) summarises high – medium quality estimates of sediment yield for 107 UK catchments. These estimates were determined to be high – medium quality when a greater than 1 year period of turbidity monitoring was available; or a rating curve was developed using automated sampling, performed at minimum on a daily basis, or weekly with the inclusion of storm events. The quality of lake based reconstruction was related to individual studies.

Table 3-4: Ranges of medium – high quality sediment yield estimates in UK catchments (reproduced from Walling *et al*., 2007).

Catchment type	Size km^2	Number	Sediment yield range t km^{-2} yr^{-1}	Sediment yield average t km^{-2} yr^{-1}
Upland Rough Pasture	<10	20	3-286	109
	10-100	3	51-169	111
Upland Agriculture	<10	4	6.7-49.7	27
	10-100	3	35-46	41
Lowland: limited anthropogenic impact	<10	1	4-9	7
Lowland: Agriculture	<10	19	8-131	51
	10-100	18	2.-58	28
	100-1000	27	1-311	46
	1000-10000	10	4-59	31
Lowland Urban	<10	1	10	10
	10-100	1	10	20

UK sediment yields range from 1- 286 t km^{-2} yr^{-1}. The Nene represents a lowland agricultural catchment with a total area of between 1000-10,000 km^2 where a sediment yield of 28-51 t km^{-2} yr^{-1} is typical (Walling *et al*., 2007).

Suspended sediment is the form in which sediment contributes to sediment yield in fine sediment based research. Bedload and dissolved load can also be considered part of sediment yield, however, are of little relevance when considering fine sediment pressures. Suspended sediment represents sediment actively being transported at the time of sampling. Suspended sediment concentration (SSC) is primarily dependent upon supply (Salant *et al*., 2008) therefore it can be expected that an increase in SSC will be associated with a greater energy available for erosion and sediment transport such as during a storm (Wood, 1977).

3.4.2. Floodplain sedimentation

Deposition of sediment on floodplains during extreme events can often result in a significant reduction in sediment yield at a catchment outlet (Walling and Owens, 2002). As a result a store of historical sediment and its associated pollutants accumulates through time in floodplain locations. In section 3.4.1 the floodplains were identified as a scale emergent feature producing a barrier between hillslopes and river channels, which impacts the degree of connectivity within a catchment. This section specifically addresses the additional role of floodplains as a store of sediment and a potential source of sediment within the context of a sediment budget.

Analyses of extreme events suggest that a single flood event has the potential to exceed the normal annual geomorphic activity (erosion) in a catchment (Gonzalez-Hidalgo *et al.*, 2013). A proportion of the sediment moved during overbank flow events will be sequestered on the floodplain. For example a study by Walling *et al.* (1999b) showed that between 39-40% of the total annual sediment yield of the River Ouse, UK, and 50% for the River Wharfe, UK, will be deposited in this way.

Rates of overbank sedimentation derived from floodplain cores are often only a few millimetres a year (Lambert and Walling, 1987). This can increase in some catchments to up to several centimetres a year, particularly in catchments heavily modified by anthropogenic activity (Marron, 1989). Table 3-5 shows historical rates of floodplain sedimentation in UK catchments. Post 1963 accumulation rates are highly variable and lie between 0 and 16,000 t km^{-2} yr^{-1} with an average rate of accumulation of 4,062 t km^{-2} yr^{-1}. Comparing the post 1963 results to the $^{210}Pb_{un}$ results for the previous 100 years shows an average reduction in accumulation rate of 10.4% in the post 1963 time period. This suggests a relatively recent trend of decreased connectivity between some UK rivers and their floodplains.

Table 3-5: Historical rates of floodplain sedimentation in selected river catchments in the UK using ^{137}Cs (over the previous 30-40 years) and $^{210}Pb_{un}$ (over the previous 100 years) chronologies (reproduced from Gruszowski, 2003).

^{137}Cs derived rate (t km^2 yr^{-1})	$^{210}Pb_{un}$ derived rate (t km^{-2} yr^{-1})	Difference in accumulation rate: ^{210}Pb - ^{137}Cs	Percentage difference (%)	Location	Reference
600-6000				River Culm, Devon	(Walling and He, 1993)
4500	4200	300	7.14	River Exe, Stoke Canon	(Walling and He, 1994)
2200	2700	-500	-18.52	River Culm, Silverton Mill	(Walling and He, 1994)
3500	3200	300	9.38	River Culm, Silverton Mill	(Walling and He, 1994)
1700	1900	-200	-10.53	River Avon Bredonfield	(Walling and He, 1994)
	700-5900			River Culm, Devon	(He and Walling, 1996)
1300	1500	-200	-13.33	River Culm, Devon	(Walling and He, 1997b)
800				River Stour, Dorset	(Walling and He, 1997a)
2060 (100-5540)				Rivers Ouse and Wharfe, Yorks	(Walling *et al.*, 1998)
1260				River Tweed	(Owens *et al.*, 1999a)
900				River Teviot	(Owens *et al.*, 1999a)
1770				Ettrick Water	(Owens *et al.*, 1999a)
9500	10400	-900	-8.65	Lower River Ouse, Yorkshire	(Owens *et al.*, 1999a)
2400	2300	100	4.35	Middle River Ouse, Yorkshire	(Owens *et al.*, 1999a)
6400	6800	-400	-5.88	Upper River Ouse	(Owens *et al.*, 1999a)
5000				River Swale, Yorkshire	(Owens *et al.*, 1999a)
1800	4200	-2400	-57.14	River Ure, Yorkshire	(Owens *et al.*, 1999a)
1700	1700	0	0.00	River Nidd, Yorkshire	(Owens *et al.*, 1999a)
1300	1100	200	18.18	River Wharfe, Yorkshire	(Owens *et al.*, 1999a)
2900	2700	200	7.41	River Culm, Silverton Mill	(Walling and He, 1999)
2800	3300	-500	-15.15	River Severn, Buildwas	(Walling and He, 1999)
900	800	100	12.50	Warwickshire Avon	(Walling and He, 1999)
2200	2000	200	10.00	River Rother, Shopman Bridge	(Walling and He, 1999)
9500	10400	-900	-8.65	River Ouse, York	(Walling and He, 1999)
2100	4600	-2500	-54.35	River Vyrnwy, Llanymynech	(Walling and He, 1999)
12200	14200	-2000	-14.08	River Severn, Atcham	(Walling and He, 1999)
1500	2800	-1300	-46.43	River Wye, Preston on Wye	(Walling and He, 1999)
8600	9500	-900	-9.47	River Severn, Tewkesbury	(Walling and He, 1999)
4600	6600	-2000	-30.30	Warwickshire Avon, Pershore	(Walling and He, 1999)
8800	10100	-1300	-12.87	River Usk, Usk	(Walling and He, 1999)
3900	3300	600	18.18	Bristol Avon, Langley Burrell	(Walling and He, 1999)
5100	6400	-1300	-20.31	River Thames, Dorchester	(Walling and He, 1999)
7000	9300	-2300	-24.73	River Torridge, Great Torrington	(Walling and He, 1999)
6000	6500	-500	-7.69	River Taw, Barnstable	(Walling and He, 1999)
5600	4300	1300	30.23	River Tone, Bradford on Tone	(Walling and He, 1999)
4500	4200	300	7.14	River Exe, Stoke Canon	(Walling and He, 1999)
3500	3200	300	9.38	River Culm, Silverton	(Walling and He, 1999)
5100	4000	1100	27.50	River Axe Colyton	(Walling and He, 1999)
400	400	0	0.00	Dorset Stour, Spetisbury	(Walling and He, 1999)
1100	1400	-300	-21.43	River Rother, Tittleworth	(Walling and He, 1999)
3900	4800	-900	-18.75	River Arun, Billingshurst	(Walling and He, 1999)
5100	7100	-2000	-28.17	River Adur, Partridge Green	(Walling and He, 1999)
1500	2300	-800	-34.78	River Medway, Penhurst	(Walling and He, 1999)
5100	4500	600	13.33	River Start, Slapton	(Walling and He, 1999)
0-16000				River Ouse, Yorkshire	(Walling *et al.*, 1999b)
0-7000				River Tweed	(Walling *et al.*, 1999b)
2000	3000	-1000	-33.33	Upper River Tweed, Scotland	(Owens and Walling, 2002)
2200	2600	-400	-15.38	Middle River Tweed, Scotland	(Owens and Walling, 2002)
1900	4800	-2900	-60.42	River Teviot, Scotland	(Owens and Walling, 2002)
900				Smisby, Leicestershire	(Walling *et al.*, 2002)
1300				River Swale, Yorkshire	(Walling and Owens, 2002)

Sediment movement and the rate of overbank sedimentation have been shown to be variable during different periods of an individual flood event, and during different flood events (Carter *et al.*, 2003). Different sediment sources also vary in importance between different flood events (Owens *et al.*, 1999b), making the long term relevance of contemporary data questionable. The sampling and dating of floodplain sediments have been used to overcome this problem. For example Owens *et al.* (1999b) showed long term changes in the sources of sediment deposited on the floodplains of the rivers Ouse and Warf; UK, during the previous 100 years, providing context to the results of their contemporary sampling programme.

3.4.3. Channel beds

Channel beds represent an important store of fine sediment in river catchments. Not only is the degradation of channel bed habitats by fine sediment considered an important ecological issue (Collins *et al.*, 2010) but the stored sediment often represents a source of easily mobilised sediment ready to be transported when flows increase (Walling and Amos, 1999).

The logistical difficulty in sampling channel bed sediment quantities over a sufficient range of river reaches and frequency of timescales has resulted in relatively few studies quantifying channel bed storage. The large spatial and temporal variation in sediment storage may be the primary reason for this (Walling *et al.*, 2003). What research has been done has indicated that typically between 2% and 10% of the total annual suspended sediment yield of a river resides on or in the channel bed (López-Tarazón *et al.*, 2012). However, in some catchments this percentage has been shown to be significantly larger; at 18% and 57% in the lowland permeable Frome and Piddle catchments respectively (Collins and Walling, 2007a). Published estimates of the quantities of sediment stored on the beds of UK catchments are provided in Table 3-6. Storage varies from below 230 t km^{-2} to over 5000 t km^{-2}.

Table 3-6: Storage of fine sediment on channel beds in UK rivers derived using the re-suspension technique developed by (Lambert and Walling, 1988) (Reproduced from Gruszowski, 2003).

Water + bed surface agitation t km^{-2}	Location	Reference
230	River Exe Devon	(Lambert and Walling, 1986; Lambert and Walling, 1988)
1730	River Swale Yorkshire	(Walling *et al.*, 1998)
1430	River Nidd Yorkshire	(Walling *et al.*, 1998)
2910	River Ouse / Ure Yorkshire	(Walling *et al.*, 1998)
1590	River Warfe Yorkshire	(Walling *et al.*, 1998)
1920	River Ouse Yorkshire	(Walling *et al.*, 1998)
640	River Tweed	(Owens *et al.*, 1999a)
1120	River Teviot	(Owens *et al.*, 1999a)
570	Ettrick water	(Owens *et al.*, 1999a)
>5000	River Piddle, Dorset	(Walling and Amos, 1999)

The storage of fine sediment on channel beds is generally in the form of either a coating of the bed surface by a mantle of sediment or the storage of sediment inside the bed, filling the pore spaces between sand and gravel particles. Mantling is especially characteristic of rivers, where sediment inputs exceed their transport capacity (Lisle and Hilton, 1992). The colonisation of sediments with benthic algae, microbial and fungal growth and subsequent formation of extracellular polymeric substances has been shown to be an important factor reducing how easily mantled sediment is mobilised (Droppo *et al*., 2001).

The accumulation of fine channel bed sediment is especially an issue in groundwater-fed permeable catchments such as in lowland UK and is likely due to the lack of episodic high flow regimes which scour channel beds and release fine sediment into suspension (Collins and Walling, 2007b). The accumulation and redistribution of sediment on channel beds has been shown to occur during the waning periods of a flood, where sediment is winnowed from riffles and deposited in pools mantling the underlying substrate (Lisle and Hilton, 1992). Walling *et al.* (1999b) and Asselman (1999) showed that fine channel bed deposits accumulated during low flows and subsequently discharged during the opening periods of high flows. Channel bed composition also played an important role in this study with sandy beds having a more consistent accumulation and remobilisation pattern, whereas gravel bed sediments were only important in one or two events during the 20 year SSC record.

4. Field Sampling Methodology

4.1. Introduction

This chapter describes the field sampling methodology used in this project; it is divided into two sections detailing palaeolimnological reconstruction and contemporary sampling methods. Each section is sub-divided to address the components of a simplified sediment budget required by Objective 4; and is designed to provide a range of sediment samples from different parts of the fluvial system, for use in a sediment fingerprinting investigation (Objectives 1, 2 and 3). A summary of all of the methods used and their relevance to the Objectives of this project is shown in Table 4-1.

Table 4-1: A summary of the methods used in the thesis and their relevance to the projects objectives.

Method	**Location**	**Objective**	**Purpose**	**Timescale**
Historical reconstruction				
Reservoir sediment coring	Sywell Reservoir	Objective 1,2 & 3	Sediment yield reconstruction and historical sediment fingerprinting	*ca*. 1-100 years
Reservoir bathymetric survey	Sywell Reservoir	Objective 4	Sediment yield reconstruction	*ca* 1-100 years
On-line lake sediment coring	Stanwick Lake	Objective 1, 2, 3 & 4	Historical sediment fingerprinting	*ca*. 1-100 years
Floodplain coring	Earls Barton, Kingsthorpe, Stanwick and Upton	Objective 1, 2, 3 & 4	Historical sediment fingerprinting and floodplain sediment accumulation rate reconstruction	*ca* 1-100+ years
Contemporary monitoring				
Stage and turbidity monitoring	Dodford and Northampton	Objective 4	Quantification of sediment yield	15 minute frequency
Time integrated suspended sediment traps	Eight tributary sub catchments	Objective 1, 2, 3 & 4	Sediment fingerprinting of suspended sediment	Monthly
Channel bed re-suspension	Nineteen tributary sub catchments	Objective 1, 2, 3 & 4	Quantification of channel bed sediment storage, fingerprinting of channel bed sediment	Quarterly
Overbank sediment deposition	Seventeen locations on the Nene's floodplain	Objective 1, 2, 3 & 4	Fingerprinting of sediment sources during high flow events	Four overbank events during a one year period.

The field sampling methodology relating to the construction of a partial sediment budget was primarily devised to address the three requirements for a suitably robust sediment budget laid out by Parsons, (2012). Namely:

"First, no sediment budget should be produced without an explicit statement of the timescale over which it is purported to be valid, or without a demonstration of process stability over that timescale.

Second, no sediment budget should include unmeasured elements, the values for which are determined simply by subtraction on the assumption of budget closure.

Third, any sediment budget must provide estimates of uncertainty associated with any reported value." (Parsons, 2012, pp.68)

The first of Parsons' requirements were fulfilled by the use of a Palaeolimnological reconstruction to assess long term (~100 years) changes in sediment provenance and sediment yield in a representative lake catchment. Additionally changing sediment accumulation rates over a ~100 year timescale and sediment provenance were established at four locations on the Nene's floodplain. Contemporary monitoring and sampling aimed to cover a wide range of flow conditions and a sufficiently large spatial area to determine monthly - quarterly changes in sediment provenance and changes in sediment yield on a 15 minute basis. The sampling was performed over a total of a 22 month period to ensure a sufficiently long time period was sampled and to gain an indication of short-term process stability.

To address Parsons' second requirement an estimate of soil erosion in-field and field to channel deposition was omitted from the sediment budget as it was judged that such an estimate could not be reliably measured within the time available for this research project. A soil erosion model could have been used and the difference between predicted soil erosion and the measured sediment yield interpreted as sediment sequestration such as that described in Banasik *et al*. (2005) however, this would violate Parsons' second requirement. This does produce a limitation of this study in that sediment yield is the only estimate of soil erosion and connectivity, which must be considered in any interpretation of the results presented in later chapters.

Parson's third requirement is addressed in the following sections, which describe the sampling methods related to each part of the sediment budget, with a justification for the methods used, together with an explanation of how estimates of uncertainty were determined.

4.2. Study catchment

4.2.1. Catchment description

The Nene river basin is located in the East Midlands, UK. The river originates south of Daventry and flows through Northampton, Wellingborough and Peterborough. The basin has a total area of 1,634 km^2. Sampling was conducted in the upper – middle Nene basin upstream of Stanwick, with a total catchment area of 1060 km^2. The maximum elevation is 226m Above Ordnance Datum (AOD) decreasing to 40 m AOD at Stanwick (Figure 4-1), The catchment follows a trend of high and steeply sloped ground in the west, gradually moving to flat ground in the east close to Oundle (Figure 4-1). Catchment lithology is primarily Jurassic marine sedimentary deposits of silts and clays with some ironstone and limestone (Figure 4-2). Deposits of Quaternary sand and gravel are found adjacent to the main river channel, and glacial diamicton is found extensively at high altitude in the centre and north of the basin. The 2007 UK Land Cover Map indicates that the catchment land utilisation is 56% cultivated, 22% pasture and 9% urban (Figure 4-3). A comparison with the land cover of the catchment in the 1930s indicates that at that time the Nene basin was approximately 50% pasture and 25% cultivated land (Stamp, 1932). Therefore, a large change in catchment land utilisation has occurred over the previous 80 years. The catchment has an average annual rainfall of 638 mm recorded at Athorp over the previous 140 years (Figure 4-4). There is little evidence of any changes to the total annual rainfall during this period.

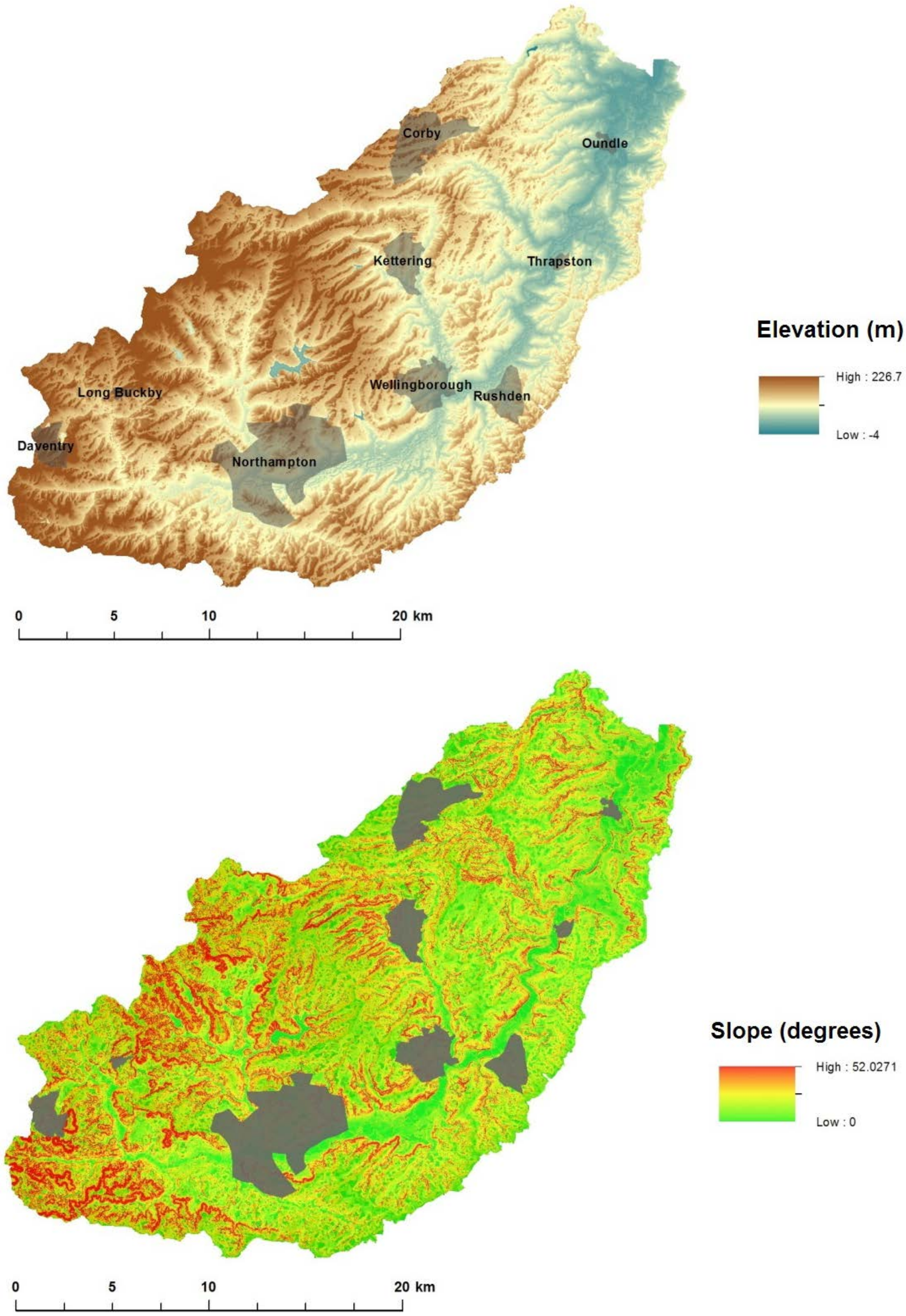

Figure 4-1: Elevation and slope of the terrain in the Nene basin.

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Figure 4-2: The Lithology of the Nene basin (British Geological Survey, 2011).

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Figure 4-3: Land Cover in the Nene basin in 1930s and 2007 (Stamp, 1932; Morton *et al*, 2011).

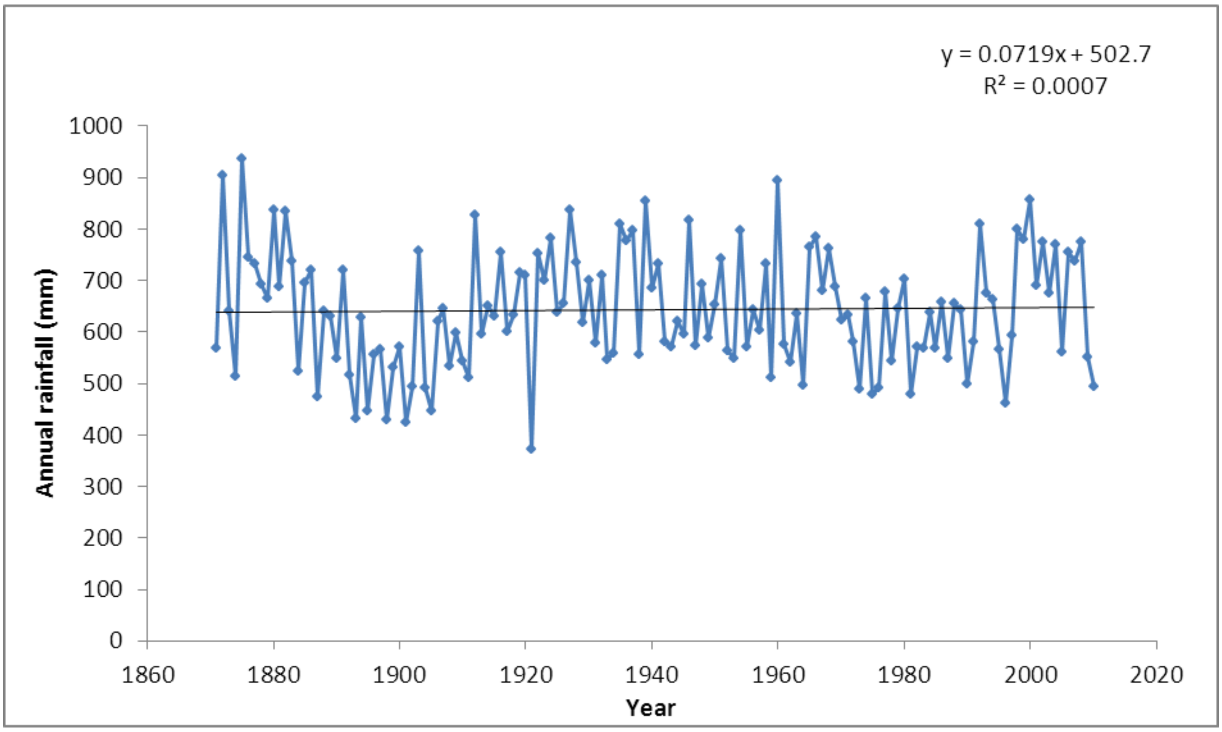

Figure 4-4: Total annual rainfall 1871 – 2010 recorded at Althorp.

The Anglian region catchment management plan (Environment Agency, 2009) reports that only 47% of surface waters in the catchment achieve good ecological and chemical status; of the reasons stated for the failures, fine sediment is suggested to be prominent although the extent of its role remains uncertain. Modifications to the river in the form of flood defences are highlighted as a major detrimental factor affecting water quality. Figure 4-5 shows the locations of the raised flood defences in the Nene river basin.

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Figure 4-5: The locations of raised flood defenses in the upper Nene river basin (Data courtesy of the Environment Agency Anglian Region).

4.2.2. Observed erosion and sediment delivery

Figure 4-6 shows photographs of the landscapes typical of the tributary catchments of the Nene basin. Cultivated land is predominantly separated from the channel by margins of grassland or woodland as show in Figure 4-6, A Figure 4-6, B, Figure 4-6, C and Figure 4-6, E. Grazed grassland is also mostly separated from river channels by a margin of woodland or riparian fencing. Where grassland was observed to be in contact with the river channel, the land was most commonly grazed by sheep with low stocking densities and little evidence of poaching or excessive erosion (Figure 4-6, A, Figure 4-6, F). However, some poaching can be observed in a few isolated areas (Figure 4-6, I). The river channel in much of catchment is shallowly incised with poorly defined channel banks (Figure 4-6, E), some sloped riparian zones are present but these are generally well vegetated (Figure 4-6, E). Evidence of channel bank erosion was visible in some river reaches in isolated areas. For example, Figure 4-6, G shows part of a stretch of channel bank in a wooded area with evidence of erosion accelerated by the presence of animal burrowing.

Some areas with a greater potential for sediment to enter the river were also observed. Figure 4-6, D shows part of a ~100m reach of channel where the river channel is deeply incised creating an easily eroded steeply sloping lightly vegetated face. Figure 4-6, J shows an artificial ditch located ~400m from any river channel however, it is connected via an underground pipe to a river channel. Numerous subsurface field drains from a neighbouring agricultural land enter the ditch, providing the potential for sediment transport to the river channel. An area of cultivated land in contact with the river channel is shown in Figure 4-6, K. This ~10m section of channel was also characterised by a deeply incised and bare channel bank showing evidence of erosion.


C
D
E
F
G
H

Figure 4-6: Photographs of the Nene basin, highlighting potential sediment sources and connectivity.

4.3. Palaeolimnological reconstruction

This section describes the methods used for historical Palaeolimnological reconstruction in this project. Figure 4-7 shows the locations of the sampling sites referred to in this section.

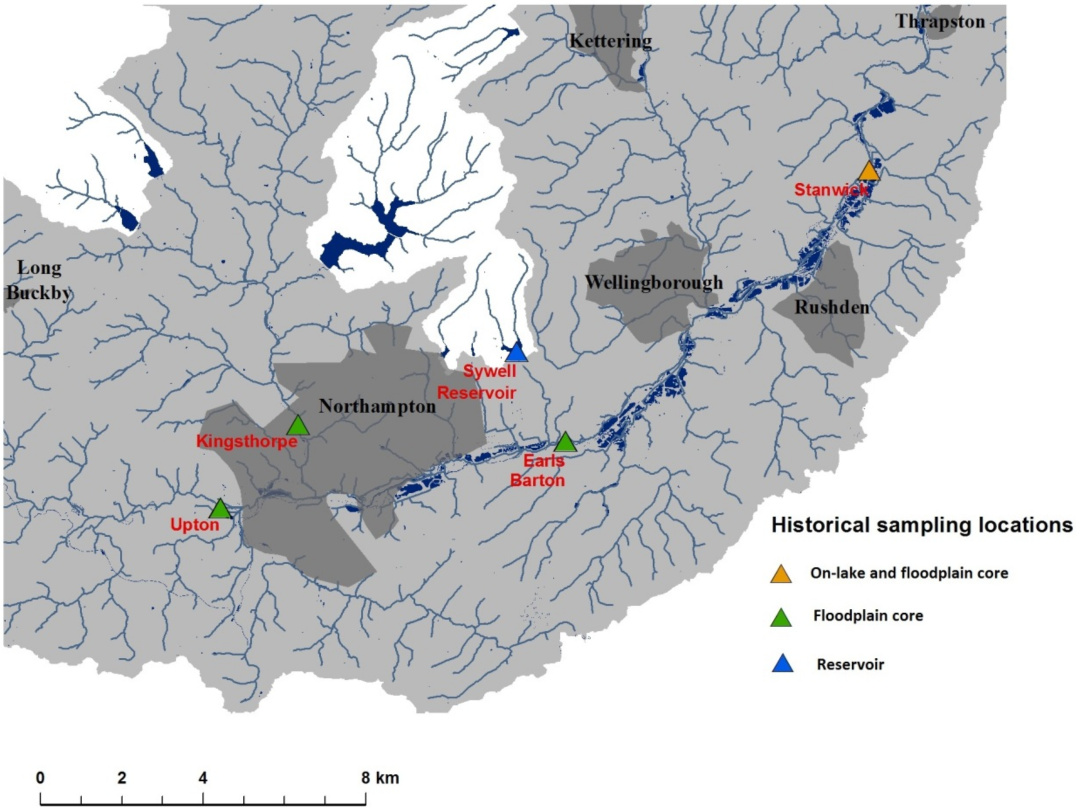


Figure 4-7: The locations of historical sediment sampling sites in the Nene basin (Surface water and town locations derived from Ordnance Survey (2009).

4.3.1. Sediment Yield

Sediment yield is a key part of a sediment budget and represents a simple figure to summarise overall sediment movement through a catchment. A discussion of its importance in a sediment budget and a list of reported estimates of sediment yields in the published literature are provided in Chapter 3.

In the UK a long term (decades to centuries) record of measured sediment yield is not available for the vast majority of catchments, meaning a surrogate source of data is required. Palaeolimnological data from depositional environments such as lakes and reservoirs represent the primary surrogate used in the literature (Foster *et al.*, 2012). As published Palaeolimnological data is currently unavailable in the Nene basin, a small lake catchment was investigated as part of this project.

The acquisition of Palaeolimnological data requires a lake with an undisturbed sediment record and with a sediment record representing a sufficiently long timescale (Foster *et al.*, 2011). In addition to these criteria, the lake catchment must also be representative of the headwater catchments of the Nene basin, trap the majority of sediment derived from catchment sources and contain a sufficient quantity of sediment for analysis. It has been shown that an increase in sediment yield in Europe is expected post-1950 (Foster *et al.*, 2011), making a minimum of 62 years accumulated sediment desirable for the purpose of assessing recent changes in sediment dynamics. Dearing and Foster, (1993) indicate that a lake – catchment ratio of ca. 30:1 in the UK generally provides both a high trap efficiency and a sufficient quantity of sediment to determine changing sediment yields in most UK catchments.

For this study, Sywell reservoir was selected as an appropriate lake catchment. It is located in the centre of the Nene basin (Figure 4-7). The catchment lithology consists of Jurassic age mudstone, sand and ironstones as well as Quaternary glacial diamicton as does much of the Nene basin as a whole. Land use has changed from being predominantly grassland in the 1930s to being dominated by cultivated land at present, as is the case in the Nene basin as a whole. On this basis the site was considered representative of headwater catchments in the Nene basin. Construction of Sywell reservoir was completed in 1906, providing a 105 year record of sediment deposition, which according to Foster *et al.*, (2011) is an adequately long record to determine sediment yield before and after the introduction of intensive agriculture in the 1950s, and evaluate decadal to century long changes. It has also been carefully managed since its construction as a water supply reservoir, so it could be ascertained through interviews with the park managers that the site had not been dredged, a key requirement of site selection (Dearing and Foster, 1993). The lake – catchment ratio is 31:1 falling close to the optimum identified by Dearing and Foster (1993) suggesting a good trap efficiency and that an adequate quantity of sediment will likely be present for analysis.

A total of 7 sediment cores were retrieved from the reservoir using a small inflatable boat and a ‘mini-Mackereth’ pneumatic corer (Mackereth, 1969) and the location of each core was recorded using a Garmin eTrex H handheld GPS (5m accuracy). The cores were collected in transparent Perspex tubes of *ca.* 5cm internal diameter and 1m length using the methods of (Foster and Walling, 1994) and were maintained in a vertical position during transport. Upon return to the laboratory, the cores were extruded and sliced into 1cm slices for analysis. Measurements of the wet density and dry density after oven drying at 40°C for each slice were recorded.

A bathymetric survey (Figure 4-8) of the reservoir was performed using echo sounding and a differential GPS in a series of nine transects (the work was performed with the assistance of Dr Jill Labadz, Nottingham Trent University, who also provided the echo sounder and differential GPS system used to locate echo sounding transects). Results were corrected to the maximum reservoir volume at the spill weir and extrapolated to produce a bathymetric map of the reservoir using ARC GIS 10 and the “topo to raster” function, based on Hutchinson and Dowling (1991).

The error associated with this estimate was explored by comparing the depths of sediment accumulated in the seven cores to produce an average depth of accumulated sediment and a standard deviation representation of variability.

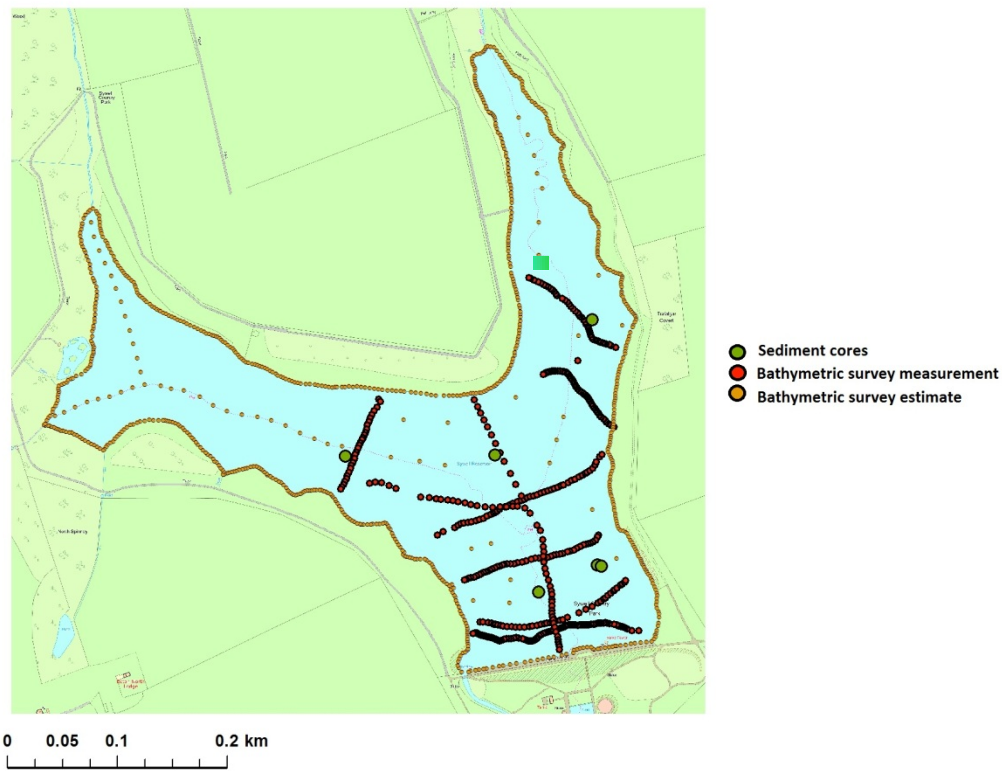


Figure 4-8: Coring locations in Sywell reservoir and the locations of the bathymetric survey measurements (Base map from Ordnance Survey (2013).

4.3.2. Historical sediment in a semi-cut off floodplain lake

Floodplain lakes have been used to investigate trends in historical suspended composition and sediment contamination (Foster *et al.*, 1998; Winter *et al.*, 2001). The term 'on-line lake' has been used to describe floodplain lakes which are in direct hydraulic contact with a river channel, and these receive sediment continuously during all flow conditions (Foster *et al.*, 1998) unlike 'offline lakes' which are only in direct contact with the river channel at high flow levels. To obtain a continuous record of suspended sediment a semi-cut off meander located at Stanwick was investigated (Figure 4-7). The location was selected to include all of the study area in the upstream catchment including the urban areas of Northampton, Wellingborough and Rushden.

Two cores were taken from the lake at the deepest point, determined using a plumb line. Cores were collected using a Perspex core tube of *ca.* 5cm diameter and 1m in length, manually pushed into the bed from an inflatable boat. The cores were maintained in an upright position during transport and the longest least disturbed core was prepared using the same methods as the reservoir cores.

4.3.3. Historical floodplain deposition

Overbank deposition on the floodplain represents both an important long term sediment store and a present day source of sediment, therefore its investigation can be regarded as a key part of a sediment budget (Walling *et al.*, 1999b) (For a discussion of the relevance of floodplain deposition in river catchments see section 3.4.2. In addition to the importance of floodplain deposition in a sediment budget, sediment movement during overbank flows also has numerous properties beneficial to determining sediment provenance. The most important property is that a large proportion of a catchment's total sediment movement often happens during brief overbank flows, providing a time effective period to sample a large proportion of a river's total sediment transport (Conaway *et al.*, 2012). Another major advantage of studying overbank flows is the greater connectivity and mixing provided by increased flow during these periods (Godfrey *et al.*, 2008). Therefore, a sediment sample taken from a floodplain is likely to be representative of the sediment derived from a large proportion of the upstream catchment (Macklin *et al.*, 1994; Bölviken *et al.*, 1996). However this does not mean that one flood can be considered representative of all overbank flows and sediment movement. Sediment movement during different flood events and rates of overbank sedimentation have been shown to be variable, with different sediment sources being mobilised during different periods of a single flood event, and during different flood events (Carter *et al.*, 2003). Sampling of floodplain sediment cores has been used to overcome these problems of intra flood variability and provide a general long term (<200yr) trend of changing sediment accumulation and provenance (Lambert and Walling, 1987; Owens *et al.*, 1999b).

A sediment core was retrieved from four locations on the Nene floodplain (Figure 4-7). These were selected to represent the different terrain types in the Nene basin and encompass the areas upstream and downstream of Northampton and Wellingborough. Four sites were investigated in order to provide a suitably robust indication of variability within the upper Nene basin. To ensure an adequately long and undisturbed record of sediment deposition, each site was investigated using historical maps and archival records to ensure that they had been both uncultivated over recent history and subject to regular flooding as suggested by Owens *et al.* (1999b) and Foster *et al.* (2011). This posed a significant challenge as many areas of the floodplain have been disturbed by the construction of a canal, construction of flood defences and by ploughing for agriculture.

Two cores were retrieved from each site using a steel percussion corer of ~ 6 cm diameter and 75 cm length. The core tube was manually driven into the floodplain surface using a sledge hammer and was retrieved using a tripod and chain hoist. On retrieval, the cores were retained in the corer during transport. Upon return to the laboratory the cores were extruded from the corer and the longest and least disturbed core was sectioned into 2cm intervals according to the method of Walling *et al.* (1999b), which aims to minimise the influence of short term flood events and focus instead at long term changes in sediment dynamics. The slices were dried at 40°C and the wet and dry density recorded.

4.4. Contemporary Monitoring

This section describes the methods used in the contemporary sediment sampling campaign of this project. Figure 4-9 shows the sampling locations referred to in this section.

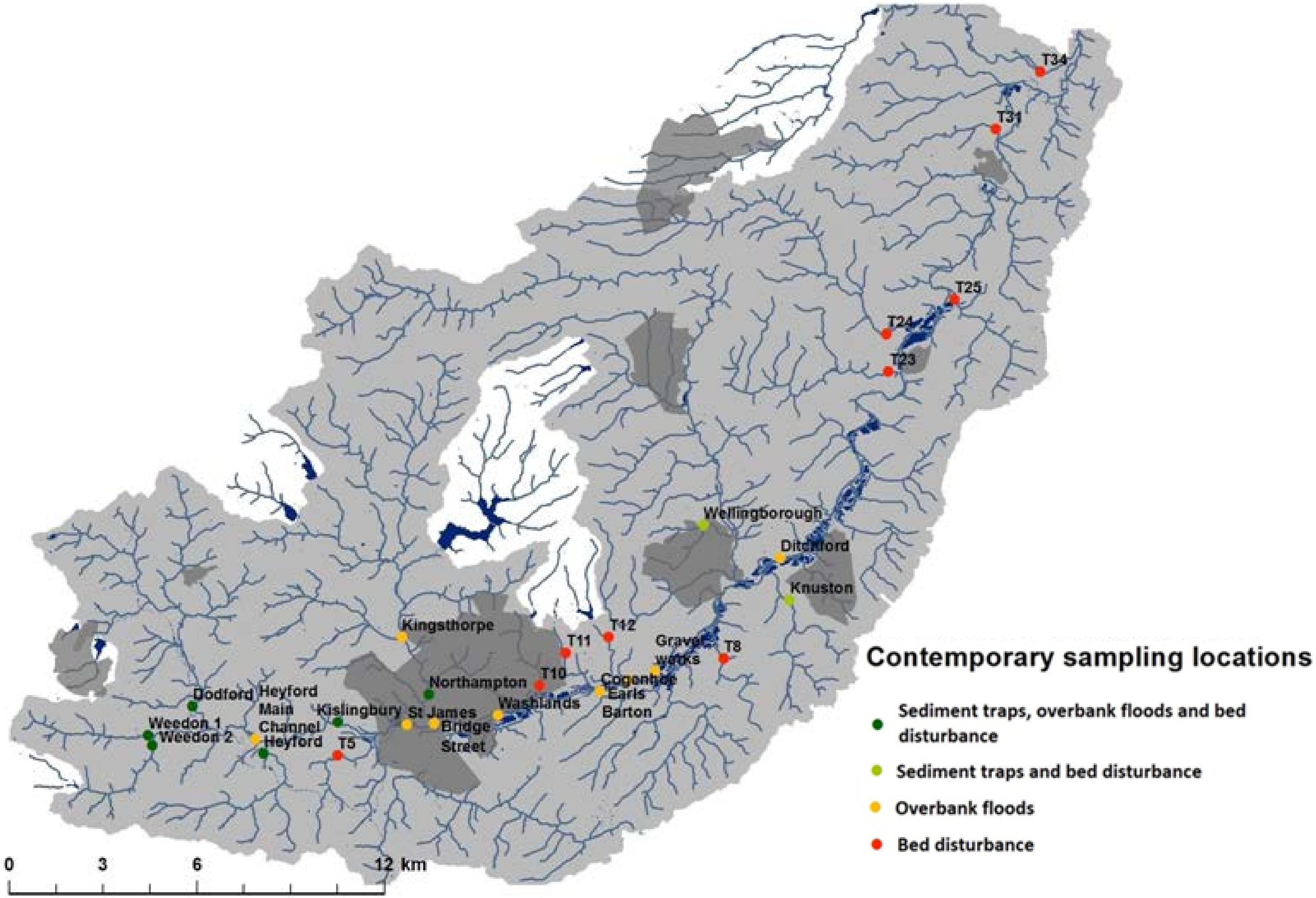


Figure 4-9: Locations of the contemporary fine sediment sampling sites (Surface water and town locations derived from Ordnance Survey (2009).

4.4.1. Stage and turbidity derived estimates of sediment yield

A disadvantage of Palaeolimnological data is the inability to examine the dynamics of individual storms or inter-storm periods. Sampling is also limited to locations where a suitable lake or reservoir is located. To overcome these limitations a continuous high resolution dataset of sediment discharge is required. Frequent manual sampling of suspended sediment combined with continuous flow measurement to produce rating curves has been used to estimate suspended sediment concentration (SSC) and create a record of suspended sediment discharge, such as those used in a 1967 - 1978 study of the Nene published by Wilmot and Collins (1981). However, this technique has the disadvantage of requiring a large number of samples over a series of high and low flow conditions, and not fulfilling this requirement can lead to a large underestimate or overestimate of sediment yield (Ferguson, 1987). Hysteresis effects can also give rise to poor rating curve regression models introducing a further source or error. Walling (1977) showed that errors of up to +280% can be encountered when estimating annual sediment yields using rating curves and of between -90% and + 900% when investigating monthly yields. The use of turbidity measurement provides an alternative to the production of rating curves. Turbidity meters are generally considered as being a more accurate means of deriving a record of SSC (Olive and Rieger, 1988; Lewis, 1996). Turbidity meters operate on the grounds that a calibration can be developed between measured turbidity and SSC, therefore an automated measurement of turbidity can act as a surrogate for very frequent manual sampling. However, limitations do exist with this method, as turbidity is not simply a measurement of SSC, rather it is a measurement of SSC, particle size and the optical properties of the river water. High productivity in river water has also lead to problems of algal growth and the fouling of sensors (Foster *et al.*, 1992).

To produce a near-continuous record of SSC sampled at 15 minute intervals, two Partech System 770 turbidity meters equipped with Partech IR-40 infrared turbidity sensors were installed in two of the Nene's major tributaries (Figure 4-10). Each sampling location was in an Environment Agency stage gauging station to provide a parallel 15 minute interval record of flow and turbidity. The sensors were fitted with covers to shield them from sunlight and limit algal growth; while this was somewhat successful, algal growth was still a problem and the record needed correcting at certain times of the year. To correct the data empirical mode decomposition (EMD) in the R statistics package based upon the method developed by

(Huang *et al.*, 1998) was used to remove the low frequency trend in the data resulting from algal fouling. An example of uncorrected and corrected data can be seen in Figure 4-11.

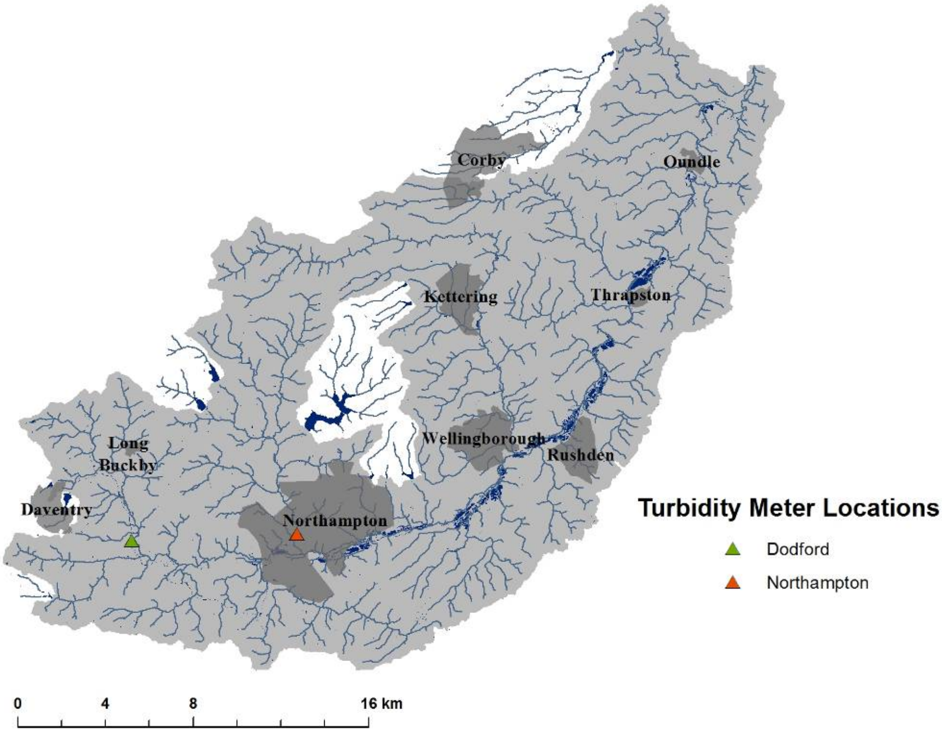


Figure 4-10: The locations and of the turbidity meters and stage gauging sites (Surface water and town locations derived from Ordnance Survey (2009).

Table 4-2 shows the dates of operation of each turbidity meter.

Table 4-2: The periods of operation of the two turbidity meters.

Site	Dates of operation
Dodford	September 2011 – August 2013
Northampton	February 2012 – August 2013

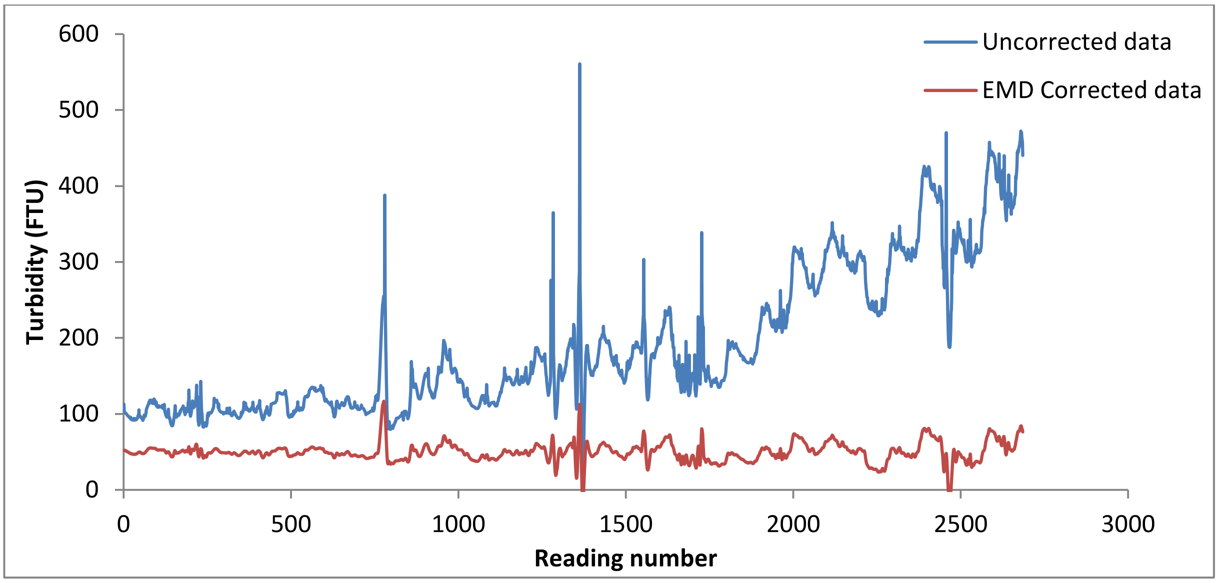


Figure 4-11: The effect of EMD correction on an example period of turbidity data affected by algal fouling

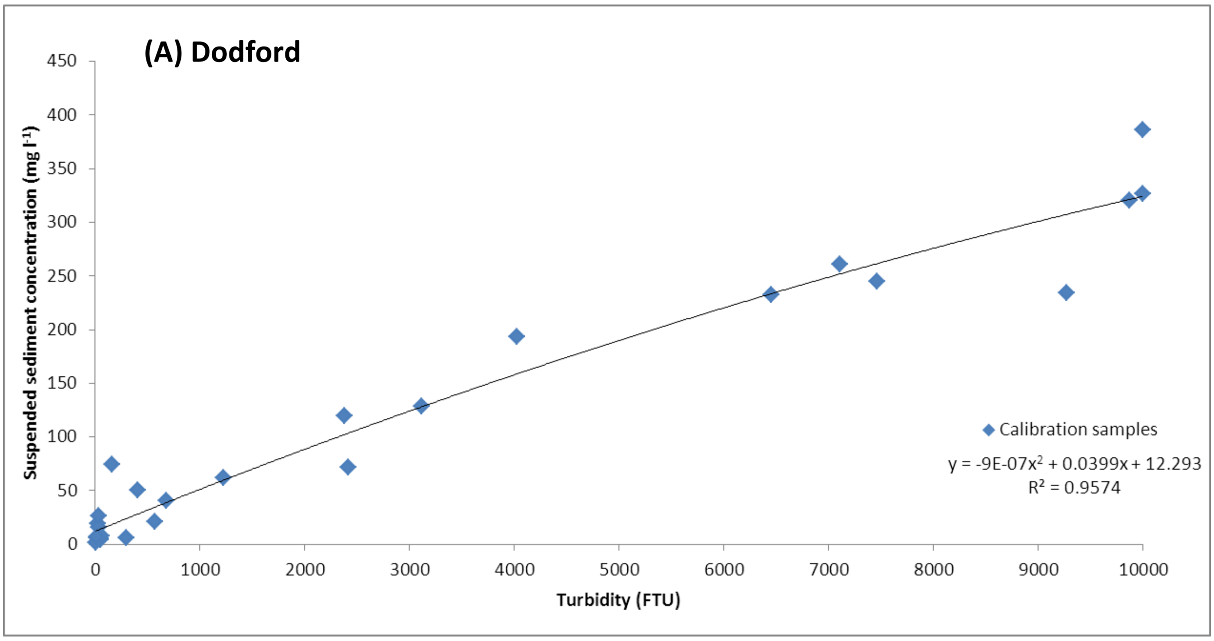
Calibrations between turbidity and SSC were established using 0.5l water samples taken from the river channel during a range of flow conditions and a range of seasons, to take account of seasonal changes in the optical properties of river water or changes in sediment properties, and to provide a sufficient range of calibration samples (Peart and Walling, 1982).

The SSC of calibration samples was determined by vacuum filtration as used by (Orwin and Smart, 2005). The bottles of water were filtered through pre-dried (at 105°C) and weighed Watman 0.45µm cellulose nitrate membrane filter paper. The resultant filter papers and sediment were dried (at 105°C) and re-weighed. SSC was calculated using Equation 4-1.

Equation 4-1:

SSC (mg l^{-1}) = (Filter paper and sediment weight (mg)- filter paper weight (mg)) / volume of sample (l)

The calibration curves developed for each meter are shown below in Figure 4-12.



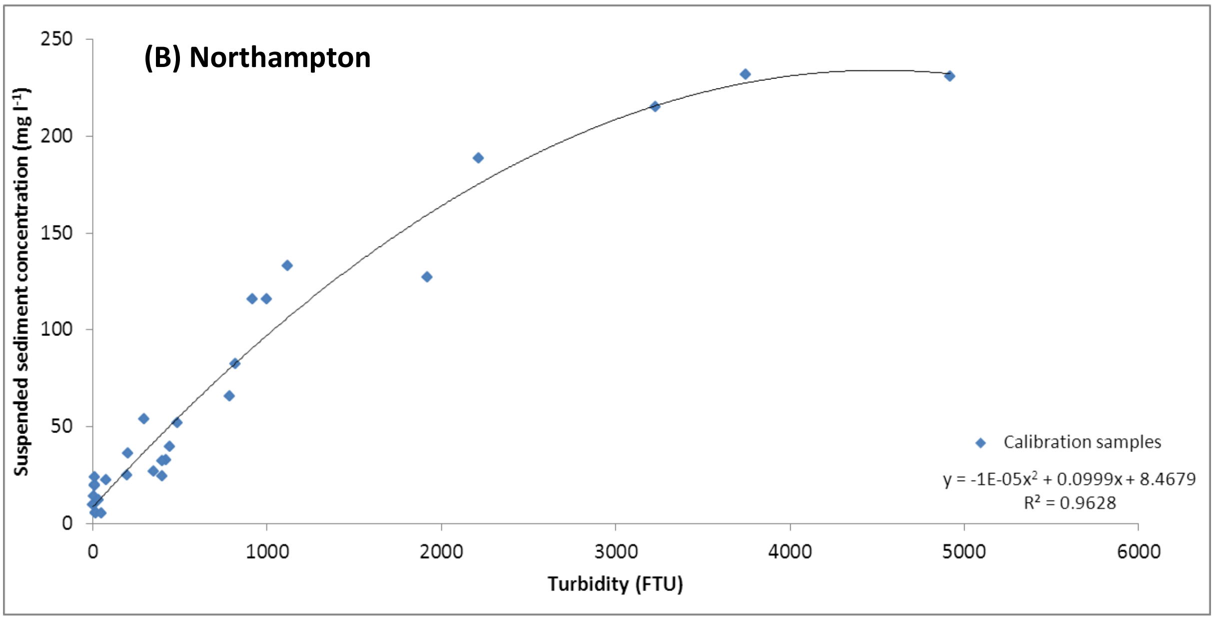


Figure 4-12: Polynomial calibration curves for the Dodford and Northampton turbidity meters.

Values above the calibration range of 9999 at Dodford were given the value of 300 mg l^{-1} and those above 5000 at the Northampton site were given the value of 250 mg l^{-1}. The figure of 9999 was the maximum at which the meter would record at Dodford and 5000 was the limit of the calibration samples at the Northampton site.

4.4.2. Contemporary suspended sediment sampling

A method was required to assess monthly changes in sediment provenance. A total of eight time-integrated suspended sediment traps were deployed across the catchment. The trap design was developed by (Phillips *et al.*, 2000) and is shown in Figure 4-13. They have been shown to effectively provide a suspended sediment sample under a range of flow conditions, and to effectively trap a sufficiently representative range of particle sizes for fine sediment investigation (Russell *et al.*, 2000). They have been successfully utilised in many sediment provenance investigations (Collins *et al.,* 2010; Smith and Blake, 2014). Alternative methods of sampling suspended sediment include the collection of bulk water samples Collins *et al.,* 1997), this method has the advantage that multiple samples can be fingerprinted in short succession, allowing for the identification of changing sediment sources over an individual flood event (Walling *et al*., 1999). However it does require the researcher to be present to collect the samples so limits the number of sites which can be investigated, and it requires the collection of logistically challenging volumes of water (50-300 l per sample).

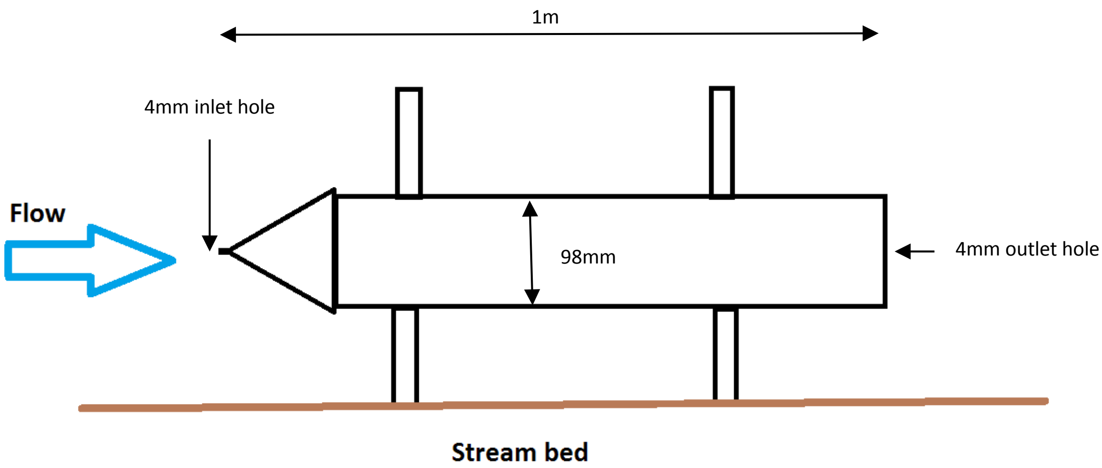


Figure 4-13: A time integrated sediment trap, as described by Phillips *et al*., (2000).

The locations of the traps were selected to cover a range of tributary sub-catchments with different geologies, land uses and topographies, while avoiding the navigable area of the Nene main channel. The locations of the traps are shown in (Figure 4-9). Each trap was emptied on a monthly basis into *ca.* 10 l plastic containers and returned to the laboratory for analysis.

Damage to traps due to high flows and vandalism meant that an uninterrupted record of samples throughout the study period was not obtained. The sites at Kislingbury and Dodford were particularly susceptible to high velocity flows and a disproportionate number of traps were lost from these sites. The range of data obtained for each trap is shown in Table 4-3.

Table 4-3: Number and timing of suspended sediment samples collected during the study period.

	Oct - Nov 2011	Nov - Dec 2011	Dec - Jan 2012	Jan - Feb 2012	Feb - Mar 2012	Mar - Apr 2012	Apr - May 2012	May - Jun 2012	Jun - July 2012	July - Aug 2012	Aug - Sept 2012	Sept - Oct 2012	Oct - Dec 2012	Dec - Jan 2013	Jan - Feb 2013	Feb - Mar 2013	Total
Weedon 1					1		1	1	1	1	1	1	1	1	1	1	11
Weedon 2	1	1	*	1	1	1	1	1	1	1	1	1	1	1	1	1	16
Dodford	1	1	1	1	1		1			1	1	1		*	1	1	12
Heyford				1	1	1	1	1	1	1	1	1	1			1	11
Kislingbury					1				1	1	1	1	1	*	1	1	9
Northampton		1			1	1		1	1	1	1	1	1	1	1	1	12
Wellingborough	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	15
Knuston	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	16
Total	4	5	4	5	8	5	6	6	7	8	8	8	6	7	7	8	79

*** Sample was collected as part of the next month's sample.**

4.4.3. Contemporary overbank sediment deposition

While sediment cores provide a record of long-term changes (<200 years) in sediment sources, an examination of sediment transported during single flood events was deemed necessary; firstly to assess inter-flood variability in sediment sources (Objective 4), and secondly due to the use of this sampling period in published sediment fingerprinting studies (Gruszowski, 2003) (Objectives 1,2 and 3). For a full discussion of overbank sedimentation see Section 3.4.2. Overbank sediment samples from four high flow events during the study period were collected once high water levels had receded to below bank-full. Sediment samples were collected from the leaves of vegetation as described by (Walling *et al.*, 1997). The primary vegetation selected was Common Comfrey (Symphytum *officinale) and* Common Nettle *(Urtica dioica)*. The vegetation was washed with native river water in a 5l plastic container, the resultant water and sediment was transported to the laboratory for analysis in 1 l Nalgene bottles. Figure 4-9 shows the locations of the sampling sites used and they were selected to cover the region of the Nene basin being sampled using suspended sediment traps, channel bed sampling and floodplain coring. The specific locations where samples were collected were determined by the presence of trapped overbank sediment.

4.4.4. Channel bed sediment storage

Channel beds represent an important store of fine sediment in a sediment budget (Objective 4). Not only is the degradation of channel bed habitats by fine sediment considered an important ecological issue (Collins *et al.*, 2010), but the stored sediment often represents a source of easily mobilised sediment, ready to be transported when flows increase (Walling and Amos, 1999). For these reasons channel bed sediment is commonly utilised in fingerprinting studies (Collins and Walling, 2007; Collins *et al*., 2013), and is necessary for the fulfilment of Objectives 1, 2 and 3. For a full discussion of channel bed sedimentation see Section 3.4.3.

The method developed by Lambert and Walling, (1988) was used to estimate the quantities of sediment stored on the bed of major tributaries, and provide a representative sample of channel bed material for further analysis. A total of 18 sites were sampled on a quarterly basis from the period June 2011 to April 2013, for a total of 7 repetitions (Table 4-4). An alternative method which is commonly utilised is the deployment of gravel traps such as used by Petticrew *et al.,* (2007), which can be used to better quantify the rates of sediment infiltration into gravel river beds. However due to the absence of a deep layer of gravel in many of the Nene's tributaries, and the requirement of this project only to quantify sediment storage, these were not utilised.

Table 4-4: Periods of bed disturbance sampling.

Sampling Period
June 2011
September 2011
January 2012
June 2012
September 2012
January 2012

Sampling was performed as close to the confluence of major tributaries and the main channel as accessibility allowed, while avoiding back water effects. Sampling locations are shown in (Figure 4-9). Conventionally, the bed disturbance method has been used on a combination of riffles and pools (Owens *et al.*, 1999a), or as a pair of samples in the centre and edge of a channel (Collins and Walling, 2007a). In the case of the Nene, the narrow width of tributaries, obscured river bed and highly variable channel bed morphology made these methods unsuitable. Therefore sampling was performed in the centre of each river channel reach.

A cylinder with a surface area of *ca.* 0.2 m^2 was pushed into the river bed creating a seal between the cylinder and bed and the depth of water was recorded. The bed within the cylinder was then disturbed to a depth of 5 cm using a wooden pole and two 0.5 l subsamples were immediately taken from the water within the cylinder. Three repetitions were performed within the *ca.* 30 m reach of river at each sampling location to provide an indication of local variability. Sediment stored on channel beds was calculated using Equation 4-2.

Equation 4-2: Calculation of sediment storage on channel beds.

$$Scb=(Sb/Vb)*Vt$$

Where Scb=sediment storage on the channel bed (kg m^{-2}), Sb= mass of sediment in the bottle (Kg), Vb= volume of bottle (litres), Vt= Volume of sampling tube (litres).

The sampling methodology used has the disadvantage of not taking into account the full temporal and spatial variability of the sediment residing on the channel beds (Collins and Walling, 2007b). It was however expected that multiple repetitions spaced evenly over the study period and spread over the Nene basin, would provide a representative picture of temporal and spatial variability.

4.5. Sediment source sampling

Sediment sources in published fingerprinting studies are most frequently classified by land utilisation (see Section 3.3 for a discussion of major sediment sources). Lithology has also been determined to be an important factor affecting tracer concentrations and has been utilised as a classification of sediment sources (Owens *et al.,* 1999b). The major sediment source types selected in the Nene were agricultural surface sources, channel banks and urban street dusts, as these have been shown to be the major contributors to in-stream sediment (Walling *et al.*, 1999a; Carter *et al.*, 2003; Walling *et al.*, 2006). However as lithology was identified to be a potential control on tracer measurements (Section 2.3) the source sampling was structured to include a representative range of lithologies present under each source group.

Sampling took place over a period of 12 months to account for any seasonal variability in source type properties (Carter *et al.*, 2003). The locations of the samples collected are shown in Figure 4-14 and the number of samples for each source group and their distributions over the various lithologies of the Nene basin are shown in Table 4-5.

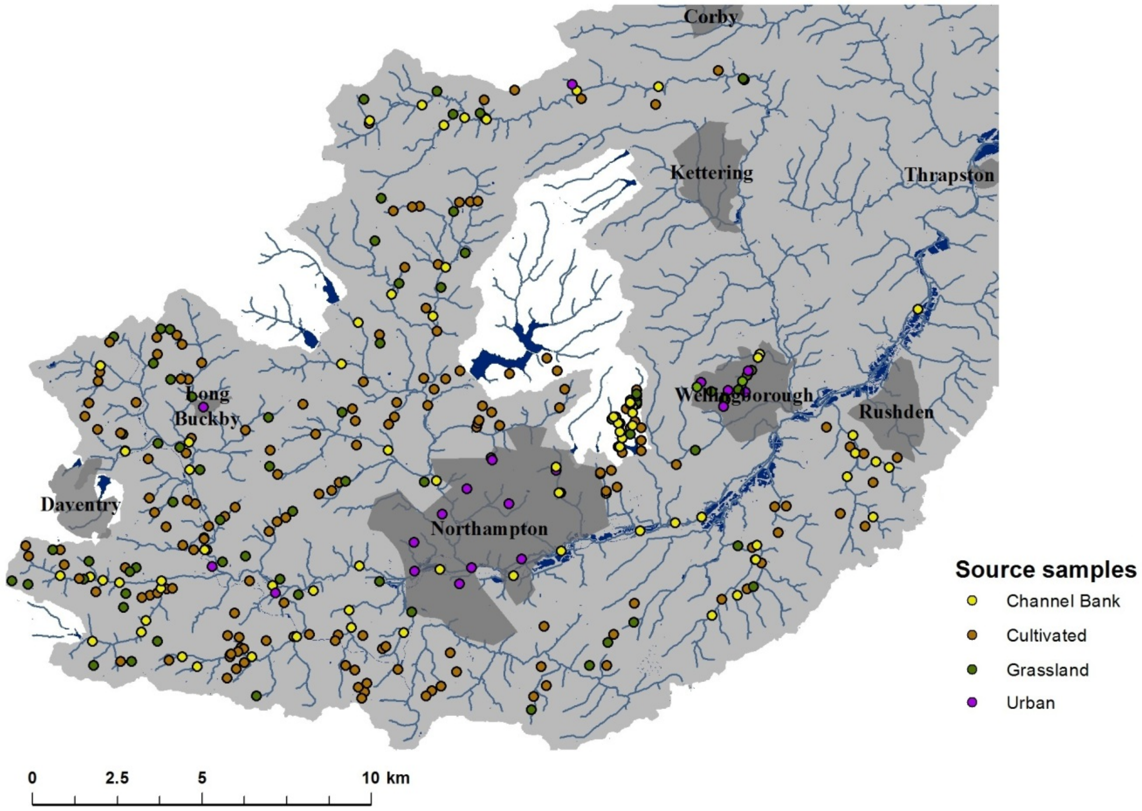


Figure 4-14: The locations of sediment source sampling (Surface water and town locations derived from Ordnance Survey (2009).

Table 4-5: The lithological and land cover distribution of source sampling.

	Total	Clay Silt Sand Gravel	Diamicton	Disturbed land	Ferrugnious Lime and Ironstone	limestone	Marlstone	Mudstone	Sand and Gravel	Sand and Ironstone	Sandstone Siltstone and Mudstone	Silts and Clays	White Sands	Unclassified
Surface agricultural sources (total)	247	21	43	5	2	12	15	53	22	39	1	26	3	5
Surface agricultural sources (Cultivated land)	173	14	34	5	1	10	14	37	12	25	1	18	2	0
Surface agricultural sources (Grassland)	74	7	9	0	1	2	1	16	10	14	0	8	1	5
Channel Banks	65													
Urban street dusts	21													

- Lithology was not considered a controlling factor on the composition of urban street dusts.
- Channel bank samples were collected on the basis of collecting a range of samples for each tributary sub-catchment investigated.

Samples of topsoils were collected from the top 2 cm of the surface using a non-metallic trowel (Carter *et al.*, 2003). Each sample was composed of an amalgamation of five sub samples taken from within a 15 m radius of a randomly selected sampling point, to further increase the representativeness of the source sampling (Collins *et al.*, 2010). Urban street dust was collected using a dustpan and brush from the material deposited at the side of a range of major and minor roads. Channel bank samples were collected from the lower and middle bank horizons of a visibly eroding channel bank. The outermost exposed 2cm of material were removed prior to sampling, in order to minimise contamination from displaced surface material or deposited fluvial sediments.

4.6. Summary

- Sampling was structured around the formation of a partial sediment budget (Objective 4) and to provide sediment samples to be used in the sediment fingerprinting investigation (Objectives 1, 2 and 3).

- Each part of the sampling methodology was structured to fulfill the requirements laid out by Parsons (2012) to produce a suitably robust sediment budget.

- Table 4-6 summarises the methods used, the sampling frequency, the sampling periods and the number of samples obtained in this project.

Table 4-6: A summary of the sediment sampling methodology.

Part of Budget	Context	Methodology	Number of Sites	Sampling Frequency	Dates of Operation
Sediment Yield: Reservoir catchment	Historical	Reservoir Cores and Bathymetric Survey	1	n/a	n/a
Sediment Yield: Turbidity	Contemporary	Turbidity Meters	2	15 Minutes	Dodford = Sept 2011 – April 2013 Northampton = Jan 2012 – April 2013
Suspended sediment	Historical	Cores from a semi cut-off meander	2	Once - Twice	n/a
Suspended sediment	Contemporary	Time integrated Sediment traps	9	Monthly	Oct 2011 - April 2013
Floodplain storage	Historical	Floodplain cores	4	Once - Twice	n/a
Overbank flows	Contemporary	Washing vegetation	16-20	Four times	April 2012, July 2012, October 2012, November 2012.
Channel Bed storage	Contemporary	Bed disturbance experiments	19	Quarterly	June 2011 – February 2013

5. Laboratory and sediment fingerprinting methodology

5.1. Introduction

This chapter begins by describing the methods used to measure the organic matter content, particle size distribution and tracer concentrations of the sediment and source samples. It then details the statistical procedure used to derive the optimum fingerprints for the un-mixing models. It concludes by describing the composition of the mathematical un-mixing model used. The methods described are relevant to Objectives 1, 2 and 3 addressing sediment fingerprinting. The sediment fingerprinting results were then used to determine sediment provenance as part of the sediment budget constructed for Objective 4.

5.2. Sample preparation

Upon return to the laboratory, sediment samples were initially de-watered by settling overnight, followed by decanting and pipetting off surplus clear water. The sediment was then oven dried at 40°C. A 40°C temperature was selected to minimise possible thermal changes to the mineral magnetic properties of the sediment which were used as fingerprint signatures (Dearing, 1999). The source and sediment samples were then gently manually disaggregated using a pestle and mortar. Source samples were sieved to <63µm to conform to common practice in sediment provenance studies, aimed at reducing potential impacts of differences in particle size on tracer concentration (Koiter *et al.*, 2013).

5.3. Particle size distribution and organic matter content

The particle size characteristics of the source and sediment was represented by the measure of specific surface area (SSA) and the organic matter content was measured as loss on ignition (LOI). These measurements have been utilised as the basis for corrections in many published sediment provenance studies. For a discussion of their use see Section 2.5. The following two sections explain how these were measured and the reasoning behind the choice of method used.

5.3.1. Particle size distribution

Suspended sediment particles in rivers have often been shown be transported as large composite particles (aggregates) rather than as discrete particles (absolute particle size)

(Walling and Woodward, 2000). It was determined that sediment in the Nene is primarily transported as discrete particles; therefore absolute particle size was selected as the most meaningful means of quantifying particle size distribution and correcting for the effects of particle size on fingerprint properties (Woodward and Walling, 2007). The majority of fingerprinting studies utilising particle size corrections use hydrogen peroxide to remove organic matter and chemical dispersion to further disaggregate particles (Collins *et al.*, 1997a), as the aggregation of particles by organic matter can lead to the underestimation of fine particle size fractions (Di Stefano *et al.*, 2010). The removal of organic matter using hydrogen peroxide, followed by chemical dispersion was selected to assess the absolute particle size distribution of the samples collected in the Nene catchment. Organic matter in the samples was first removed using 10 ml of 30% hydrogen peroxide added to ~ 0.1 g of soil or sediment. The samples were left for 24 hours at room temperature and then heated at 70°C until bubbling had stopped; 5 ml of 3% sodium hexametaphosphate solution was then added to the cooled samples and left to stand for 2 minutes before analysis (Gray *et al.*, 2010).

Laser granulometry was used to measure the particle size distribution of the source and sediment samples. A number of methods exist for quantifying < 63µm particle size distribution including: microscopy, sedimentation techniques, optical and electrical sensing zone methods and laser light scattering techniques (*ie*. laser granulometry). Sedimentation methods using pipette or hydrometer based analysis have been commonly used in published literature (Galehouse, 1971; Plumb, 1981). These methods have a number of requirements which must be carefully controlled for such as: temperature to avoid convection currents, concentrations of sediment used must be low enough to avoid interactions between particles and the density and shape of all of the sediment particles are assumed to be equal (Konert and Vandenberghe, 1997). These methods are also very time consuming and require large samples *ca.* 10-50 g (Di Stefano *et al.*, 2010). Laser granulometry has the advantage of very fast analysis time (typically <5 minutes per sample), it requires no manual calibration and can quantify a wide range different sized particles. The technique has also been shown to have a higher accuracy and better reproducibility then sieving and pipette sedimentation alternatives (Konert and Vandenberghe, 1997). A drawback of laser granulometry is that any estimate of SSA assumes that sediment particles are spherical and measurement occurs only in two dimensions, so particle size is calculated using cross sectional area. As a result it has been argued that this method underestimates the clay particle size fraction (Loizeau *et al.*, 1994). Given its advantages and the availability of laser granulometry at the University of Northampton it was selected for use in this study.

The sediment and source samples were added to 500 ml Type 1 ultrapure water in a Malvern Hydro 2000 unit, where the sample was subjected to two minutes of ultrasonic dispersion immediately prior to analysis (Blott *et al.*, 2004). Each sample was measured for a total of 60 seconds at 8-12% obscuration (Blott *et al.*, 2004), using a Malvern Instruments laser granulometer, and the characteristics in Table 5-1 were recorded. Due to time constraints each sample was only analysed once; however, preliminary tests of the methodology confirmed consistency between the results of three consecutive repetitions.

Table 5-1: Particle size sorting characteristics as used by Foster *et al.* (2008).

Measurement	Description and units
D10	The 10th percentile (µm)
D50	The 50th percentile (µm)
D90	The 90th percentile (µm)
Span	A sorting index defined as (D90-D10) / D50
Specific Surface Area (SSA)	A measure of the surface area of the whole particle size distribution based on the assumption that all particles are spherical ($m^2\ g^{-1}$)

5.3.2. Organic matter

Loss on ignition (LOI) is the most common method to quantify the organic content of soils and sediments utilised in the majority of sediment provenance studies (Collins *et al.*, 1997). Loss on ignition has the disadvantage that water can be lost from clay minerals during heating, resulting in an overestimation of organic content. As a result LOI can only be considered a semi-quantitative technique (Dankers, 1983). A more accurate estimation of organic content can be derived using wet oxidation followed by titration with ferrous ammonium sulphate or combustion followed by the collection and measurement of evolved carbon dioxide (Schumacher, 2002) as used by Smith and Blake (2014). Heiri *et al.*, (2001) found that a reasonably consistent result (~2% error) could be obtained using LOI, providing a consistent sample mass, temperature and heating time were used. For this reason, and the insufficient time available for the use of a wet oxidation technique, LOI was selected as a measurement of organic matter in soils and sediments.

High temperature LOI has been demonstrated to be unsuitable on highly carbonaceous soils and can lead to the liberation of water from clay minerals (Ball, 1964). For this reason, low temperature LOI was used following the method of Grimshaw *et al.*, (1989). Ceramic crucibles were heated in an oven at 105°C to remove any residual moisture and their mass was recorded to three decimal places of a gram. One to two grams of sample was weighed into each crucible and oven dried at 105°C for 2 hours and the mass of the sediment and crucible together were recorded. The full crucibles were placed in a Carbolite muffle furnace at 450°C for 4 hours. The hot crucibles were allowed to cool for 5 minutes in a desiccator before the crucibles were weighed again. Loss on ignition was calculated using the following formula.

Equation 5-1: Loss on ignition

Loss on Ignition (%) = (pre-ignition weight - post–ignition weight) / pre-ignition weight) *100

5.4. Analysis of Tracers

The tracers used in this study were selected on the basis of being the most commonly utilised in published sediment provenance studies (D'Haen *et al*., 2012) . For a full discussion of the tracer groups used, with reference to published literature, see Section 2.3.

5.4.1. Mineral magnetic signatures

The measurement of mineral magnetic signatures in this study used ca. 10g of the prepared source and sediment samples packed tightly to a depth of ca. 2 cm in 10ml sample pots. The measurements performed, equipment used and relevant calculations made, are shown in Table 5-2 and follow the protocols laid out by (Lees, 1997). The analyses were performed in the order in which they appear in the table.

Table 5-2: Magnetic measurements used as by Foster *et al*., (2008), measurements highlighted in bold were used as fingerprinting tracers.

Property	Measured (M) or Derived (D)	Units	Instrument / calculation used
Low frequency susceptibility (χ_{lf})	M	10^{-6} m^3 kg^{-1}	Bartington Instruments MS2b sensor (470 Hz)
High frequency susceptibility (χ_{hf})	M	10^{-6} m^3 kg^{-1}	Bartington Instruments MS2b sensor (4700 Hz)
Frequency dependant susceptibility (χ_{fd})	D	10^{-9} m^3 kg^{-1}	$((\chi_{lf} - \chi_{hf})/m)*100$ (m = sample mass)
Anhysteretic Remanent Magnetisation ($ARM_{(40\mu T)}$)	M	10^{-3} Am^2 kg^{-1}	Molspin® anhysteretic remanent magnetiser, Molspin® slow-speed spinner magnetometer
Saturation Isothermal Remanent Magnetisation (SIRM)	M	10^{-3} Am^2 kg^{-1}	Molspin® pulse magnetiser, Molspin® slow-speed spinner magnetometer
Soft Isothermal Remanent Magnetisation ($IRM_{(-100mT)}$)	M	10^{-3} Am^2 kg^{-1}	Molspin® slow-speed spinner magnetometer
Susceptibility of ARM (χ_{arm})	D	10^{-6} m^3 kg^{-1}	ARM x 3.14 x 10
S Ratio	D	Dimensionless	-1 x (IRM_{100mT} / $IRM_{0.88T}$
Hard Isothermal Remanent Magnetisation (HIRM)	D	10^{-3} Am^2 kg^{-1}	IRM_{1T}/(1-Sratio))/2

Ten repeat measurements of ten individual sub-samples of sediment were performed to estimate magnetic signature measurement errors. Each sample was removed from the sample container and randomised in a pestle and mortar between measurements. The average measurement and standard deviation was calculated for each sample and used to calculate the coefficient of variation in Table 5-3. The average coefficient of variation of all ten sub samples was used to quantify the error associated with the tracer measurement.

Table 5-3: Established measurement errors for magnetic susceptibility and remanence measurements.

	Low frequency susceptibility (10^{-6} m^3 kg^{-1})				Frequency dependant susceptibility (10^{-9} m^3 kg^{-1})		
Sample	**Mean**	**Standard deviation**	**Coefficient of variation (%)**		**Mean**	**Standard deviation**	**Coefficient of variation (%)**
Sediment trap December – January 2012 Northampton	0.42	0.004	0.9		19.54	3.54	18.1
Sediment trap September – October 2012 Kislingbury	0.37	0.003	0.79		15.53	2.19	14.12
Bed sediment September 2012 Knuston	0.15	0.003	2.23		4.62	4.87	105.45
Upton floodplain core slice 4	0.23	0.001	0.63		3.23	1.73	53.50
November flood Ditchford	0.53	0.005	1.02		26.87	1.93	7.17
Sediment trap December – January 2012 Wellingborough	1.25	0.006	0.47		49.35	1.58	3.21
Bed sediment September 2012 Northampton	0.86	0.004	0.41		28.47	4.86	17.06
Stanwick floodplain core slice 24	0.30	0.001	0.40		16.94	2.22	13.11
October flood Heyford	0.26	0.002	0.75		9.16	3.60	39.34
Sediment trap January – February Weedon 1	0.25	0.001	0.41		10.44	0.77	7.35
Average			.80				15.59

	Saturation Isothermal Remanent Magnetisation (10^{-3} Am^2 kg^{-1})				Soft Isothermal Remanent Magnetisation (10^{-3} Am^2 kg^{-1})				Hard Isothermal Remanent Magnetisation (10^{-3} Am^2 kg^{-1})		
Sample	**Mean**	**Standard deviation**	**Coefficient of variation (%)**		**Mean**	**Standard deviation**	**Coefficient of variation (%)**		**Mean**	**Standard deviation**	**Coefficient of variation (%)**
Suspended March – April Northampton	6.22	0.47	7.58		4.73	0.46	9.79		0.74	0.02	2.73
Suspended May - June Heyford	3.39	0.04	1.20		2.48	0.06	2.38		0.46	0.02	4.56
November flood Ditchford	6.59	0.08	1.16		5.04	0.10	1.97		0.78	0.04	5.66
October Flood Heyford	3.03	0.03	0.85		2.12	0.04	1.93		0.46	0.03	6.15
Stanwick floodplain core slice 24	2.41	0.01	0.55		1.78	0.02	1.29		0.32	0.01	4.48
Upton floodplain core slice 4	2.67	0.01	0.45		1.71	0.05	2.81		0.48	0.02	4.75
Average			**1.96**				**3.36**				**4.72**

5.4.2. Radionuclides

Radioactive decay can result in the emission of alpha, beta particles and gamma rays. Gamma rays are the most commonly measured in sediment due to the practical constraints of measuring alpha and beta particles which are easily blocked by air or solid matter (Wallbrink *et al.*, 2003). Radionuclide activity in this study was determined by high resolution, low-level gamma spectrometry using Ortec hyper-pure germanium (HPGe) detectors as used by Foster *et al.* (2007) and based on the methods described by Gilmore

(2008). Hyper-pure germanium (HPGe) gamma detectors provide a measurement of gamma decays of elements at known decay energies, measuring activity concentrations of specific radionuclides. Liquid-scintillation counting can provide better detection efficiency but lower resolution and is most commonly used to measure beta decay, so was not employed in this research (Papastefanou, 2009).

Samples of source and sediment of *ca.* 3 g were packed to a depth of 4 cm in PTFE sample pots and sealed with a turnover cap and paraffin wax. They were left to equilibrate for a minimum of 21 days to allow for in-growth of ^{222}Ra (Pennock and Appleby, 2002). A summary of the radionuclides measured in this study is provided in Table 5-4.

Table 5-4: A summary of radionuclides used as environmental tracers in this thesis (after Foster *et al.*, 2007).

Isotope	Half Life	Origin	Measured Decay energy (Kev)	Notes
^{137}Cs	30yr	Anthropogenic: Fallout from high-yield thermonuclear weapons tests	661.62	First detectable occurrence 1954, peaks in 1963 & 1986 (Cambray *et al.*, 1989)
^{210}Pb$_{un}$	22.3 yr	Atmospheric fallout Primordial	46.52	Atmospheric from ^{222} Rn (Radon Gas) ^{226}Ra is formed from the ^{238}U decay series.
^{234}Th	24.1 day	Primordial	63.29	^{238}U decay series
^{235}U	7.04 x 10^8 yr	Primordial	185.72	^{235}U decay series
^{214}Pb	26.8 min	Primordial	295.22, 351.99	^{238}U / ^{226}Ra decay
^{228}Ac	6.14 hr	Primordial	338.40, 911.07	^{232}Th decay series
^{212}Pb	10.6 hr	Primordial	238.63, 300.09	^{232}Th decay
^{40}K	1.28 x 10^9 yr	Primordial	1460.75	Primordial

Samples were measured for a minimum of one day (>86,400s) and the resulting spectra were analysed by calculating the number of photon counts at each decay energy. The area of each peak was manually identified using Ortec Gamma Vision software, version 6.08. The results were corrected for detector efficiency, background interference, sample mass, surface area and storage time.

The measurement error of each tracer was determined using the error associated with the calculated net area of each radionuclide decay peak, which was provided by the Gamma Vision software. The used values were derived as an average of the 253 samples measured at the time of calculation, results are presented in Table 5-5.

Table 5-5: Error associated with radionuclide activity measurements.

	Average Coefficient of variation
$^{210}Pb_{un}$	3.61
^{226}Ra	4.32
^{137}Cs	14.79
^{228}Ac	7.23
^{40}K	3.60
^{234}Th	11.45
^{235}U	10.47
^{212}Pb	1.25

5.4.3. Geochemistry

Five commonly utilised methods exist for the measurement of geochemical tracers, inductively coupled plasma (ICP) atomic absorption spectroscopy (ICP-AAS), ICP optical emission spectroscopy (ICP-OES), ICP mass spectroscopy (ICP-MS) and X-ray fluorescence (XRF). ICP-AAS limits analysis to one element at a time and is not as sensitive as ICP-OES (Fassel and Kniseley, 1974) so was not used in this study. ICP-OES has an extensive record of use in published fingerprinting studies; however ICP-OES is often affected by spectral overlap requiring the careful examination of resulting spectra. It is also not as sensitive at low element concentrations as ICP-MS due to spectral overlap creating a continuous background (Olesik, 1990). ICP-MS has as a result been utilised heavily in sediment fingerprinting studies (Collins and Walling, 2007c). ICP-OES however is less expensive, and is available at the University of Northampton and for this reason the method was selected for this study.

Results obtained by ICP-based methods and energy dispersive X-ray spectrometry have been shown to be almost comparable (Alomary *et al.*, 2012). X-ray based methods have the disadvantages that samples must be homogenously distributed throughout the cross sectional area to be measured and penetration of X-rays into sample material is limited to near the surface of sediment particles. They can also exhibit poor detection of elements with atomic weights lower than Sodium. These methods are however non-destructive unlike ICP based methods (Shackley, 2011) and have been successfully utilised in sediment fingerprinting studies (Smith and Blake, 2014).

For the preparation of samples in this study, approximately 0.8 g $^{+}/_{-}$ 0.05g of sample was weighed into tetraflouromethacrylate (TFM) vessels. Microwave digestion in *aqua regia* has been shown to extract a greater percentage of the total metal content of a sample than alternatives, such as *aqua regia* digestion on a hotplate (Chen and Q Ma, 1999) and microwave and hotplate nitric acid digestion (Tighe *et al.*, 2004) . While the method is not as effective as microwave digestion with hydrofluoric acid combined with *aqua regia* it does remove the need to use hazardous Hydrofluoric acid which was avoided for health and safety reasons. Therefore, a mixture of 2ml 70% analytical reagent grade nitric acid, 6ml 37% analytical reagent grade hydrochloric acid and 2ml type 1 ultrapure water was added to each tube to form the *aqua regia* digestion fluid (Chen and Q Ma, 1999). The samples were digested by microwave digestion in a CEM Mars 6 digestion unit using the digestion procedure outlined in Table 5-6.

Table 5-6: Breakdown of the microwave digestion temperature, power and heating time.

Stage	Temperature (°C)	Power (watts)	Duration (minutes)
1	Ramp to 120	1000	8
2	Hold at 120	1000	3
3	Ramp to 170	1500	10
4	Hold at 170	1500	3
5	Ramp to 180	1500	4
6	Hold at 180	1500	20
7	Cool	n/a	20

The digested samples were diluted to 50ml in volumetric flasks using Type 1 ultrapure water and after a period of settling for *ca.* 5 minutes, a subsample was decanted into 10ml polypropylene centrifuge tubes for analysis. Samples were analysed using a Thermo iCAP 6500 Duo View ICP-OES. A range of 30 samples randomly selected from a number of sampling sites were initially analysed with a 1 mg kg^{-1} multi-element standard to determine the elements of sufficient concentration to be successfully detected, and wavelengths free of interference from other elements. Of the usable elements determined (Table 5-7) a range of four standards were made up around the concentrations found in the trial samples. The standards used were Fisher Assurance SPEX Certi Prep Standards at 1000 mg kg^{-1} or 10,000 mg kg^{-1} made to volume with Type 1 ultrapure water.

Table 5-7: The elements and wavelengths used for ICP-OES geochemical tracer analysis.

Element	Wavelength (nm)	Element	Wavelength (nm)
Al	396.1	**Mn**	259.3
As	193.7	**Na**	589.5
Ba	493.4	**Nd**	406.1
Ca	317.9	**Ni**	231.6
Co	228.6	**P**	177.4
Cr	267.7	**Pb**	220.3
Cu	327.3	**Ti**	336.1
Fe	238.2	**V**	290.8
Ga	294.3	**Y**	371.0
Gd	335.0	**Yb**	328.9
K	766.4	**Zn**	206.2
La	412.3	**Zr**	343.8
Mg	279.5		

During the analysis each sample was measured three times and the average taken as the final result (McKinstry *et al*., 1999). The samples were digested in batches of 40 tubes, of each batch one tube contained a blank for the assessment of contamination during the digestion procedure. Table 5-8 shows the average contamination present in blank samples containing only *aqua regia* and ultra-pure water for each geochemical tracer analysed. The average error recorded for all spikes was 16.6% with a standard deviation of 11.7%.

Table 5-8: Average contamination associated with geochemical element measurement determined by blank samples.

Element	Average contamination (mg/l)	Standard deviation
Al	26.45	26.24
As	0.02	0.16
Ba	0.62	2.33
Ca	106.41	106.56
Co	0.02	0.03
Cr	3.49	6.70
Cu	0.45	0.81
Fe	92.48	96.57
Ga	0.47	1.08
Gd	-0.07	0.29
K	14.66	12.99
La	-0.07	0.36
Mg	5.27	6.25
Mn	2.34	4.07
Na	12.35	9.72
Nd	3.53	17.44
Ni	1.18	2.50
P	5.79	8.16
Pb	0.30	0.96
Ti	-0.60	1.25
V	0.10	0.33
Y	0.04	0.06
Yb	0.01	0.01
Zn	2.37	1.91
Zr	0.12	0.18

A certified reference material (CAN-STSD-1) was analysed for two repetitions to determine the detection efficiency of the methodology used. Table 5-9 shows both the total concentration of elements expected in the reference material and the *aqua regia* extractable fraction compared to the concentrations found during two repetitions of the analysis procedure used in this study.

Table 5-9: The amount of sediment element concentration recovered by the microwave digestion and ICP analysis procedure, determined using a certified reference material (mg kg^{-1}).

Element	Quantity measured using the analysis procedure of this thesis	Certified value	Aqua regia extractable value
Al	5081.63		
As	17.52	23	17
Ba	338.80	630	
Ca	8090.46		
Co	7.88	17	14
Cr	21.36	67	28
Cu	19.51	36	36
Fe	14802.27	4700	3500
Ga	0.62		
Gd	0.48		
K	314.79		
La	3.68	30	
Mg	2846.78		
Mn	3989.60	3950	3740
Na	67.06		
Nd	27.10	28	
Ni	10.53	24	18
P	1306.69		
Pb	28.75	35	34
Ti	92.70	4600	
V	33.09	98	47
Y	16.53	42	
Yb	1.96	4	
Zn	126.32	178	165
Zr	1.68	218	

Analytical error for each element was established using three repeat measurements of six sediment samples. The average coefficient of variation was calculated and used as the quantification of error, and is shown for each element in Table 5-10.

Table 5-10: Errors associated with the measurement of geochemical tracers.

Element	Average Coefficient of variation (%)	Element	Average Coefficient of variation (%)
Al	13.52	Mn	6.85
As	8.22	Na	26.12
Ba	11.31	Nd	7.96
Ca	4.68	Ni	31.53
Co	3.03	P	3.26
Cr	20	Pb	20.75
Cu	9.36	Ti	30.06
Fe	4.19	V	11.12
Ga	4.8	Y	8.68
Gd	6.18	Yb	8.57
K	20.95	Zn	4.94
La	21.69	Zr	10.2
Mg	13.07		

5.5. Sediment fingerprinting methodology

The sediment fingerprinting methodology used is outlined in Figure 5-1. The following section describes each stage of the procedure, outlining the procedure used and the reasoning behind the fingerprinting methodology. Chapter 2 provides a discussion of published sediment fingerprinting methodologies, from which this methodology was derived.

The different tracer groups used to fingerprint the sediment were investigated both alone and in combinations of two groups. For the remainder of the fingerprinting methodology each group is treated separately until the results derived with them are compared in the results sections to fulfil Objectives 1, 2 and 3. A list of tracer groups and their abbreviations used in future figures are provided in
Table 5-11.

Table 5-11: Tracer groups used and their abbreviations.

Tracer group	Abbreviation
Mineral magnetics	Mag
Mineral magnetics with lithogenic radionuclides	Mag litho
Mineral magnetics with fallout radionuclides	Mag fallout
Mineral magnetics with geochemistry	Mag geochem
Geochemistry with lithogenic radionuclides	Geochem litho
Geochemistry with fallout radionuclides	Geochem fallout
Geochemistry	Geochem
Lithogenic radionuclides with fallout radionuclides	Litho fallout
All tracer groups combined	All

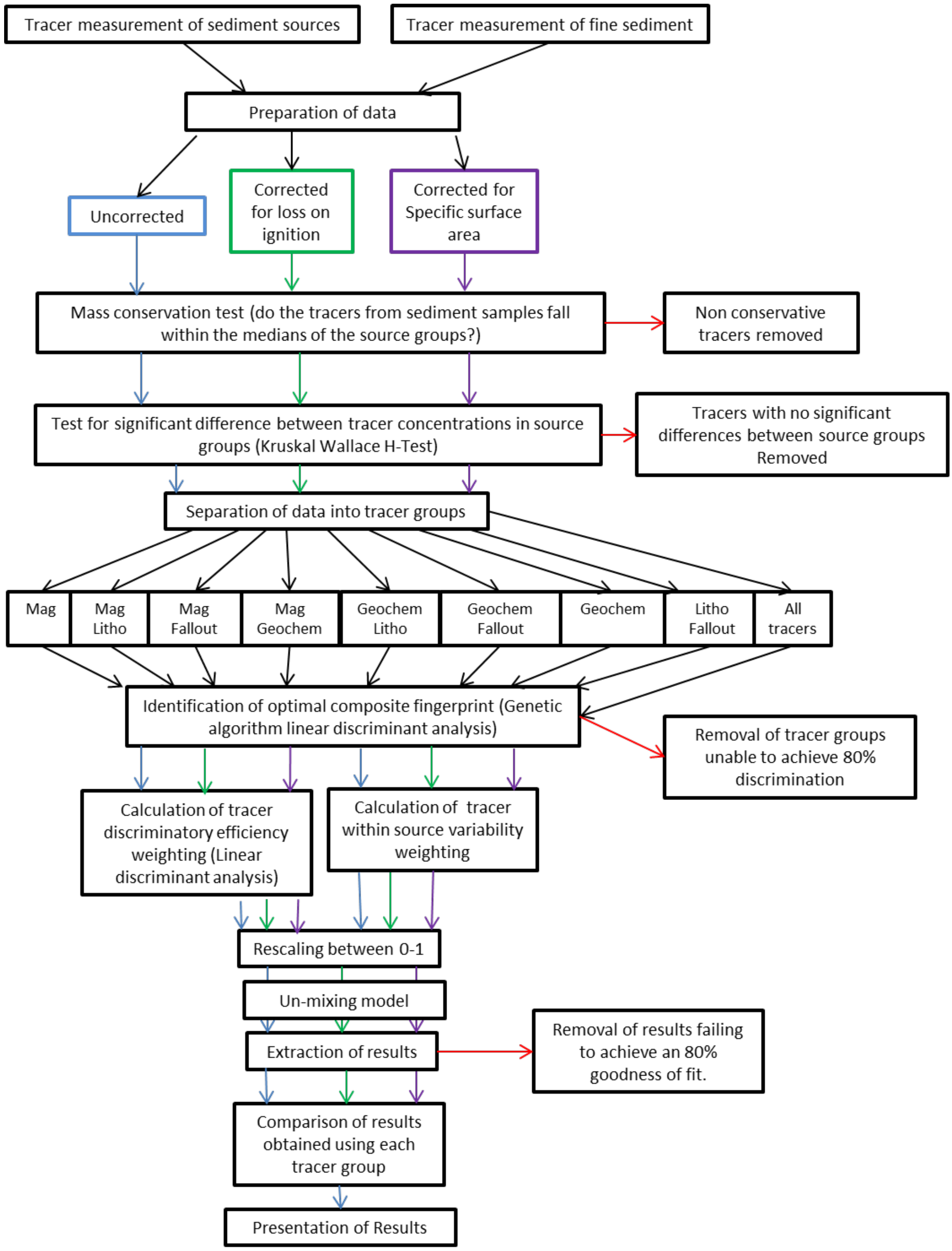


Figure 5-1: A Flow diagram of the sediment fingerprinting procedure.

5.5.1. Allocation of source samples

The sediment source groups used in this study were channel banks, surface agricultural land and urban street dusts. These were selected on the basis of their importance as sediment sources in UK catchments, as described in Chapter 3.

Due to sampling and analytical constraints a discrete set of source samples was not acquired for every tributary sub-catchment investigated, an issue also highlighted in a recent study by Smith and Blake (2014). Instead surface agricultural land samples were pooled into five regions, each of which consisted of comparable lithologies and land utilisations (Figure 5-2 A). Likewise channel banks were split into three regions representing the upstream, middle and downstream regions of the study area (Figure 5-2B). When fingerprinting the recently deposited overbank sediment samples Figure 4-9 all source samples in the upstream catchment were used. This resulted in a total of 8 regions of the Nene basin, where different combinations of source samples were used.

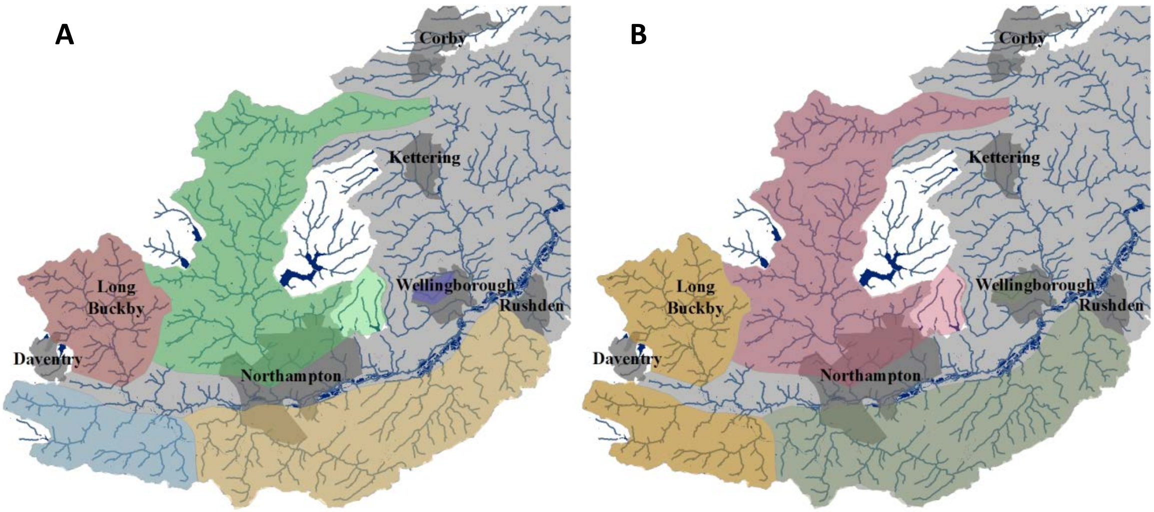


Figure 5-2: The division of the study area into surface source (A) and channel bank (B) regions for the separation of source samples.

The data for each source and sediment sample was corrected for organic enrichment (Equation 5-2), particle size SSA (Equation 5-3) and left uncorrected, to fulfil the requirements of Objective 3. Many published studies calculate these corrections on the basis of the mean organic content and particle size distribution of the source groups compared to the mean of the sediment samples, to form a correction factor for each source group e.g.

Rowan *et al*. (2012). As it was found that many sediment cores were affected by down-core trends in organic matter and particle size distribution, a single correction factor was considered to be unsuitable to represent the entire core. For this reason all sediment and source samples were given an individual correction factor based upon the methods of Collins *et al*. (1997). For a full discussion of the use of these corrections in published fingerprinting studies see chapter 2.

Equation 5-2: Tracer organic enrichment correction.

$$\text{Organic corrected value} = T(1/(1-(LOI/100)))$$

Where T- measured tracer concentration and LOI= loss on ignition (%).

Equation 5-3: Tracer particle size correction.

$$\text{Particle size corrected value} = T/SSA.$$

Where T= measured concentration value and SSA= specific surface area.

5.5.2. Mass conservation test and statistical procedure

The determination of composite fingerprints was based on the published developments in sediment fingerprinting outlined in chapter 2. Data for suspended and recently deposited sediment were initially screened for conservatism using a mass conservation test as used by Wilkinson *et al*. (2012), which removed tracers which did not fall between the highest and lowest medians of the included source groups. It was found that this mass conservation test was failed by almost all tracers when fingerprinting historically deposited sediment. For this reason the mass conservation test of Collins *et al*. (1997) was used for these cores. This test required sediment tracer concentrations to fall between the highest median + 1 median absolute deviation and the lowest median – 1 median absolute deviation of any included source group. When over 20% of samples from each sampling location (e.g. Suspended sediment in the Weedon 1 sampling site, or slices of the Kingsthorpe floodplain cores) fell outside of the median source values, the tracer was judged to violate the assumption that it is representative of the sediment sources and was removed from further analysis. Some leeway on this requirement was permitted when tracer failed by very small amounts, or the requirement was tightened if tracers failed by exceptionally large amounts. No guidelines for this threshold exist in published literature so the 20% value was selected on the basis that only the most conservative tracers should pass the test, but acknowledging that variability in the natural environment is likely to result in some anomalous samples.

The optimum composite fingerprint was determined by a two stage statistical procedure based upon the methodology used by Collins *et al.* (2013) and Collins *et al*. (1997). The ability of tracers to discriminate between source groups was initially tested using a Kruskal Wallace H test.

The tracers in each group passing the initial Kruskal Wallace test were included in a genetic algorithm based linear discriminant analysis (GA-LDA) consisting of an initial variable selection step, followed by a linear discriminant analysis. The genetic algorithm uses a fitness function to assess the robustness of the model proposed by each individual group of tracers; this method has been shown to generate the maximum value from a dataset of tracers (Collins *et al.,* 2012).

The analysis was initially programmed to select three tracers and was repeated with the addition of one extra tracer until additional tracers did not improve the discriminatory efficiency of the fingerprint. A 1% Improvement caused by the addition of a tracer was judged to be an appropriate cut-off for the inclusion of additional tracers, as it was found that without such a cut-off, fingerprints would often include close to 20 tracers, which is a number not encountered in published fingerprinting studies.

Any fingerprint failing to achieve at least an 80% correct classification of samples into their respective source groups was not included in any further analysis. This was done to reduce the likelihood that the differences between tracer group provenance predictions were due to failure to adequately differentiate between sediment sources. The value of 80% was selected as published fingerprinting studies were found to rarely use a fingerprint with a lower discriminatory efficiency.

5.5.3. Un-mixing modelling

The un-mixing model selected for this study was based upon that used by Collins *et al.*, (2010). The structure of the model is shown in Equation 5-4.

Equation 5-4: The structure of the un-mixing model (Collins *et al.,* 2010).

$$\sum_{i=1}^{n}\left\{\left(C_i-\left(\sum_{s=1}^{m}P_sS_{si}Z_sO_sSV_{si}\right)\right)/C_i\right\}^2 W_i$$

Where C_i = concentration of fingerprint property (*i*) in time-integrated suspended sediment sample; P_s = the optimised percentage contribution from source category (*s*); S_{si} = median concentration of fingerprint property (*i*) in source category (*s*); *Z* = particle size correction factor for source category (*s*); *O* = organic matter content correction factor for source category (*s*); SV_{si} = weighting representing the within-source variation of fingerprint property (*i*) in source category (*s*); W_i = tracer discriminatory weighting; *n* = number of fingerprint properties comprising the optimum composite fingerprint; *m* = number of sediment source categories.

Weightings have been utilised in many recent sediment fingerprinting papers such as, Collins *et al*. (2010) and Collins *et al.* (2013), although other authors do not use weightings e.g. Smith and Blake, (2014). Weightings were utilised in this study as it was found by Collins *et al*. (2010) that the precision of source apportionment was improved by their incorporation.

Weightings operate by increasing the impact of specific tracers on the un-mixing model based on their positive attributes, such as a smaller within source variability in tracer concentration, or the ability of tracers to differentiate between sediment sources.

The weightings applied for within source tracer variability and tracer discriminatory efficiency in this study were calculated using Equation 5-5 and Equation 5-6 based on the methods used by Collins *et al*. (2010).

Equation 5-5: Within source tracer variability weighting.

Within source tracer variability weighting = 1- (Σn (MAD/Median)/n)

Where MAD = Median absolute deviation.

Equation 5-6: Tracer discriminatory efficiency weighting.

Tracer discriminatory weighting = E_t/E_a

Where E_t= Discriminatory efficiency of each individual tracer and E_a= minimum discriminatory efficiency of any used tracer.

The model was programmed using Microsoft Excel and the Solver add in, a visual basic macro ran the model for Monte Carlo 3000 iterations through a range of random source values within one median absolute deviation of the measured median. Measurements of tracers for sediment samples in the model were assigned a random value within the coefficient of variation determined for its measurement error, which can be seen in Table 5-3, Table 5-5 and Table 5-10.

6. Fingerprinting historically deposited sediment

6.1. Introduction

This chapter addresses Objectives 1, 2, and 3 of this thesis by conducting a fine sediment fingerprinting investigation, using historically deposited sediment in lakes and on floodplains. It forms one of two chapters which address these objectives; Chapter 7 follows a similar structure to this chapter and investigates the fingerprinting of suspended and recently deposited overbank and channel bed sediment, in further fulfilment of Objectives 1, 2, and 3.

The results in this chapter are split into three sections. In the first section a sediment fingerprinting study was conducted using different fingerprints of three different tracer groups. The results obtained using each tracer group were then compared in order to determine the differences between their sediment provenance predictions. These differences provided an indication of the uncertainty associated with the use of the tracers, fulfilling Objective 1 of this thesis.

In the second section, the differences between the tracer groups' predictions determined for Objective 1, were compared to potential causes of tracer non-conservatism, to fulfil Objective 2. The predicted contribution from channel banks made by one tracer group of e.g. 50% was subtracted from the predicted contribution from a second tracer group of e.g. 70%, to quantify the difference between the tracer groups' predictions, of e.g. 20%. This difference was calculated for every slice in each core and for all combinations of tracer groups, to produce a table of the differences between the tracer group provenance predictions. Pearson correlation coefficients were then calculated between these differences and the sediment organic matter content and particle size distribution. Correlation coefficients were also calculated for ratio based indicators of alterations to mineral magnetic signatures. In this way the probable reasons for the differences between tracer group provenance predictions were identified.

In Section 3 data corrections based on organic enrichment and particle size distribution were applied to the tracer groups, when either of these factors had been shown in section 2 to be likely causal factors of the differences between tracer group predictions. It was then determined if the application of the data corrections reduced the differences between their sediment provenance predictions, fulfilling Objective 3.

6.2. Sediment tracer concentrations chronology, organic matter content and particle size distribution.

The sediment cores used in this section were retrieved using the methods laid out in sections 4.3.2. and 4.3.3. Using the 1963 peak in ^{137}Cs fallout and first detectable occurrence of ^{137}Cs at 1958 (Foster, 2006) (Figure 8-1, Figure 8-5), each core was estimated to contain a record of sediment accumulated over the previous ~100-150 years.

Prior to fingerprinting the sediment, down-core plots of loss on ignition (LOI) and specific surface area (SSA) were constructed to provide an indication of changes to the sediments' organic content and particle size distribution during its deposition and post-depositional storage. LOI (Figure 6-1A) is enriched above the median LOI of surface agricultural (10.44 %) and channel bank (7.47 %) source samples in all cores other than Sywell reservoir and most of the Kingsthorpe floodplain core (Table 6-1). All cores show an up-core increase in LOI, with the core at Earls Barton showing a particularly large increase, and being composed predominantly of organic matter in the uppermost 6 cm of the core. SSA (Figure 6-1B) is higher than the maximum sediment source group median of 1.18 m^2 g^{-1} in all cores except for the Kingsthorpe floodplain core, indicating a fining of sediment particle size. Most cores have a ~50% increase in SSA over the source group medians, although between a depth of 20 and 54 cm the Earls Barton core has over double the SSA of the source groups. It is therefore clear that LOI and SSA is significantly different from the source material in most of the cores.

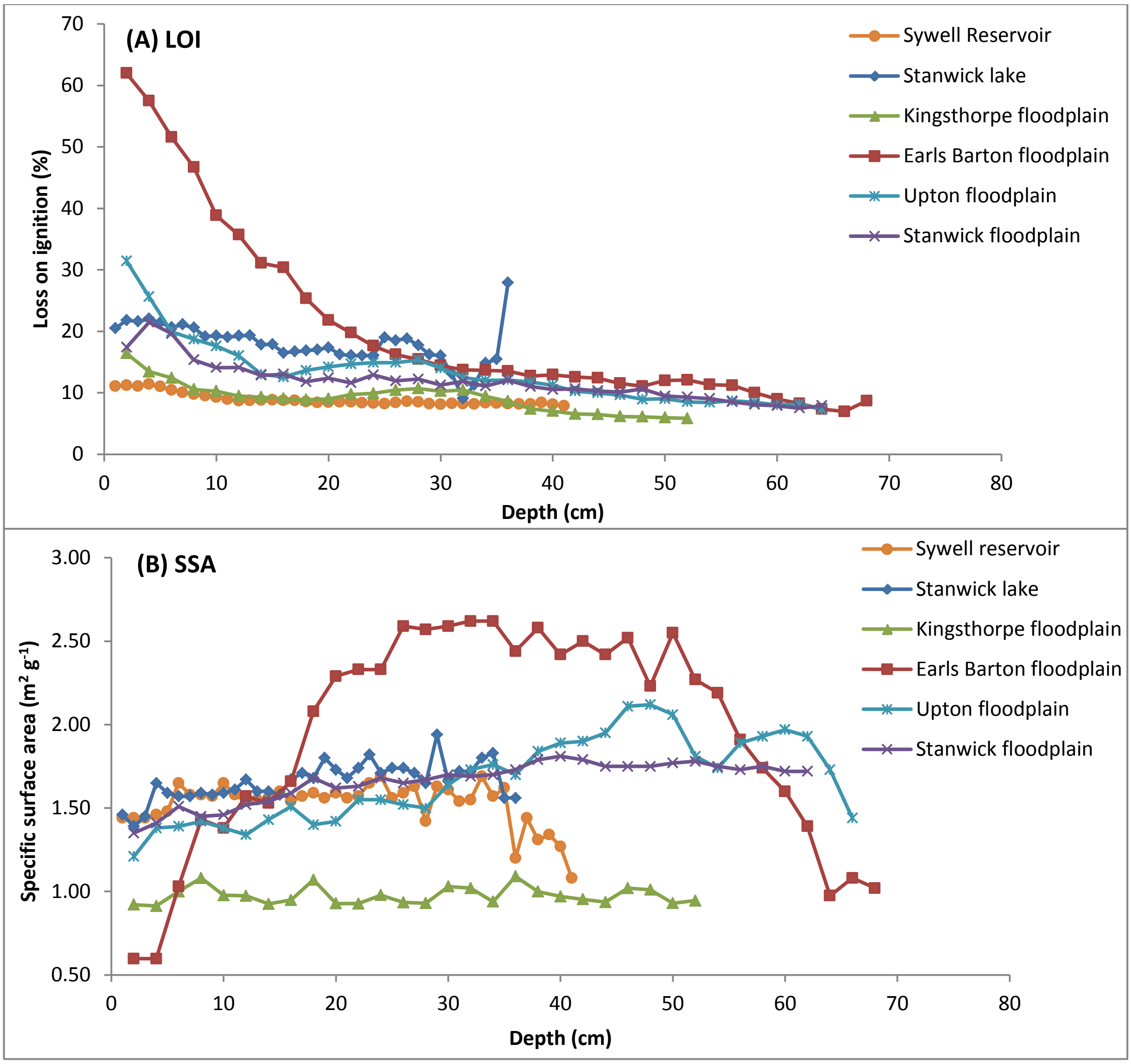


Figure 6-1: Down-core profiles of the loss on ignition (LOI, A) and Specific surface area (SSA, B) of the sediment cores.

Table 6-1: Median tracer concentrations in sediment source groups reported with median absolute deviations.

	Surface Agriculture	Median absolute	**Chanel Banks**	Median absolute deviation	**Urban dusts**	Median absolute deviation
LOI (%)	10.44	1.23	7.47	1.03	21.34	2.57
SSA (m^2 g^{-1})	1.18	0.10	1.16	0.08	0.90	0.07
X_{lf} (10^{-6} m^3 kg^{-1})	0.38	0.18	0.22	0.05	**3.73**	0.45
X_{fd} (10^{-9} m^3 kg^{-1})	21.41	14.19	6.81	3.39	**124.75**	20.12
Xarm (10^{-6} m^3 kg^{-1})	3.67	2.36	1.46	0.66	**9.44**	0.91
IRM1T (10^{-5} m^3 kg^{-1})	4.50	2.18	2.53	0.96	**34.11**	2.62
IRM_{-100} (10^{-5} m^3 kg^{-1})	-3.49	1.85	-1.68	0.74	**-25.98**	3.08
HIRM (10^{-5} m^3 kg^{-1})	0.52	0.18	0.40	0.09	**4.57**	0.59
^{226}Ra (mBq g^{-1})	31.25	8.30	**34.54**	9.94	10.31	2.80
^{137}Cs (mBq g^{-1})	**2.89**	1.24	0.16	0.16	0.75	0.39
^{228}Ac (mBq g^{-1})	32.86	6.17	**36.89**	6.19	15.91	4.71
^{40}K (mBq g^{-1})	612.58	84.17	**645.74**	91.08	388.96	51.66
^{234}Th (mBq g^{-1})	**20.27**	5.55	18.16	4.90	6.79	1.28
^{235}U (mBq g^{-1})	**2.28**	0.96	2.23	0.95	0.93	0.28
^{212}Pb (mBq g^{-1})	34.25	6.05	**38.40**	5.33	19.89	2.18
Al (mg kg^{-1})	9488.73	1463.34	8841.46	1974.21	**11868.20**	693.92
As (mg kg^{-1})	22.62	9.23	**24.95**	9.44	17.68	1.64
Ba (mg kg^{-1})	59.02	12.61	64.29	15.81	**195.50**	19.56
Ca (mg kg^{-1})	5570.06	1877.22	8284.87	4270.21	**35837.93**	10581.46
Co (mg kg^{-1})	9.46	2.80	**10.82**	2.52	8.51	1.03
Cr (mg kg^{-1})	42.62	17.36	37.49	9.20	**74.19**	14.51
Cu (mg kg^{-1})	21.62	4.20	20.75	4.52	**222.47**	49.74
Fe (mg kg^{-1})	34929.08	11191.21	**42631.25**	12194.19	40927.50	4052.42
Ga (mg kg^{-1})	4.77	2.55	3.13	1.97	**5.08**	0.74
Gd (mg kg^{-1})	2.60	1.15	**2.94**	1.42	1.12	1.10
K (mg kg^{-1})	**1343.61**	323.03	947.59	229.36	1271.75	197.28
La (mg kg^{-1})	15.33	3.85	**15.75**	4.22	14.95	1.73
Mg (mg kg^{-1}))	1708.98	403.85	1776.62	493.32	**8917.81**	1402.17
Mn (mg kg^{-1})	647.86	244.88	608.39	208.75	**1765.83**	242.99
Na (mg kg^{-1})	61.04	22.72	94.92	36.56	**299.17**	87.08
Nd (mg kg^{-1})	28.76	8.12	**38.30**	6.73	24.95	2.05
Ni (mg kg^{-1})	25.93	9.86	24.84	4.00	**37.36**	4.95
P (mg kg^{-1})	**1354.41**	374.61	1018.04	249.95	1319.66	160.01
Pb (mg kg^{-1})	30.98	7.83	26.47	7.18	**107.45**	17.62
Ti (mg kg^{-1})	23.98	10.63	21.61	8.39	**79.26**	20.57
V (mg kg^{-1})	52.19	18.60	53.18	15.06	**59.75**	3.84
Y (mg kg^{-1})	14.15	4.09	**17.62**	3.99	12.93	1.07
Yb (mg kg^{-1})	1.78	0.56	**2.29**	0.52	1.88	0.14
Zn (mg kg^{-1})	85.27	23.06	85.82	12.68	**853.82**	290.51
Zr (mg kg^{-1})	5.84	1.51	7.43	1.54	**9.32**	1.33

6.3. Statistical determination of composite fingerprints

The statistical procedure described in Section 5.5.2. was used to identify the composite fingerprint for each core and each tracer group. The fingerprint used was the one that was best able to discriminate between the channel bank, surface agriculture and urban street dust sediment sources. The statistical procedure consisted of an initial mass conservation test, followed by a two-step statistical determination of the composite fingerprint. The following sections provide a brief reminder of each part of the statistical procedure and presents the tracers and fingerprints passing and failing each stage.

The lithogenic radionuclides, geochemistry, and mineral magnetic tracer groups were used to fingerprint the sediment cores alone, in combinations of two groups, and as a final single group consisting of all tracers. The combinations of groups used are shown in Table 6-2, along with the abbreviation for each group used in the figures and tables in this chapter.

Table 6-2: The tracer groups used to fingerprint historically deposited sediment and their abbreviations.

Tracer group fingerprint	Abbreviation
Mineral magnetics	Mag
Mineral magnetics and lithogenic radionuclides	Mag litho
Mineral magnetics and geochemistry	Mag geochem
Geochemistry and lithogenic radionuclides	Geochem litho
Geochemistry	Geochem
All tracer groups combined.	All

A mass conservation test was used to remove any tracers falling outside of the median +/- one median absolute deviation of the source groups shown in Table 6-1 (Section 5.5.2.). The tracers failing this test are shown in Table 6-3. In addition to the information shown in Table 6-3 it was found that a large number of tracers failed the mass conservation test in the Stanwick lake core above 19cm depth, and the Upton floodplain core below 28cm depth. For this reason the fingerprinting was only conducted on the sections above and below these depths, and the results shown only relate to these more conservative sections of the cores.

Table 6-3: Tracers failing the mass conservation test for each core and each correction.

Sywell reservoir			Stanwick Lake			Kingsthorpe floodplain		
Uncorrected	**Organic corrected**	**Particle size corrected**	**Uncorrected**	**Organic corrected**	**Particle size corrected**	**Uncorrected**	**Organic corrected**	**Particle size corrected**
XARM	XARM	XARM	HIRM	IRM-100	Xlf	HIRM	HIRM	HIRM
^{234}Th	^{235}U	HIRM	^{234}Th	HIRM	IRM-100	Cu	^{40}K	^{234}Th
^{235}U	Ca	^{40}K	^{235}U	^{226}Ra	HIRM	Ga	^{234}Th	^{235}U
Ca	Gd	Ba	As	^{228}Ac	^{40}K	Gd	^{235}U	Cu
Gd	Ni	Ca	Ca	^{234}Th	^{212}Pb	K	Cu	Ga
K	Ti	Co	Co	^{235}U	Al	Nd	Ga	Gd
Ni		Cr	Cr	^{212}Pb	As	P	Gd	Nd
Ti		Ga	Fe	As	Co		K	P
		Gd	Ga	Ca	Cr		Nd	
		Mn	La	Co	Fe		P	
		Nd	Mn	Cr	Ga		Pb	
		Ni	Nd	La	Gd			
		P	P	Mn	La			
		Ti	Ti	Na	Mg			
		Y	V	P	Mn			
		Yb		Ti	Nd			
		Zn			Ni			
		Zr			P			
					Ti			
					V			
					Y			
					Yb			

Stanwick floodplain			Upton floodplain			Earls Barton floodplain		
Uncorrected	**Organic corrected**	**Particle size corrected**	**Uncorrected**	**Organic corrected**	**Particle size corrected**	**Uncorrected**	**Organic corrected**	**Particle size corrected**
HIRM	IRM-100	SIRM	XARM	XARM	XARM	Xlf	Xlf	Xlf
^{226}Ra	^{226}Ra	IRM-100	^{226}Ra	^{226}Ra	^{226}Ra	Xfd	Xfd	Xfd
^{228}Ac	^{228}Ac	HIRM	^{228}Ac	^{228}Ac	^{228}Ac	XARM	XARM	XARM
^{235}U	^{235}U	^{40}K	^{235}U	^{235}U	^{40}K	SIRM	SIRM	SIRM
^{212}Pb	^{212}Pb	Al	^{212}Pb	^{212}Pb	^{235}U	IRM-100	IRM-100	IRM-100
Al	Cr	Co	Al	Al	Al	HIRM	HIRM	HIRM
Cr	Cu	Cr	As	As	Ca	^{228}Ac	^{226}Ra	^{40}K
Cu	Gd	Cu	Ga	Co	Fe	^{234}Th	^{228}Ac	^{234}Th
Fe	K	Fe	Gd	Gd	Gd	^{235}U	^{234}Th	^{235}U
Gd	La	Gd	K	K	K	^{212}Pb	^{235}U	As
K	Mg	K	La	La	La	Al	^{212}Pb	Co
La	Yb	La	Mg	Mg	Mg	Co	Al	Cr
Mg		Mg	P	Nd	P	Cu	As	Cu
P		Na	V	P		Fe	Co	Ga
Ti		Ni	Y	V		Ga	Fe	K
		P	Yb	Y		Gd	Ga	La
		Ti	Zr	Yb		La	Gd	Mn
				Zr		Mn	K	Nd
						Na	La	P
						Nd	Mn	Pb
						P	Na	Ti
						Ti	Nd	V
						V	P	Zn
						Y	Ti	
						Yb	V	
						Zr	Y	
							Yb	
							Zr	

The two-step statistical procedure was then used to select the optimum composite fingerprint for each tracer group at each coring location (Section 5.5.2.). Firstly a Kruskal–Wallis *H* test was used to remove any tracers which did not show a significant difference in concentration between at least two of the sediment sources (Table 6-4). Due to the highly distinctive urban street dusts group (Table 6-1) it was found that the majority of tracers passed this test.

Table 6-4: Tracers failing the Kruskal–Wallis *H* test (p=0.05) for each core and each correction.

Sywell reservoir			Stanwick lake			Kingsthorpe floodplain		
Uncorrected	**Organic corrected**	**Particle size corrected**	**Uncorrected**	**Organic corrected**	**Particle size corrected**	**Uncorrected**	**Organic corrected**	**Particle size corrected**
-	Co	-	-	Fe	-	Co	Co	Co
	Fe					La	Fe	Fe
	La					V	La	Y
							V	Yb
							Yb	

Stanwick floodplain			Upton floodplain			Earls Barton floodplain		
Uncorrected	**Organic corrected**	**Particle size corrected**	**Uncorrected**	**Organic corrected**	**Particle size corrected**	**Uncorrected**	**Organic corrected**	**Particle size corrected**
Ga	As	-	-	-	As	-	-	Fe
V	Co							

The selection of the optimum composite fingerprint was performed using the tracers passing the mass conservation test and Kruskal–Wallis *H* test. A Genetic Algorithm based Linear Discriminant Analysis (GA-LDA) was used to identify the optimum composite fingerprint for each tracer group in each core. Any composite fingerprint which failed to correctly discriminate between 80% of source samples was removed from further analysis, with the aim of minimising the uncertainty introduced by source discrimination, rather than tracer behaviour. A value of 80% was selected, as a review of published fingerprinting studies found that composite fingerprints were rarely used which failed to achieve at least this amount of discrimination.

Table 6-5 shows the composite fingerprints which were formed for each tracer group for each core. In the Sywell reservoir and Kingsthorpe floodplain cores a composite fingerprint was able to be used for all tracer groups. The LOI and SSA in these two cores was the most comparable to the sediment source samples, providing an indication that some impact of alterations to sediment LOI and SSA may be affecting the fingerprinting in other cores, where fewer composite fingerprints could be formed (Table 6-1). The Earls Barton and Stanwick floodplain cores could be fingerprinted with the fewest tracer groups. The Earls Barton core was indicated to have the most LOI and SSA values in comparison to the sediment sources, indicating that tracer may be the most heavily altered in these cores.

Table 6-5: The composite fingerprints, fingerprint discriminatory power and average goodness of fit of un-mixing model outcomes.

Sywell reservoir

Uncorrected	**Correctly classified (%)**	**Average Goodness of Fit**								
Mag	81	0.74	Xlf	Xfd	SIRM	IRM-100	HIRM			
Mag litho	81	0.95	Xlf	Xfd	^{226}Ra	^{40}K	^{212}Pb			
Mag geochem	94	0.92	Xfd	Co	Fe	La	Mg	P	V	Yb	Zn
Geochem litho	91	0.94	^{226}Ra	Fe	La	Mg	P	V	Yb	Zr	
Geochem	93	0.92	Cr	La	Mg	P	V	Yb	Zn		
All	95	0.91	^{226}Ra	Xfd	Fe	La	Mg	V	Yb	Zr	
Organic corrected											
Geochem	91	0.55	Al	Gd	Mg	Nd	P	V	Yb		

Stanwick lake

Uncorrected	**Correctly classified (%)**	**Average Goodness of Fit**						
Mag	<80							
Mag litho	81	0.75	Xfd	XARM	SIRM	IRM-100	^{212}Pb	
Mag geochem	As ‘All’							
Geochem litho	88	0.89	^{40}K	Al	Cu	K	Mg	Y
Geochem	88	0.94	Al	Ba	K	Yb	Zr	
All	89	0.68	Xfd	Al	K	Mg	Y	Zr

Kingsthorpe floodplain

Uncorrected	**Correctly classified (%)**	**Average Goodness of Fit**							
Mag	80	0.95	Xlf	Xfd	XARM				
Mag litho	81	0.63	Xfd	XARM	^{228}Ac	^{40}K			
Mag geochem	92	0.90	XARM	IRM-100	Ca	Mn	Y		
Geochem litho	83	0.71	^{228}Ac	Ba	Ca	Cr	Ti		
Geochem	86	0.91	Ba	Ca	Cr	Mg	Y	Zn	
All	90	0.77	Xlf	^{212}Pb	Ca	Cr	Ti	Yb	
Mag fallout*	87	0.93	^{137}Cs	Ca	Cr	Mg	Y		
Geochem fallout*	83	0.88	^{137}Cs	Xlf	Xfd	XARM	SIRM		
Organic corrected									
All	90	0.82	Xlf	^{212}Pb	Ca	Cr	Na	Ti	Y
Mag litho	82	0.71	XARM	IRM-100	^{228}Ac	^{212}Pb			
Geochem	83	0.91	Ba	Ca	Cr	Y	Zn		

Earls Barton floodplain

Uncorrected	**Correctly classified (%)**	**Average Goodness of Fit**							
Mag	<80								
Mag litho	<80								
Mag geochem	<80								
Geochem litho	As "Geochem"								
Geochem	88	0.91	Ba	Ca	K	Mg	Pb	Zn	
All	89	0.88	^{40}K	Ba	Ca	K	Mg		
Particle size corrected									
All	83	0.90	^{228}Ac	^{212}Pb	Al	Ba	Ca	Mg	Y

Upton floodplain

Uncorrected	Correctly classified (%)	Average Goodness of Fit						
Mag	<80							
Mag litho	82	0.75	Xlf	Xfd	SIRM	IRM-100	HIRM	^{234}Th
Mag geochem	As ‘All’							
Geochem litho	As "Geochem"							
Geochem	83	0.77	Co	Cu	Ni	Pb	Ti	
All	90	0.55	Xfd	Ba	Co	Cu	Pb	
Organic corrected								
Mag litho	83	0.75	Xlf	Xfd	SIRM	IRM-100	HIRM	^{234}Th
Geochem	81	0.77	Ba	Ca	Co	Cu	Pb	Ti
Particle size corrected								
Geochem	83	0.77	As	Co	Cu	Ti	Y	

Stanwick floodplain

Uncorrected	Correctly classified (%)	Average Goodness of Fit									
Mag	<80										
Mag litho	<80										
Mag geochem	As ‘All’										
Geochem litho	82	0.92	^{234}Th	As	Ba	Co	Ni	V	Yb	Zr	
Geochem	<80										
All	84	0.84	Xfd	IRM-100	Ba	Ca	Co	Ni	Yb		
Organic Corrected											
Geochem litho	82	0.76	Al	As	Ba	Ca	Co	Ni	Ti	Y	
All		0.51	Xlf	SIRM	IRM-100	Al	Ca	Na	Y		
Particle size corrected											
Geochem litho	83	0.76	^{226}Ra	^{228}Ac	^{234}Th	As	Ba	Mn	V	Yb	Zr
All	85	0.51	Xlf	XARM	IRM-100	^{226}Ra	Ca	Y	Zr		

*Two additional ^{137}Cs containing tracer groups were included in the top 10 cm of the Kingsthorpe core, the use of this group is discussed in section 6.4.

6.4. Quantifying differences between the sediment provenance predictions of different tracer groups

This section compares the sediment provenance predictions made by each of the different tracer groups in each of the cores, to contribute to the fulfillment of Objective 1 of this thesis. The provenance predictions are only shown for those tracer groups which produced a composite fingerprint which was able to correctly classify >80% of source samples. All results shown in this section are uncorrected for particle size distribution and organic matter content. To simplify the analysis of results, only the predicted contributions from channel banks are discussed in detail, as this was indicated to be the dominant sediment source in most cores (Figure 6-2), and its prediction was considered to be representative of the overall results of the un-mixing models. This section firstly describes the differences between the median Monte Carlo predicted contribution from channel banks in each slice of core, made by the different models, before discussing the range of uncertainty indicated by the Monte Carlo analysis in each of the models.

The median predicted contribution from channel banks made by the different tracer groups at the base of the Sywell reservoir core ranged from 31% made by 'All' tracer group up to 100% made by mineral magnetic signatures alone (Figure 6-2A). In the middle and upper sections of the core, this difference decreased to between a 45% and 95% predicted contribution made by the different tracer groups. Most tracer groups show little change in predicted sediment provenance through the down-core profile, indicating a consistent trend in their predictions, although individual peaks and troughs do not consistently occur in the predictions made by all of the tracer groups.

The Stanwick lake core (Figure 6-2B) has a difference in predictions of up to 100% between tracer groups containing mineral magnetic signatures and those containing geochemical tracers. The down-core trends in sediment provenance produced by mineral magnetic based and geochemistry based tracer groups were also different.

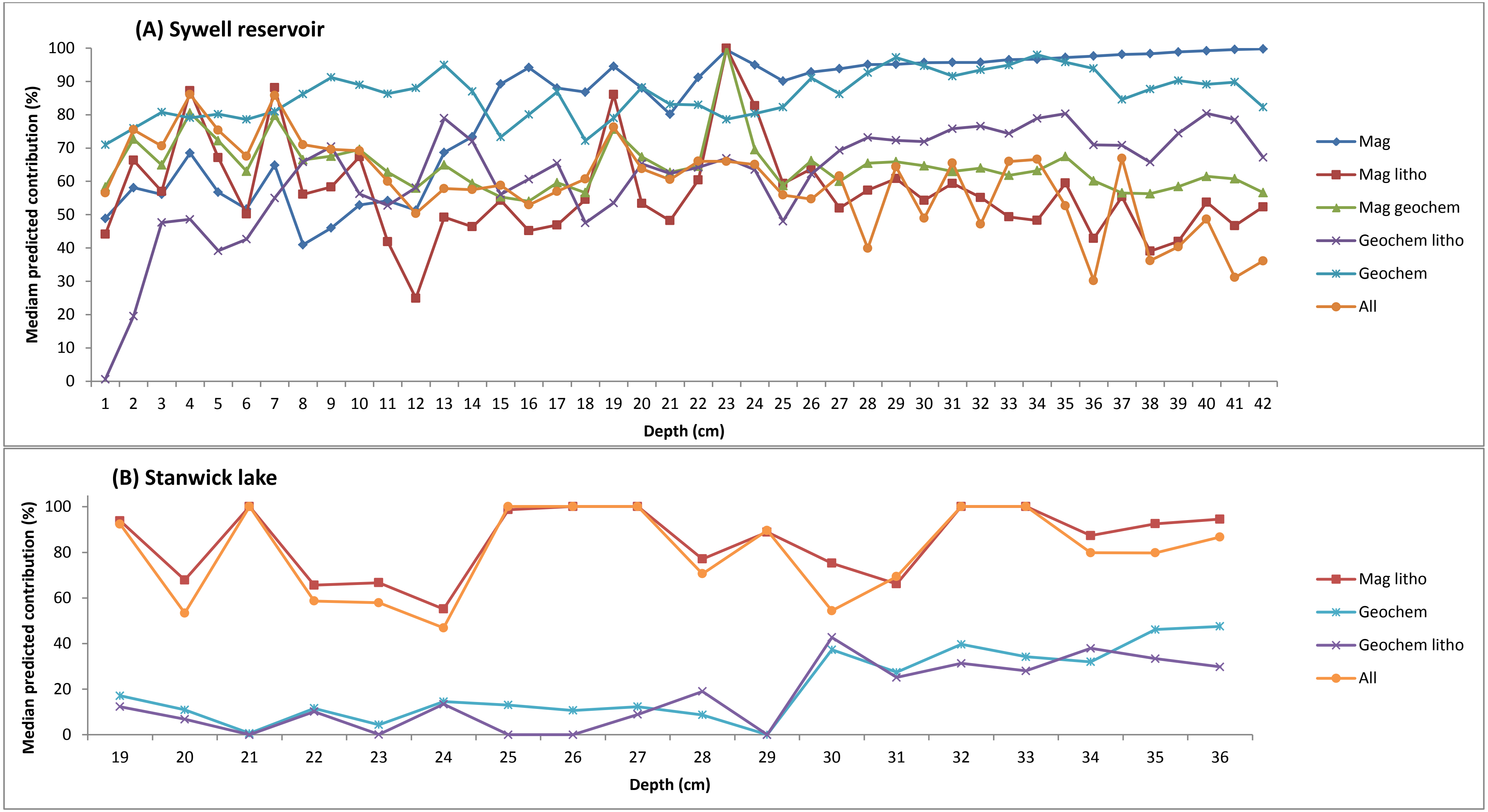
All of the tracer groups in the Kingsthorpe floodplain core (Figure 6-2C) predict widely different contributions of sediment from channel banks, ranging from between a 0% to a 95% contribution. The largest differences were found between the predictions produced by mineral magnetic signatures and geochemical tracers, although the addition of lithogenic radionuclides to any tracer group combination resulted in a lower predicted contribution from channel banks. In this core two additional tracer groups were used (Mag fallout and

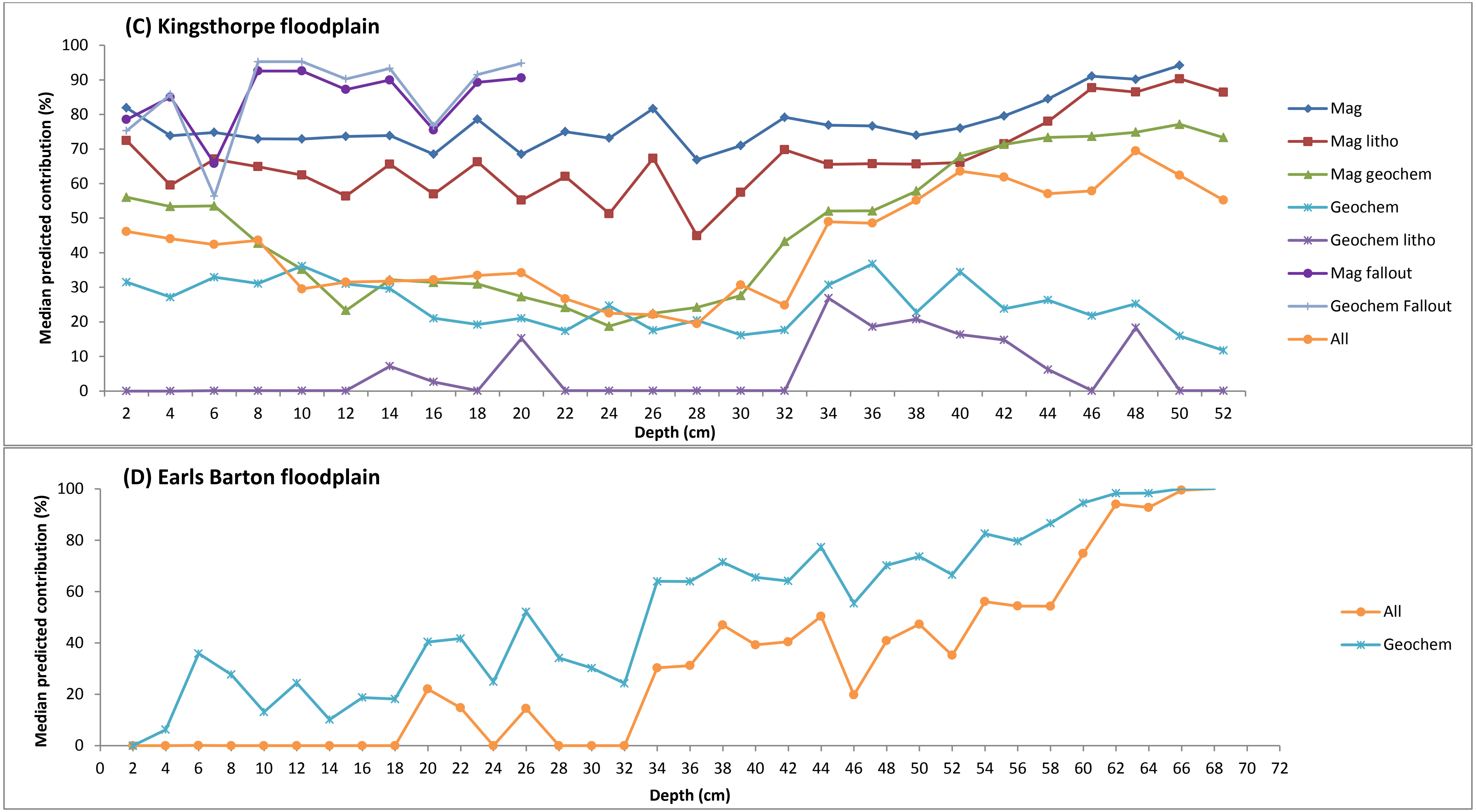
Geochem fallout), these contained the fallout radionuclide ^{137}Cs. ^{137}Cs was able to be used because there was no indication of additional ^{137}Cs fallout after the peak centered upon 1963 (Figure 8-5). Results presented by Walling, (2012) also showed that ^{137}Cs fallout after the 1970s was negligible in the UK. Therefore, the predictions of these two additional tracer groups could be compared in this core. The fingerprints which used fallout radionuclides predicted a contribution most similar to mineral magnetic signatures, although differences of up to 23% are seen between the predictions of these two groups. As in the Stanwick lake core, down-core trends in changing sediment provenance were found to be different in the predictions of many tracer groups.

The predictions of two tracer groups were compared in the Earls Barton core (Figure 6-2D). Both fingerprint predictions show a very similar down-core trend, however, the 'All' tracer group (containing geochemical and lithogenic radionuclides), decreased the predicted contributions from channel banks by up to 38%, from the prediction made by the Geochem group.

In the Upton floodplain core (Figure 6-2E) the 'All' tracer group and Mag litho group predict that almost all sediment originates from channel banks throughout the down-core profile. In comparison the Geochem fingerprint predicts a trend of decreasing contributions from channel banks, which is up to 89% different to the "All" and Mag litho groups.

Between a 22% to a 38% difference between predictions were found in the bottom two thirds of the Stanwick floodplain core when using the 'Geochem litho' group and the 'All' tracer group to fingerprint the sediment (Figure 6-2F). The difference increased to a maximum of a 64 % at the top of the core. As in many of the other cores, the two tracer groups predicted different down-core trends.


(A) Sywell reservoir
Mediam predicted contribution (%)
Depth (cm)
Mag
Mag litho
Mag geochem
Geochem litho
Geochem
All
(B) Stanwick lake
Median predicted contribution (%)
Depth (cm)
Mag litho
Geochem
Geochem litho
All


(C) Kingsthorpe floodplain
Median predicted contribution (%)
100
90
80
70
60
50
40
30
20
10
0
2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52
Depth (cm)
Mag
Mag litho
Mag geochem
Geochem
Geochem litho
Mag fallout
Geochem Fallout
All
(D) Earls Barton floodplain
Median predicted contribution (%)
100
80
60
40
20
0
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62 64 66 68 70 72
Depth (cm)
All
Geochem

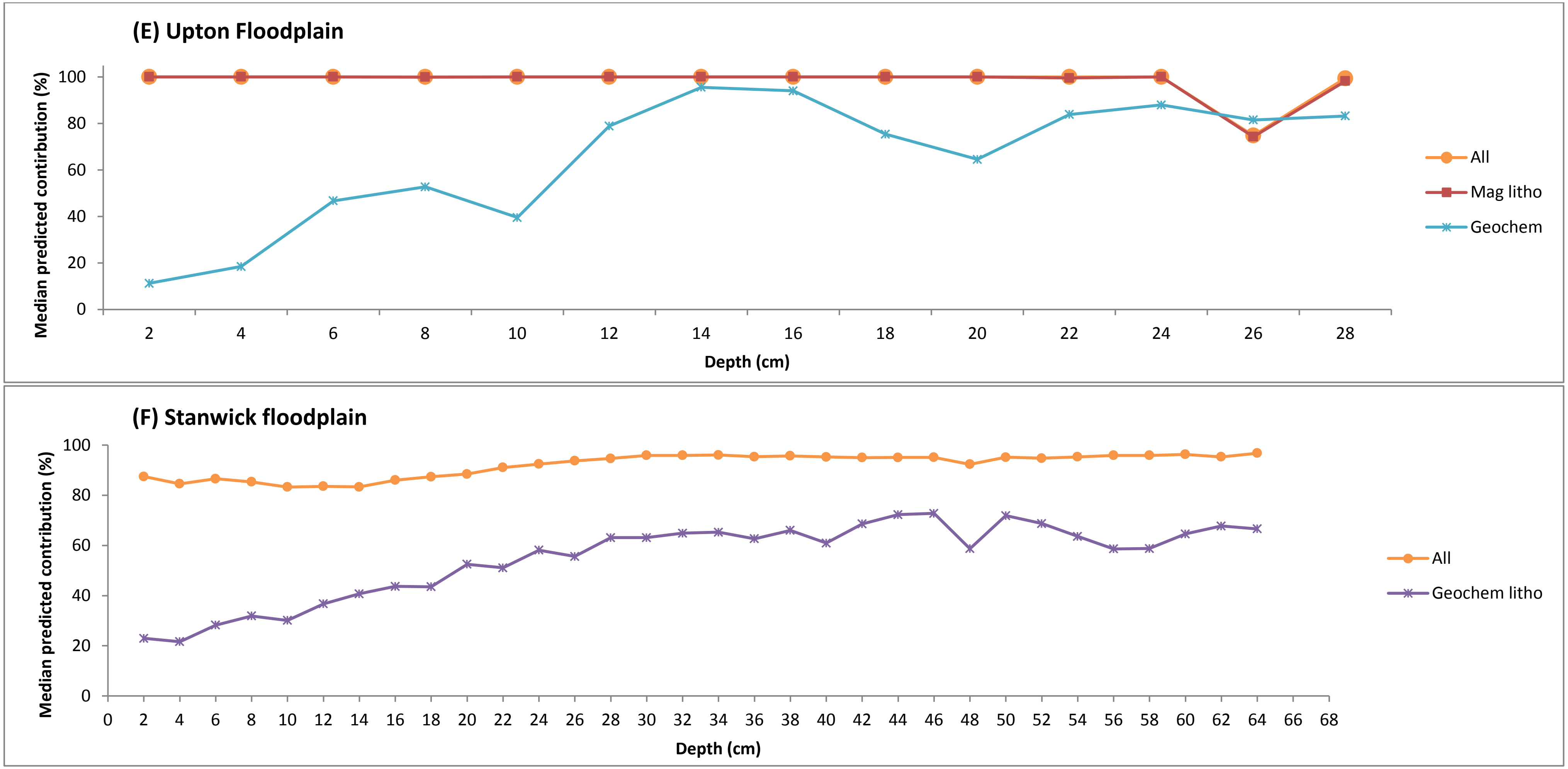


Figure 6-2: Down core plots of the median predicted contributions from channel banks derived using the different uncorrected tracer fingerprints and historically deposited sediment.

While median tracer group predictions provide a simple way to present fingerprinting results and have been used alone for this purpose by authors such as Owens *et al.* (1999); the use of Monte Carlo uncertainty analysis has become the common way to express the range of uncertainty associated with un-mixing model predictions. The uncertainty indicated by the Monte Carlo analysis when fingerprinting the lake and floodplain cores is shown in Table 6-6. The range between the median contributions (shown in Figure 6-2) and the 25th and 75th percentile Monte Carlo predictions are shown as an average for each core.

The range of uncertainty between the 25th and 75th percentile Monte Carlo predictions was found to be between 2.5% and 82.3%, with an average range for all tracer groups at all sites of 29.3%. It is clear that the indicated uncertainty between the 25th and 75th percentiles do not account for many of the large differences between tracer group median predications shown in Figure 6-2. Using a wider range of percentiles, such as between the 5th and 95th percentile Monte Carlo results, would be expected to indicate a larger range of uncertainty, which may include the full range of medians obtained by different tracer groups. However, a proper representation of uncertainty would require error bars of up to 100% in many of the cores, to incorporate all of the tracer group median predictions, meaning that no determination of sediment provenance could be determined from the modelling.

Table 6-6: The median and the 75th and 25th percentile Monte Carlo predicted contributions from channel banks of the results shown in Figure 6-2.

	Mag	Mag litho	Mag geochem	Geochem litho	Geochem	All	Mag fallout	Geochem fallout
Sywell Reservoir								
75th percentile	89.0	73.3	73.2	78.0	95.6	82.0		
Median	81.8	56.8	64.7	62	84.9	59.4		
25th percentile	56.2	27.6	53.9	44.8	70.6	34.8		
Stanwick Lake								
75th percentile		89.6		29.5	31.4	86.4		
Median		84.4		16.59	20.42	79.6		
25th percentile		79.3		4.5	9.9	73.0		
Kingsthorpe floodplain								
75th percentile	87.5	78.7	59.3	43.6	89.1	66.0	86.5	88.4
Median	77.7	67	46.9	5.7	31.5	42.1	84.7	85.5
25th percentile	65.9	45.1	29.5	0.06	6.8	16.2	82.1	81.5
Earls Barton floodplain								
75th percentile					73.6	56.0		
Median					53.4	31.2		
25th percentile					31.9	14.5		
Upton floodplain								
75th percentile		101.7			79.9	99.4		
Median		100			62.43	98.3		
25th percentile		97.2			37.2	96.9		
Stanwick floodplain								
75th percentile				67.3		107.3		
Median				54.9		92.05		
25th percentile				42.1		76.8		

The results of this section have indicated that had any of the tracer groups been used in isolation, a prediction of sediment provenance would have been derived using a composite fingerprint able to differentiate between the source groups, and an acceptable goodness of fit would have been found in the un-mixing model, indicating the fingerprinting had been successfully used. However, the different provenance predictions produced when using different tracer groups has shown that the results derived would likely be entirely determined by the tracer group chosen for use. As a result, the results derived would be unlikely to be a reflection of actual sediment provenance, or a realistic indication of historical changes in sediment sources.

As multiple tracer groups have been used to fingerprint cores in this section, the uncertainties associated with tracer selection have been quantified by the fingerprinting methodology. However, without an independent means of identifying which tracer group(s) best reflect(s) changing sediment provenance, it is not possible to precisely determine the dominant sediment sources or historical trends in almost all of the cores investigated. Sywell reservoir has the most consistent predictions made by the different tracer groups. The predictions made by the different tracer groups show that channel banks have contributed between 50 and 100% of the sediment to the reservoir throughout the ~110 years of deposition, meaning that some success can be judged to have been achieved when fingerprinting this core.

6.5. The effects of changes to the sediment organic content, particle size distribution and chemical alterations of sediment on the tracer group provenance predictions.

This section fulfils Objective 2 of this thesis by investigating the potential reasons for the differences between the tracer group provenance predictions observed as part of Objective 1.

As changing sediment provenance is represented by the tracer fingerprint predictions, comparing individual tracer groups' provenance predictions to factors which can potentially cause tracer non-conservatism such as LOI, would likely provide some indication of the LOI of the changing sources of the sediment. Instead of this, the differences between the predictions of two tracer groups were compared to potential causes of tracer non conservatism, as they were considered to be more representative of the error caused by tracer behaviour.

The average difference between tracer group fingerprint predictions in each core slice was quantified by subtracting the predicted contribution of one tracer group from the predicted contribution of the second tracer group, between the 5th and 95thpercentiles of the 3000 ranked Monte Carlo results. The average difference between these 2700 Monte Carlo results for each slice of core was then taken as a quantitative expression of the differences between tracer group predictions. The differences were correlated in a Pearson Correlation analysis with LOI, SSA, and ratios which indicate the alteration of mineral magnetic signatures in the sediment. These ratios are described in the following sections.

The following sections examine the results of the correlation analyses identifying the impacts of LOI, SSA and also the alterations of magnetic minerals on the differences between tracer group predictions. Each of these potential controls on tracer conservatism are examined in turn, with a discussion of the result in relation to the published literature, and a discussion of the potential specific changes they could be making to individual tracers.

6.5.1. The organic enrichment of sediment

The Pearson correlation analysis (Table 6-7) showed that the differences between most tracer group predictions in the Kingsthorpe, Upton, and Stanwick floodplain cores and in the Sywell reservoir core are significantly correlated with the loss on ignition of the sediment. In the Upton floodplain core and Sywell reservoir core, as LOI increases the predicted contribution of sediment from channel banks made by groups containing mineral magnetic signatures increases in relation to groups containing geochemical tracers. In the Kingsthorpe core, as LOI increases, mineral magnetic signatures predict lower contributions from channel banks than geochemical tracers, showing the opposite trend to Upton and Sywell.

Table 6-1 showed that mineral magnetic signatures are lowest in concentration in channel banks, so a dilution of magnetic signatures by organic matter would be expected to cause an increase in the predicted contribution of sediment from channel banks. On this basis, it is suggested that the increased predicted contribution of sediment from channel banks made by mineral magnetic containing tracer groups in Upton and Sywell, when sediment LOI increases, could be due to the dilution of mineral magnetic signatures by organic matter. Published literature has shown that mineral magnetic signatures are not associated with the organic fraction of the sediment, as organic matter is only weakly diamagnetic (Smith, 1999; Lees, 1999). Therefore this result is what would be expected from mineral magnetic theory. The fact that a similar result was not encountered in the other cores analysed suggests that other causes of tracer non-conservatism are of more importance and are likely masking the impacts of organic matter dilution. In the Kingsthorpe floodplain core there is an increase in the predicted contribution of sediment made by geochemical and lithogenic radionuclide tracers, in relation to mineral magnetic signatures, when LOI increases. This result is the opposite of that expected according to magnetic theory. An explanation for this may be a result of the association of geochemical or radionuclide tracers with the organic fraction. For example, calcium is used in most composite fingerprints in this core and is found in high concentrations in the channel banks source group in relation to the surface agriculture source group. Therefore, an increase in the concentration of Ca, caused by the enrichment of organic matter (Figure 6-1), would result in an increased predicted contribution from channel banks when the LOI of the sediment increases, masking the effects of the dilution of mineral magnetic signatures by organic matter. Although it cannot be shown which tracers are associated with organic matter in the Nene using the available data, it has been shown in published literature that organic matter can concentrate between 1-10% of dry weight of Co, Cu, Fe, Pb, Mn, Mo, Ni, Ag, V, and Zn (Swanson *et al*., 1966). Charlesworth *et al*. (2003) showed that between 7.7% and 90.6% of Cd, Cu, Ni, Zn and Pb present in urban street dusts in Coventry, (a town close to Northampton in the East Midlands, UK) were concentrated within the organic fraction of urban street dusts. The potential effects of an increase in tracer concentrations associated with organic matter can also be seen on tracer groups not containing mineral magnetic signatures, such as the Geochem litho compared to the Geochem group in the Kingsthorpe (Table 6-7C) and Sywell cores (Table 6-7A). There exists therefore a large potential for the enrichment of geochemical tracers in the cores caused by the increased organic matter content of the sediment.

6.5.2. Changes to sediment particle size

The specific surface area of the sediment is highly correlated with most differences between the tracer groups' sediment provenance predictions in the Earls Barton, Stanwick and Upton floodplain cores (Table 6-7).

In the Earls Barton floodplain core, as the specific surface area (SSA) of the sediment increases, the prediction of the 'All' tracer group (containing geochemical tracers and ^{40}K) decreases in relation to the prediction of the Geochem tracer group (Table 6-7E). ^{40}K has low activities in urban street dusts compared to the other sediment sources (Table 6-1). It can therefore be identified that any reduction in sediment ^{40}K activity caused by a change in sediment SSA would result in a greater predicted contribution from urban street dusts and a reduced contribution from the other sediment sources. However, published literature has shown ^{40}K to be concentrated within small clay minerals (Tsabaris et al., 2007), suggesting an inconsistency between the results found in the Nene and prior knowledge of tracer behaviour. An alternative explanation for this result is that Pb and Zn are present in the geochemistry fingerprint and not in the 'All' tracer fingerprint. Both of these elements were shown to be in high concentrations in urban street dusts (Table 6-1), and have also been shown to be typically associated with larger particle size fractions in urban soils and sediment (Horowitz and Elrick, 1987; Pye et al., 2007). Therefore the selective deposition of only fine particles on the floodplain (as was indicated to occur in Figure 6-1), would cause the loss of large particles. The loss of Pb and Zn with these large particles would decrease the predicted contributions from urban street dusts made by the geochemistry tracer group, which would increase the predicted contributed from channel banks.

The opposite trend to that found in the Earls Barton core was seen in the Stanwick floodplain core (Table 6-7F); as SSA increases so does the predicted contribution made by the Geochem litho tracer group in relation to the 'All' tracer group. Likewise, in the Upton floodplain core the geochemistry group predicts increased contributions from channel banks in comparison to the 'All' tracer group as sediment SSA increases. In both of these cores the 'All' tracer group contains mineral magnetic signatures while the other tracer groups do not. In the published literature a positive relationship between geochemical tracers and SSA has been shown to commonly occur (Koiter et al., 2013) while the relationships with mineral magnetic signatures have been shown to be far more complex (Foster *et al.*, 1998; Oldfield *et al.*, 2009). Therefore, a potential interpretation of this result is that an increase in sediment SSA is resulting in a linear increase in geochemical tracer concentration in the core, changing the sediment provenance prediction. As shown by Foster *et al.* (1998) and Oldfield *et al*. (2009) magnetic signatures are likely not to follow the same positive linear relationship, resulting in a discrepancy in the predictions made by magnetic minerals and other tracers. However, it has been shown by Russell *et al*. (2001) that many traces other than mineral magnetism can exhibit non-linear relationships with SSA; so tracer behaviour in reality is likely to be more complex than this generalisation.

6.5.3. Alterations to mineral magnetic signatures

This sub-section repeats the Pearson correlation analysis using ratios which indicate the loss of specific sized magnetic grains in the same way that SSA and LOI were used. Mineral magnetic signatures have been shown to be affected by numerous processes which can cause the loss or alteration of specific sized magnetic grains. For example, smaller magnetic grains are preferentially dissolved before larger grains (Karlin and Levi, 1983) which would cause a reduction in the concentration of those magnetic signatures which incorporate measurement of small magnetic grains (Xlf, Xfd and Xarm), in relation to signatures which also account for larger grains (SIRM and HIRM) (Anderson and Rippey, 1988). The opposite trend of disproportionally low SIRM and HIRM concentrations in relation to Xlf and Xarm would be indicative of the loss of larger magnetic grains, through a process such as selective transport or deposition. Such a process was suggested as a potential explanation for a discrepancy in mineral magnetic signatures between a lake and its upstream floodplain by Foster *et al.* (1996). Therefore, by examining the ratios of mineral magnetic signatures indicative of large magnetic grains, compared to signatures indicative of small magnetic grains, an indication as to any process causing mineral magnetic non-conservatism can be gained (Anderson and Rippey, 1988).

Whilst this section only directly investigates the non-conservatism of mineral magnetic signatures, due to their potential to indicate the loss of specific grain sizes; the diagenesis of geochemical tracers has been shown to occur in research such as that presented by Mayer *et al.* (1982). It is also well documented in other research, such as that produced by Burdige (1993) that metals in the environment are often associated with the iron oxide fraction of soils and sediments. Therefore, the processes causing the dissolution of magnetic iron oxides would also be expected to cause the dissolution of the geochemical and lithogenic radionuclide tracers associated with the iron oxides fraction of sediment. On this basis magnetic minerals were considered as indicators of the processes which could potentially be affecting different types of tracer in the sediment.

In addition to processes of chemical dissolution and selective transport which can alter mineral magnetic signatures, the in-growth of bacterially derived magnetite and autogenic

Griegite has been shown to alter mineral magnetic signatures in deposited lake sediment (Oldfield and Wu, 2000; Oldfield et al., 2003). Bacterially produced magnetite is characterised by small stable single domain magnetite grains (< ~0.1μm), which are a primary contributor to the Xarm signature of lake sediments (Moskowitzet al., 1993). For this reason a value greater than 2 for the ratio of Xarm / Sirm suggests that the bacterial magnetite is beginning to dominate the mineral magnetic signature, and is therefore overprinting the detrital signature (Foster et al., 2008). The formation of autogenic Greigite, an iron sulphide, has been shown to occur in freshwater and slightly brackish lake or estuarine sediments. The presence of this mineral is indicated by a Sirm / Xlf ratio in excess of 30 (Snowball and Thompson, 1988). As the Xarm / Sirm and Sirm / Xlf ratios are also ratios of the loss or gain of large magnetic grains in relation to small magnetic grains, they were used as indicators of both the in-growth and dissolution of minerals in lake cores, as well as processes of selective deposition of fine particles and dissolution of minerals in floodplain cores.

Figure 6-3A shows that in the source samples there is a strong relationship between Xlf and SIRM (Spearman rank p=0.000, r=0.913). Therefore a change in sediment source is unlikely to alter the ratio between these two signatures. For this reason this ratio can be confidently used as an indicator of the non-conservatism of magnetic signatures. The relationship between Xarm and Sirm is also strongly linear for channel bank and surface agricultural source samples; however the urban street dust samples do not follow this relationship. Therefore, the results derived using this ratio should be carefully interpreted where a large proportion of urban sediment is likely to be present.

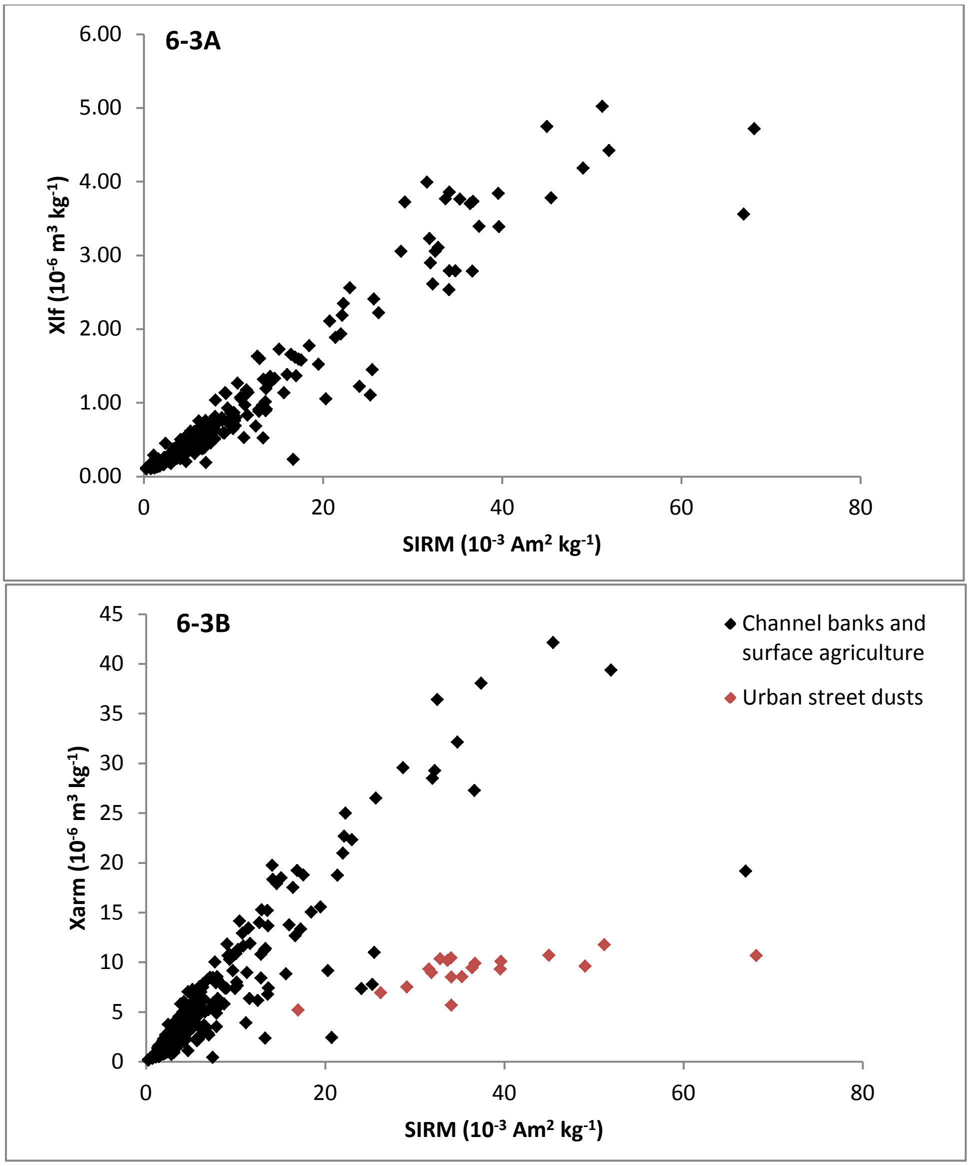


Figure 6-3: The relationships between Xlf and SIRM (A), and Xarm and SIRM (B) in sediment source samples.

The Xarm/ Sirm ratio in the Sywell reservoir core exceeded a value of 2 in the majority of core slices, indicating the likely in-growth of bacterial magnetite (Foster *et al.,* 2008) (Table 6-7 A). Xarm is most sensitive to the presence of bacterially produced stable single domain magnetite (Oldfield, 2007), which is an explanation for why this tracer failed the mass conservation test (Table 6-3). However, an impact on other magnetic mineral signatures would still be expected, as magnetic minerals are being added to the sediment and contribute to magnetic susceptibility (Xlf) and remanence (Sirm, Irm-100mt) (Oldfield, 2007). The impact of this in-growth in Sywell reservoir is seen in the form of a positive correlation between the Xarm / Sirm ratio and four of the differences between tracer group predictions. The Sirm / Xlf ratio shows the opposite trend and is positively correlated with a decrease in predicted contributions from channel banks made by mineral magnetic signatures in comparison to other tracer groups. These results indicate an increase in small remanence carrying minerals in relation to larger minerals, as would be expected with the in-growth of small stable single domain bacterial magnetite. It can be noted that the consistency between the predictions of mineral magnetic signatures and other tracers in the Sywell core is greater than in most other cores (Figure 6-2A); suggesting that the in-growth of magnetite is having less of an impact on fingerprint provenance predictions than the processes causing the tracer non-conservatism occurring in other cores for different reasons.

In the Kingsthorpe floodplain core (Table 6-7 C), twelve of the fifteen differences between tracer group predictions were significantly correlated with the Xarm / Sirm ratio, and fourteen were significantly correlated with the Sirm / Xlf ratio. Correlation coefficients were generally high and ranged from 0.46 to 0.8 and 0.43 to 0.9 respectively, indicating that alterations to magnetic minerals are potentially an important process affecting tracers in this core. When the Xarm / Sirm ratio increased, the predicted contribution from channel banks made by mineral magnetic signatures decreased. The opposite trend was seen with the Sirm / Xlf ratio; when this ratio increased, the predicted contribution made by magnetic minerals also increased. These results indicate that when a greater proportion of large remanence carrying magnetic grains were present in relation to small grains, mineral magnetic tracers predicted a greater contribution of sediment originating from channel banks.

Due to the low mineral magnetic signatures in the channel bank source group (Table 6-1), an increase in the concentration of magnetic minerals in the sediment would cause a reduction in the predicted contribution from channel banks, and a decrease in the concentrations of magnetic minerals would cause an increased predicted contribution from channel banks. It is therefore possible that the dissolution of small magnetic grains in the deposited sediment is reducing the magnetic mineral signatures and therefore increasing the predicted contributions from channel banks made by mineral magnetic signatures. The dissolution of iron oxides in gleyed soil horizons has been previously shown to occur by Dearing *et al*. (1985). The gleying of waterlogged floodplain sediments would result in the loss of the mineral magnetic signatures and geochemical and lithogenic radionuclide tracers associated with iron oxides, and may be occurring in the Kingsthorpe core. An alternative explanation is that the selective transport of only small magnetic minerals to the floodplain is decreasing the proportion of large magnetic minerals present, and therefore increasing the predicted contribution from channel banks; however the coarse SSA of the sediment in this core shown in Table 6-1 suggests that this is not occurring.

In the Stanwick floodplain core (Table 6-7 F) the Xarm / Sirm and Sirm / Xlf ratios were significantly correlated with the differences between the predictions made by the Geochem litho group and the predictions made by the 'All' tracer group. The 'All' group contained both mineral magnetic signatures and geochemical tracers. As in the Kingsthorpe core the Xarm / Sirm ratio is strongly and positively correlated with a decreased predicted contribution from channel banks made by mineral magnetic signatures. An increased Sirm / Xlf ratio was correlated with an increased predicted contribution of sediment from channel banks. As in the Kingsthorpe core this suggests that either the removal of larger magnetic grains by selective fine particle size deposition or the dissolution of smaller magnetic minerals may be occurring, reducing the magnetic signatures when the Sirm / Xlf ratio decreases. As the specific surface area of sediment in this core is increased by ~50% over the sediment source samples (Figure 6-1), the process of selective deposition of only small magnetic grains on the floodplain is the most probable explanation for the discrepancy between tracer group predictions. However, it has been shown that small magnetic grains can contribute a disproportionally high amount of the overall magnetic signatures of soils and sediment (Dunlop and Argyle, 1997), contradicting this idea. It can however be considered that large haematite minerals of between 10-100 μm in diameter have been shown to be formed by combustion in urban environments and are major contributors to the magnetic signatures of urban material (Sheng-Gao and Shi-Qing, 2008). The loss of these larger minerals would therefore be expected to remove much of the highly magnetic minerals of anthropogenic origin, and could cause a reduction of magnetic signatures as particle size decreased.

The magnetic ratios did not prove to be significantly correlated with the differences in predictions in the Upton floodplain core (Table 6-7D), despite the large differences between predictions of mineral magnetic tracers and geochemical tracers; suggesting that the tracers are more affected by the organic enrichment, chemical dissolution and particle size alterations than any selective loss of different size magnetic grains. However, all magnetic mineral tracers failed the range test in the Earls Barton core and the bottom half of the Upton core (which was not included in this section of the analysis). Therefore, there is the additional consideration that, in these cores, the loss of all magnetic mineral grain sizes was occurring in at least part of the cores. The floodplain in both of these coring locations was observed to be heavily waterlogged, with much of each core having a blue tinted gleyed appearance, suggesting that the magnetic minerals were significantly affected by dissolution. The 100% contribution of sediment from channel banks predicted by magnetic signatures in the Upton core, which is unlikely to be a true reflection of sediment sources in the Nene, probably reflects this process (Figure 6-2E).

Another consideration when using magnetic mineral signatures to fingerprint sediment, not previously discussed, is the assumption of linear additivity. Lees (1997) showed that errors of up to 2% occur with susceptibility measurements, and up to 16% with remanence measurements due to a lack of linear additivity. In the Nene, contrasts in median mineral magnetic signatures in the source groups range from 30% (HIRM) up to 214% (Xfd) (Table 6-1). Therefore significant errors to predictions made using HIRM could be caused through non-linear additivity effects, although for other magnetic signatures a 16% error would likely be minor in relation to the differences between source group medians.

The results in this section have suggested that a significant alteration has occurred to magnetic minerals in most of the cores examined. It should however be emphasised that geochemical and radionuclide tracers are also likely to be subject to alterations caused by dissolution and the selective transport of larger or finer mineral size fractions. In Figure 6-2E it was shown that when ^{137}Cs was used as a tracer in the Kingsthorpe floodplain core, its predictions were closer to those of magnetic minerals than any other tracer group. As ^{137}Cs has been shown to be rapidly and strongly sorbed to soil particles (Taylor *et al.*, 2012). Therefore, it is likely that this tracer exhibits a greater amount of conservatism than the mineral magnetic, geochemical and lithogenic radionuclide tracers. Therefore, it is likely that in the Kingsthorpe floodplain cores the magnetic mineral signatures provide a more accurate prediction of sediment provenance than the other tracer groups, despite the alterations which have been indicated to have affected them.

Table 6-7: Pearson correlation coefficients (r) and associated p values for correlations between differences between tracer group predictions and loss on ignition (LOI), specific surface area (SSA), and the Xarm/Sirm and Sirm/Xlf ratios. Statistically significant (p<0.05) values are highlighted in green.

(A) Sywell Reservoir

		LOI	SSA	Xarm/Sirm	Sirm/Xlf
Mag - Mag litho	Correlation Coefficient	-.640	-.269	.009	-.592
	Sig. (2-tailed)	.000	.093	.956	.000
	N	40	40	40	40
Mag - Mag geochem	Correlation Coefficient	-.441	-.170	.189	-.491
	Sig. (2-tailed)	.004	.295	.244	.001
	N	40	40	40	40
Mag - Geochem litho	Correlation Coefficient	-.087	-.117	-.109	.232
	Sig. (2-tailed)	.593	.474	.502	.149
	N	40	40	40	40
Mag - Geochem	Correlation Coefficient	.753	.184	-.118	.305
	Sig. (2-tailed)	.000	.255	.468	.056
	N	40	40	40	40
Mag - All	Correlation Coefficient	-.594	-.200	.341	-.421
	Sig. (2-tailed)	.000	.215	.031	.007
	N	40	40	40	40
Mag litho - Mag geochem	Correlation Coefficient	.209	-.175	.033	-.176
	Sig. (2-tailed)	.196	.279	.838	.277
	N	40	40	40	40
Mag litho - Litho geochem	Correlation Coefficient	-.090	-.389	.132	-.234
	Sig. (2-tailed)	.579	.013	.417	.147
	N	40	40	40	40
Mag litho - Geochem	Correlation Coefficient	-.402	-.153	-.075	-.598
	Sig. (2-tailed)	.010	.346	.644	.000
	N	40	40	40	40
Mag litho - All	Correlation Coefficient	.486	.098	-.219	.089
	Sig. (2-tailed)	.001	.546	.174	.587
	N	40	40	40	40
Mag geochem - Litho geochem	Correlation Coefficient	.167	-.272	.449	.210
	Sig. (2-tailed)	.304	.090	.004	.193
	N	40	40	40	40
Mag geochem - Geochem	Correlation Coefficient	-.692	-.219	.002	-.578
	Sig. (2-tailed)	.000	.174	.988	.000
	N	40	40	40	40
Mag geochem - All	Correlation Coefficient	-.546	-.261	.360	-.270
	Sig. (2-tailed)	.000	.104	.023	.092
	N	40	40	40	40
Litho geochem - Geochem	Correlation Coefficient	.472	-.024	.223	.367
	Sig. (2-tailed)	.002	.886	.166	.020
	N	40	40	40	40
Litho geochem - All	Correlation Coefficient	-.070	-.364	.515	.010
	Sig. (2-tailed)	.667	.021	.001	.950
	N	40	40	40	40
Geochem- All	Correlation Coefficient	-.753	-.178	.059	-.519
	Sig. (2-tailed)	.000	.272	.716	.001
	N	40	40	40	40

(B) Stanwick lake

		LOI	SSA	Xarm/Sirm	Sirm/Xlf
Mag litho - Geochem litho	Correlation Coefficient	.389	.358	.309	-.323
	Sig. (2-tailed)	.111	.145	.213	.191
	N	18	18	18	18
Mag litho - Geochem	Correlation Coefficient	.352	.376	.354	-.337
	Sig. (2-tailed)	.152	.124	.150	.171
	N	18	18	18	18
Mag litho - All	Correlation Coefficient	.030	-.332	-.024	.399
	Sig. (2-tailed)	.906	.179	.926	.101
	N	18	18	18	18
Geochem litho - Geochem	Correlation Coefficient	-.247	-.487	-.692	.298
	Sig. (2-tailed)	.324	.040	.001	.229
	N	18	18	18	18
Geochem litho - All	Correlation Coefficient	.352	.153	-.003	-.162
	Sig. (2-tailed)	.152	.543	.990	.521
	N	18	18	18	18
Geochem - All	Correlation Coefficient	.265	.371	.207	-.311
	Sig. (2-tailed)	.287	.130	.409	.210
	N	18	18	18	18

(C) Kingsthorpe floodplain

		LOI	SSA	Xarm/Sirm	Sirm/Xlf
Mag - Mag litho	Correlation Coefficient	.571	-.156	-.648	.797
	Sig. (2-tailed)	.002	.447	.000	.000
	N	26	26	26	26
Mag - Mag geochem	Correlation Coefficient	.545	-.087	-.796	.940
	Sig. (2-tailed)	.004	.673	.000	.000
	N	26	26	26	26
Mag - Geochem litho	Correlation Coefficient	-.062	-.082	.227	-.298
	Sig. (2-tailed)	.764	.690	.264	.139
	N	26	26	26	26
Mag - Geochem	Correlation Coefficient	-.354	-.097	.350	-.559
	Sig. (2-tailed)	.076	.636	.080	.003
	N	26	26	26	26
Mag - All	Correlation Coefficient	-.582	.264	.468	-.657
	Sig. (2-tailed)	.002	.192	.016	.000
	N	26	26	26	26
Mag litho - Mag geochem	Correlation Coefficient	.289	-.028	-.620	.783
	Sig. (2-tailed)	.152	.892	.001	.000
	N	26	26	26	26
Mag litho - Geochem litho	Correlation Coefficient	-.247	-.022	.460	-.567
	Sig. (2-tailed)	.223	.917	.018	.003
	N	26	26	26	26
Mag litho - Geochem	Correlation Coefficient	-.447	.027	.515	-.723
	Sig. (2-tailed)	.022	.897	.007	.000
	N	26	26	26	26
Mag litho - All	Correlation Coefficient	-.564	.250	.529	-.718
	Sig. (2-tailed)	.003	.218	.005	.000
	N	26	26	26	26
Mag geochem - Geochem litho	Correlation Coefficient	-.446	.083	.715	-.887
	Sig. (2-tailed)	.022	.685	.000	.000
	N	26	26	26	26
Mag geochem - Geochem	Correlation Coefficient	-.574	.074	.718	-.895
	Sig. (2-tailed)	.002	.721	.000	.000
	N	26	26	26	26
Mag geochem - All	Correlation Coefficient	-.531	.191	.648	-.851
	Sig. (2-tailed)	.005	.349	.000	.000
	N	26	26	26	26
Geochem litho - Geochem	Correlation Coefficient	-.591	.066	.252	-.432
	Sig. (2-tailed)	.001	.750	.214	.027
	N	26	26	26	26
Geochem litho - All	Correlation Coefficient	-.637	.321	.405	-.559
	Sig. (2-tailed)	.000	.110	.040	.003
	N	26	26	26	26
Geochem - All	Correlation Coefficient	-.652	.354	.468	-.602
	Sig. (2-tailed)	.000	.076	.016	.001
	N	26	26	26	26

(D) Upton floodplain

		LOI	SSA	Xarm/Sirm	Sirm/Xlf
Mag - Mag litho	Correlation Coefficient	.019	-.019	-.101	-.002
	Sig. (2-tailed)	.949	.949	.730	.994
	N	14	14	14	14
Mag - Geochem	Correlation Coefficient	.871	-.571	-.240	-.081
	Sig. (2-tailed)	.000	.033	.409	.782
	N	14	14	14	14
Mag - All	Correlation Coefficient	.415	-.355	-.198	.141
	Sig. (2-tailed)	.140	.212	.497	.631
	N	14	14	14	14
Mag litho - Geochem	Correlation Coefficient	.871	-.571	-.240	-.081
	Sig. (2-tailed)	.000	.033	.409	.782
	N	14	14	14	14
Mag litho - All	Correlation Coefficient	.362	-.358	-.277	.198
	Sig. (2-tailed)	.203	.209	.337	.497
	N	14	14	14	14
Geochem - All	Correlation Coefficient	-.878	.573	.253	.068
	Sig. (2-tailed)	.000	.032	.383	.817
	N	14	14	14	14

(E) Earls Barton floodplain (an Xarm measurement was unavailable for this core due to equipment failure)

		LOI	SSA
All - Geochem	Correlation Coefficient	.239	-.809
	Sig. (2-tailed)	.173	.000
	N	34	34

(F) Stanwick floodplain

		LOI	SSA	Xarm/Sirm	Sirm/Xlf
Geochem litho - All	Correlation Coefficient	-.790	.876	.783	-.812
	Sig. (2-tailed)	.000	.000	.000	.000
	N	31	31	31	31

6.6. The effectiveness of simple organic enrichment and particle size corrections

This section contributes towards Objective 3 of this thesis by investigating the effects of organic matter and particle size data corrections on the consistency between tracer group fingerprinting predictions.

Section 6.5 showed that changes to the organic content of sediment were likely to be a controlling factor in the differences between tracer group provenance predictions in the Sywell reservoir, Kingsthorpe floodplain, Upton floodplain and Stanwick floodplain cores. Therefore, an organic enrichment data correction would be expected to improve the consistency between tracer fingerprint predictions in these cores.

Changes to the specific surface area (SSA) of the sediment were shown to be a potential controlling factor on the differences between tracer group predictions in the Sywell reservoir, Upton floodplain, Stanwick floodplain and Earls Barton floodplain cores. Therefore, a particle size data correction would also be expected to improve the consistency between tracer group predictions in these cores.

This section uses the simple SSA and LOI corrections described in Section 5.5 to determine the extent to which they reduce the differences between the provenance predictions of the tracer group fingerprints. The corrections were applied only to those cores where LOI and SSA corrections were indicated to be of potential benefit in Section 6.5. Plots of the median predicted contributions of sediment from channel banks derived using the different fingerprints before and after corrections are shown in Figure 6-4.

Sywell Reservoir (Figure 6-4A)

It was indicated in Section 6.5 that an organic enrichment correction would potentially be of benefit in this core. On this basis an organic correction was applied to the geochemistry tracer group. The correction caused very little impact on the predictions of this tracer group. An exception to this is an anomalous period of results occurring between 25cm and 35cm, which resulted in a prediction of 0% of sediment originating from channel banks. An examination of the tracer concentrations in this core showed that Gd was the cause of this anomalous period, suggesting a period of non-conservatism of this tracer. It is therefore apparent that this correction has had very little beneficial effect on this tracer group. A composite fingerprint able to correctly classify >80% of source samples could not be established in order to test the impact of the organic correction on magnetic minerals, indicating a loss of discriminatory power caused by the correction. A potential problem with tracer use is therefore highlighted, as tracer discriminatory power may be derived from differences in the organic content or particle size distribution of the source groups. Despite this failure of magnetic minerals to achieve 80% discrimination, the organic correction was applied to the mineral magnetic tracer group, on the basis that organic matter is only weakly diamagnetic (Smith, 1999; Lees, 1999) and therefore a robust justification for the use of this correction exists. The correction had a minimal impact on the provenance prediction of magnetic minerals, with an average of a less than 1% change occurring. This therefore indicates that the processes of tracer non-conservatism causing large differences between the predictions of tracer groups in this core are causing much bigger alterations to the tracers than the dilution of mineral magnetic signatures by organic matter.

Stanwick lake (Figure 6-4B)

An organic correction was applied to the magnetic Mag litho fingerprint in the Stanwick lake core. Although organic matter was not indicated to be a potentially causal factor of the differences between tracer group predictions in Section 6.5, organic matter has been shown to be only weakly diamagnetic providing a robust justification for the use of this correction. The correction had very little impact on the prediction made, changing it by an average of 5.8%. This highlights that, as in the Sywell reservoir core, the dilution of magnetic minerals by organic matter in the sediment has a minor impact on the fingerprinting results derived using mineral magnetic tracers.

Upton floodplain (Figure 6-4C)

Both an organic enrichment correction and a particle size correction were indicated in Section 6.5 to be of potential benefit to the fingerprinting of sediment in the Upton floodplain core. The fingerprinting in this core was characterised in Figure 6-2E by a very large difference in the predictions made by tracer groups containing mineral magnetic signatures and groups containing geochemical tracers, indicating a large potential for improvement by the corrections.

In the Upton core an organic correction did not change the prediction made by the Mag litho fingerprint that 100% of the sediment originated from channel banks. The organic correction increased the predicted contribution made by geochemical tracers by up to 56% in the uppermost half of the core, bringing the estimate closer to that made by the Mag litho group. Therefore an organic enrichment correction may be of some benefit to the geochemical tracers.

The particle size correction had little impact on the geochemical tracer group; it also resulted in a failure of the Mag litho group to achieve 80% discrimination after the mass conservation test and discriminant analysis. It therefore appears that a particle size correction is of little benefit when fingerprinting sediment in this core.

Stanwick floodplain (Figure 6-4D)

In Section 6.5 both the organic enrichment and particle size corrections were indicated to be of potential benefit when fingerprinting the Stanwick floodplain core. When the corrections were applied, both corrections were shown to result in a large change to the tracer groups' predictions. The particle size corrected 'All' fingerprint and the uncorrected Geochem litho fingerprint produced the most comparable predictions in the top half of the core. The uncorrected Geochem litho and organic corrected 'All' fingerprints predict very similar contribution from channel banks in the bottom half of the core. It therefore appears that the corrections can be of benefit in different parts of the core. Although without an independent source of sediment provenance information, if this conclusion is correct cannot be ascertained.

Kingsthorpe floodplain (Figure 6-4E and Figure 6-4F)

Section 6.5 indicated that an organic correction was likely to be of potential benefit towards improving the agreement between the tracer group fingerprinting predictions in the Kingsthorpe floodplain core.

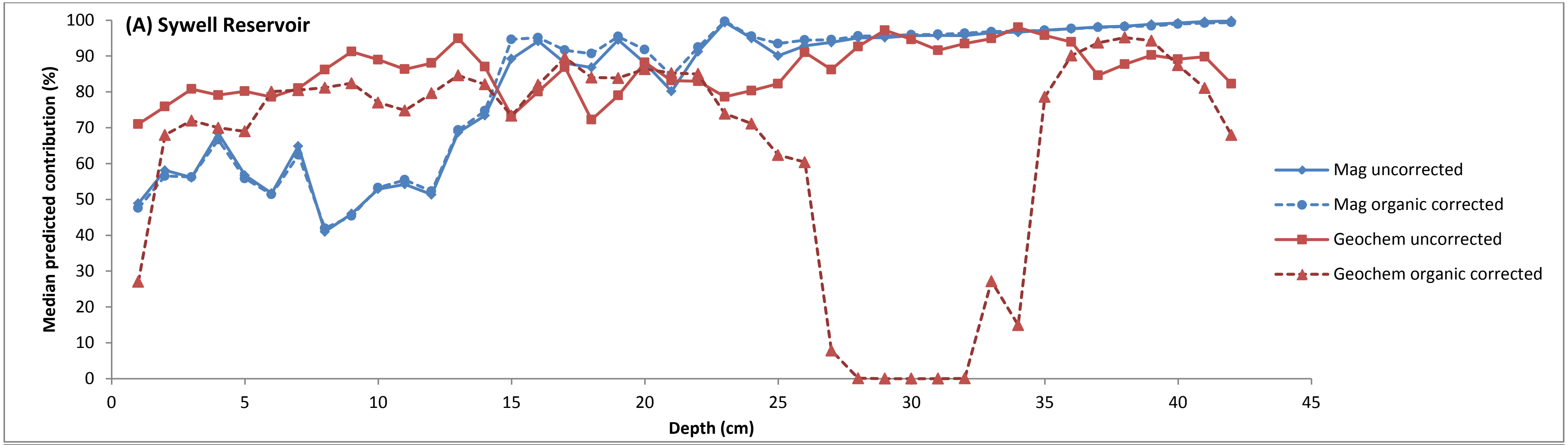
The organic matter data correction was applied to two composite fingerprints containing magnetic mineral tracers, which were the Mag litho and 'All' groups; the predictions of these groups was compared to the geochemistry group (with and without an organic correction).

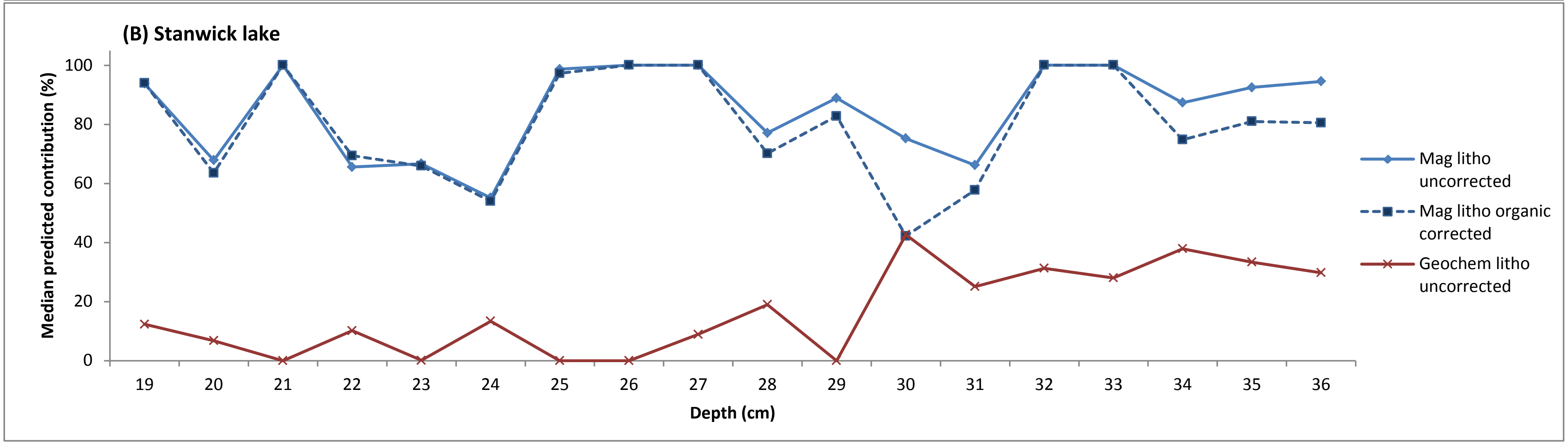
The provenance predictions of the geochemistry and 'All' tracer fingerprints were in close agreement above a depth of 34cm in their uncorrected state, as a result the organic correction applied to either group resulted in a larger difference between their provenance predictions in this section of the core. Below 34cm the two uncorrected tracer groups become less in agreement. Applying the organic correction to either tracer groups in this section of the core was shown to bring their provenance predictions closer together, suggesting that the correction is may be of some benefit. However, due to the different trend observed in the top 34 cm of the core, if the correction was applied to the entire core its overall effect would be detrimental.

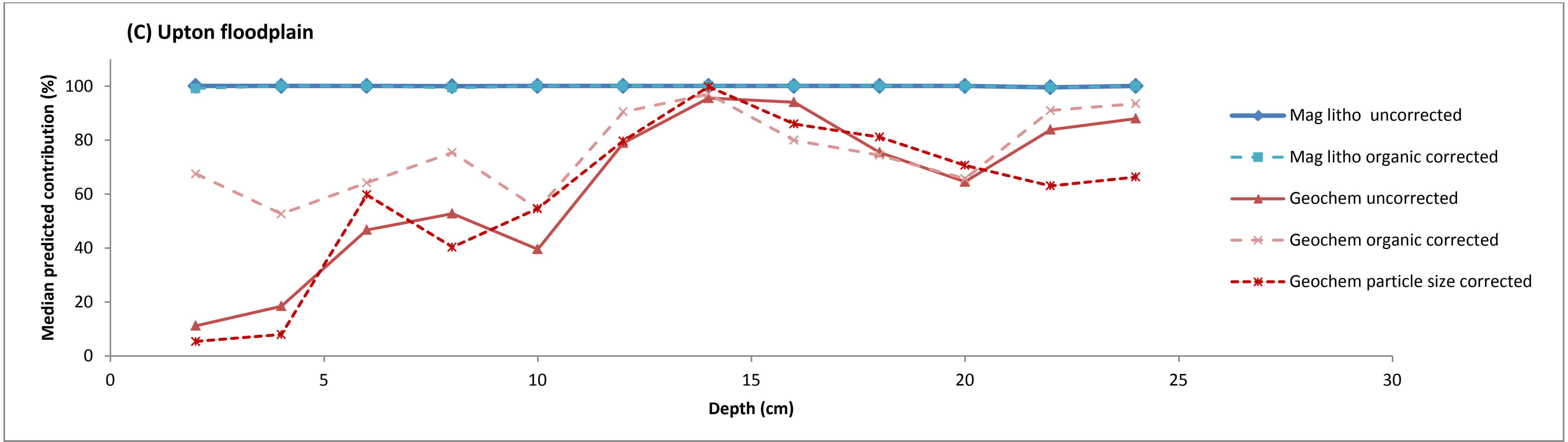
When an organic correction was applied to the Mag litho group it had very little impact on its sediment provenance prediction, even though the dilution of magnetic signatures has been shown to be an important process in the published literature (Lees, 1999). The results in this core therefore indicate that, as in the Sywell and Stanwick lake cores, dilution effects have a relatively minor impact on the sediment fingerprinting results, compared to other sources of tracer non-conservatism, and therefore the organic correction (which assumes dilution by organic matter) has little impact. The organic correction, when applied to the Geochem group brings it closer to the prediction of the uncorrected Mag litho group, which as in the comparison with the 'All' group suggests that the correction may be of some benefit.

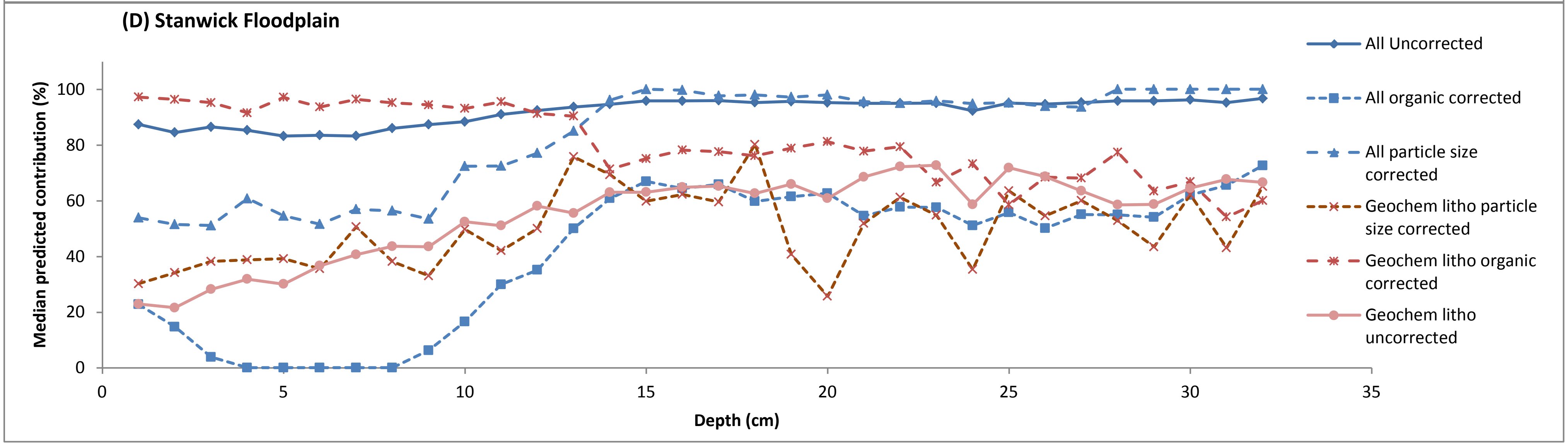
Earls Barton floodplain (Figure 6-4G)

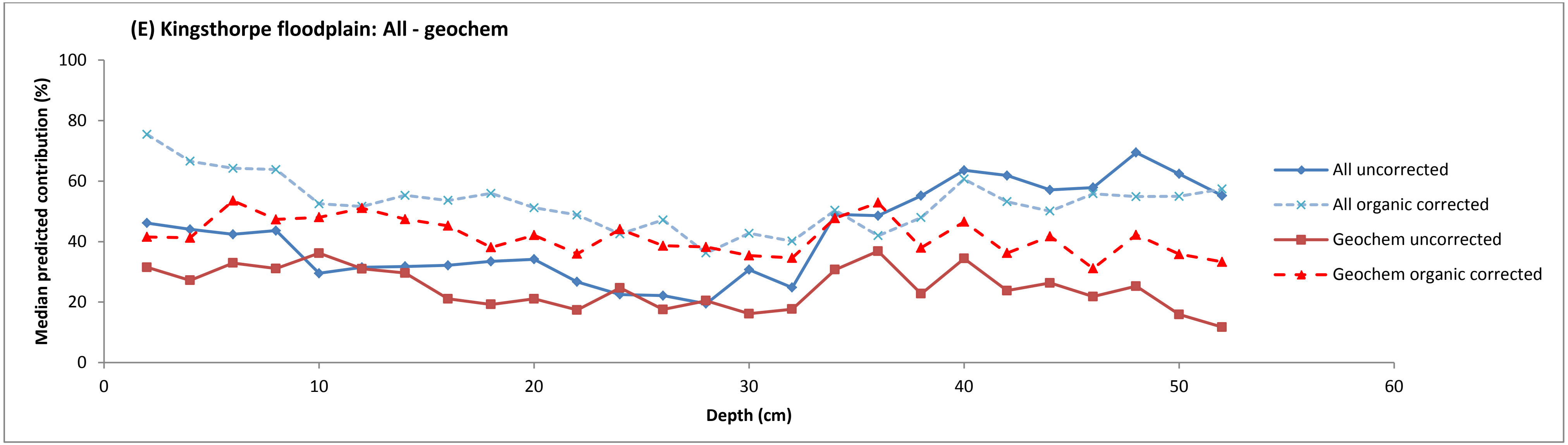
A particle size correction was indicated to be potentially of benefit in the Earls Barton floodplain core in Section 6.5. When this correction was applied to the 'All' tracer group its prediction decreased to a 0% contribution from channel banks throughout most of the down-core profile. This result appears unrealistic when considering the importance of channel banks, suggested by many tracer groups in the other cores, indicating that the correction is detrimental to the fingerprinting. It was found a reduction in the number of tracers able to pass the mass conservation test, and a loss of tracer discriminatory efficiency occurred when a particle size correction was applied to the Geochem litho group, which meant the correction could not be tested.

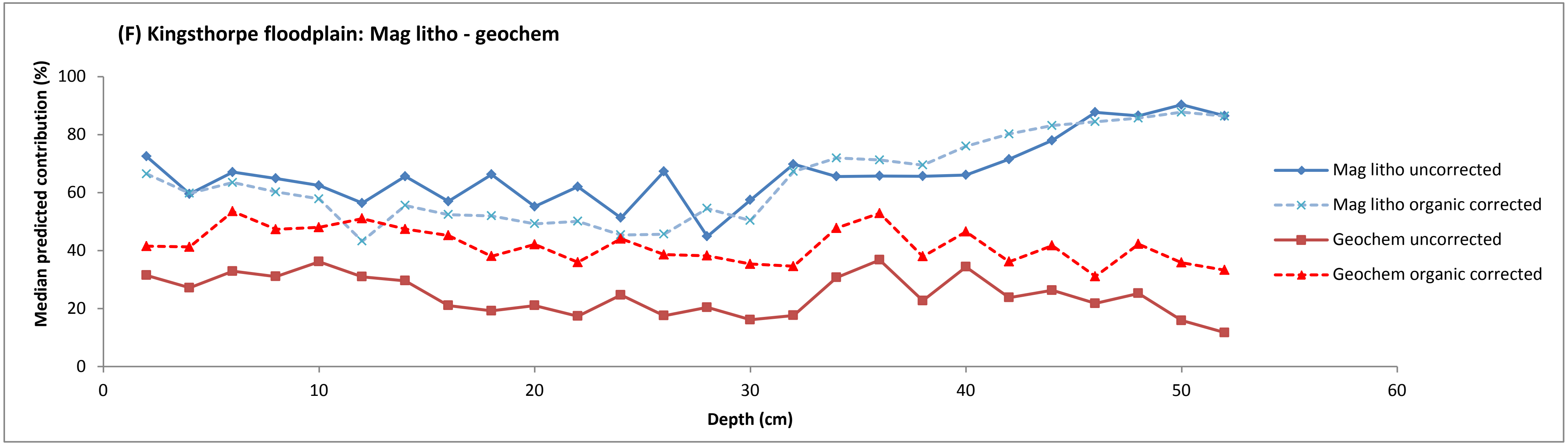

(A) Sywell Reservoir
Median predicted contribution (%)
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
40
45
Depth (cm)
Mag uncorrected
Mag organic corrected
Geochem uncorrected
Geochem organic corrected


(B) Stanwick lake
Median predicted contribution (%)
100
80
60
40
20
0
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
Depth (cm)
Mag litho uncorrected
Mag litho organic corrected
Geochem litho uncorrected


(C) Upton floodplain
Median predicted contribution (%)
Depth (cm)
Mag litho uncorrected
Mag litho organic corrected
Geochem uncorrected
Geochem organic corrected
Geochem particle size corrected


(D) Stanwick Floodplain
Median predicted contribution (%)
Depth (cm)
All Uncorrected
All organic corrected
All particle size corrected
Geochem litho particle size corrected
Geochem litho organic corrected
Geochem litho uncorrected


(E) Kingsthorpe floodplain: All - geochem
Median predicted contribution (%)
100
80
60
40
20
0
0
10
20
30
40
50
60
Depth (cm)
All uncorrected
All organic corrected
Geochem uncorrected
Geochem organic corrected


(F) Kingsthorpe floodplain: Mag litho - geochem
Median predicted contribution (%)
100
80
60
40
20
0
0
10
20
30
40
50
60
Depth (cm)
Mag litho uncorrected
Mag litho organic corrected
Geochem uncorrected
Geochem organic corrected

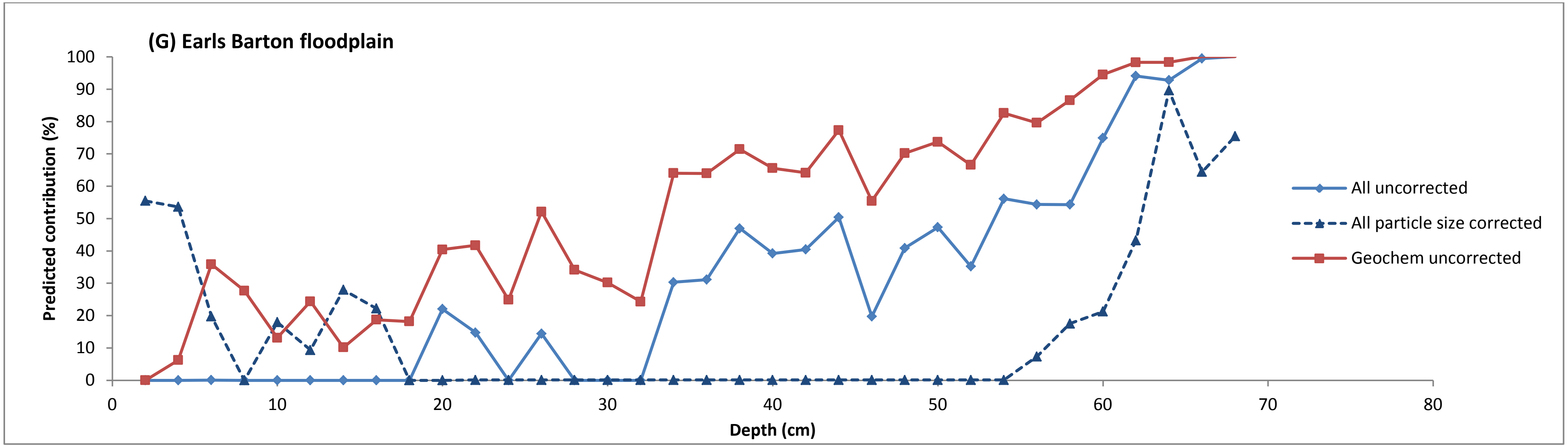


Figure 6-4: The effects of the organic and particle size corrections on the median predicted contributions from channel banks in the sediment cores.

In this section it was found that the organic correction resulted in little effect on the predictions of mineral magnetic tracers. It appeared to be potentially of benefit in the Stanwick, Upton and Kingsthorpe floodplain cores when applied to fingerprints containing geochemical tracers. It was however difficult to determine if the correction was genuinely of benefit without an independent measurement of sediment provenance.

The particle size correction appeared to improve the predictions of the 'All' tracer group in the top 10cm of the Upton floodplain core. In the Earls Barton core the correction appeared to have a detrimental effect on the 'All' tracer group. And in the Stanwick floodplain core it was found to be difficult to determine if the particle size correction was of benefit.

It can therefore be concluded that the use of corrections was problematic, despite the fact that they were only used when the results related to Objective 2 indicated them to be of potential benefit. The loss of specific magnetic mineral fractions provides a potential explanation for the complex outcomes of the corrections. The dissolution of iron oxides suggested to be occurring in the Kingsthorpe and Stanwick floodplain cores indicates changes to tracers unrelated to particle size and organic enrichment of the sediment. It is also likely that the corrections do not represent the true relationships between tracers and organic matter and particle size. For example the particle size correction assumes a linear relationship between SSA and tracers and corrects accordingly (Koiter *et al.*, 2013). Foster *et al.* (1998) and Oldfield *et al.* (2009) showed that the relationship between particle size and mineral magnetic signatures was more complex than a linear relationship. Therefore, the correction would not be expected to correct adequately for the effects of changing sediment particle size on magnetic minerals.

The organic enrichment correction assumes that tracers are not associated with the organic fraction of the sediment (Lees, 1999). While this assumption has been shown to apply to mineral signatures, other tracers have been shown to readily associate with organic matter. An example of this is the proposed association of geochemical tracers with organic matter in the Kingsthorpe floodplain core, the effects of which would be made worse by the correction.

7. Fingerprinting suspended and recently deposited overbank and channel bed sediment.

7.1. Introduction

This chapter addresses Objectives 1, 2 and 3 of this thesis. The previous chapter (Chapter 6) addressed these objectives when fingerprinting historically deposited sediment. This chapter continues the investigation of these objectives by fingerprinting suspended and recently deposited overbank and channel bed sediment (hereafter referred to as 'river sediment'). The chapter is structured into three sections each based upon investigating one of the objectives.

In the first section (7.2) (Objective 1) a fine sediment fingerprinting investigation was conducted using the different fingerprints of mineral magnetic, geochemical, fallout radionuclide and lithogenic radionuclide tracers listed in Table 5-11. The section first explores the ability of tracers to successfully pass each stage of the statistical composite fingerprint determination procedure (outlined in section 5.5.2.). Un-mixing models were then run for all of the river sediment samples using composite fingerprints composed of the different tracer groups outlined in Table 5-11. The sediment provenance predictions made by the different tracer groups were compared, to determine the percentage differences between their predictions, and the differences between their predicted monthly trends in changing sediment provenance.

In the second section (7.3) (Objective 2) the differences between the provenance predictions of the fingerprints were compared to the organic content and particle size distribution of the sediment samples in order to determine if these factors are potentially causes of the differences observed. The investigation of Objective 2 is then continued by examining the uncertainty associated with within-source variability in tracer concentrations and the size of the contrasts in tracer concentration between source groups.

The final section (7.4) addresses Objective 3 by applying data corrections for the sediment organic content and particle size distribution to the tracer signatures. It was determined if the corrections increased the percentage of samples passing the mass conservation test for each tracer and if they improved the discriminatory efficiency of the tracers. The section concludes by determining if there was an improved consistency between tracer group sediment provenance predictions when the tracer signatures were corrected.

7.2. The differences between tracer group provenance predictions

This section addresses Objective 1 of this thesis, by conducting a fine sediment fingerprinting investigation using multiple combinations of different tracer groups, and quantifying the differences between their sediment provenance predictions. The results in this section all utilise data which are uncorrected for organic content or particle size distribution. The ability of tracers to pass the mass conservation test and discriminate between sediment sources is a key part of tracer use. Therefore, this section begins by describing the behaviour of each tracer used during the mass conservation test and statistical determination of composite fingerprints (outlined in Section 5.5.2.).

7.2.1. Mass conservation test

A mass conservation test was used to identify any tracer that might have been altered significantly during sediment transport (Wilkinson *et al*., 2012). The test operated by identifying any tracer in each sediment sample which fell outside of the median values of the included source groups (Table 7-1). These tracers were determined to have failed the test. Figure 7-1 shows the percentage of the total number of river sediment samples collected where each tracer passed the mass conservation test. The results showed that most mineral magnetic signatures (1A) and radionuclide tracers (1B) pass this test for the majority of sediment samples. However, many geochemical tracers (1C) appear to perform poorly.

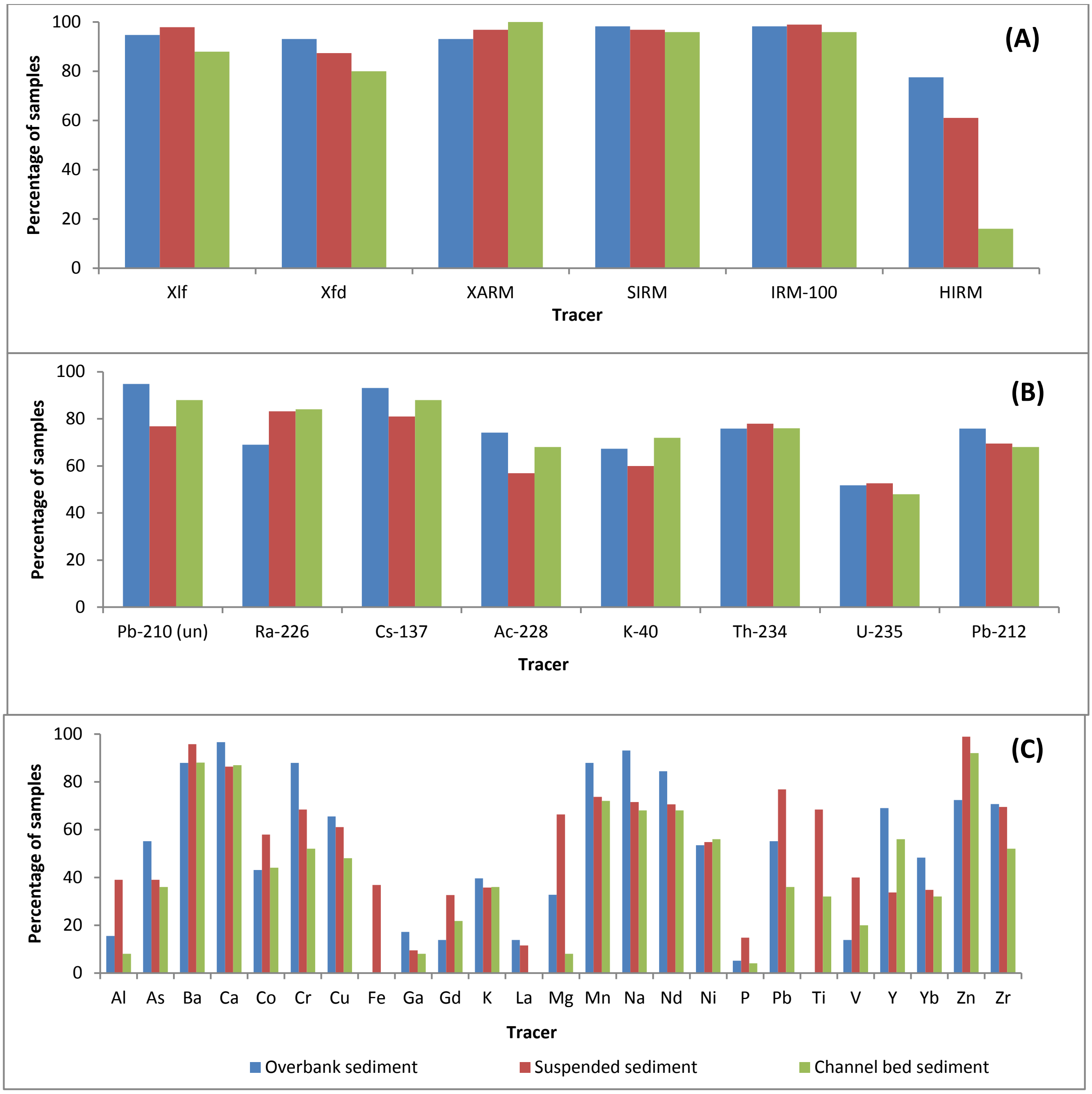


Figure 7-1: The percentage of river sediment samples passing the mass conservation test for each tracer.

A comparison was made between the proportion of samples passing the mass conservation test and the largest inter- source contrasts in tracer concentration (maximum median tracer concentration in any source group – minimum median tracer concentration in any source group). This comparison was made to determine if the results of the mass conservation test were a function of the properties of the source group tracer concentrations, rather than being an equal representation of tracer non-conservatism, for all tracers. The results of this comparison, shown in Figure 7-2, indicated that the ability of tracers to pass the mass conservation test was primarily a function of the inter-source group contrasts in tracer concentration. As many of the geochemical tracers exhibited small contrasts in concentration between the source groups, this explains their observed poor performance in the test (Figure 7-1). A linear relationship was observed for most of the tracers, however, Ga, Gd, Ti, Mg, Cu, HIRM and $^{210}Pb_{un}$ did not follow this linear relationship, indicating that for these 7 tracers more sediment samples failed the range test than would be expected by the inter-source group contrasts in tracer concentration. These seven tracers may therefore be more non-conservative in the environment than others used. Potential reasons for their non-conservatism can be speculated upon, for example P and Cu are found in high concentrations in sediments close to sewage treatment effluent releases, and HIRM has been shown to be significantly affected by non-linear additivity effects (Lees, 1997).

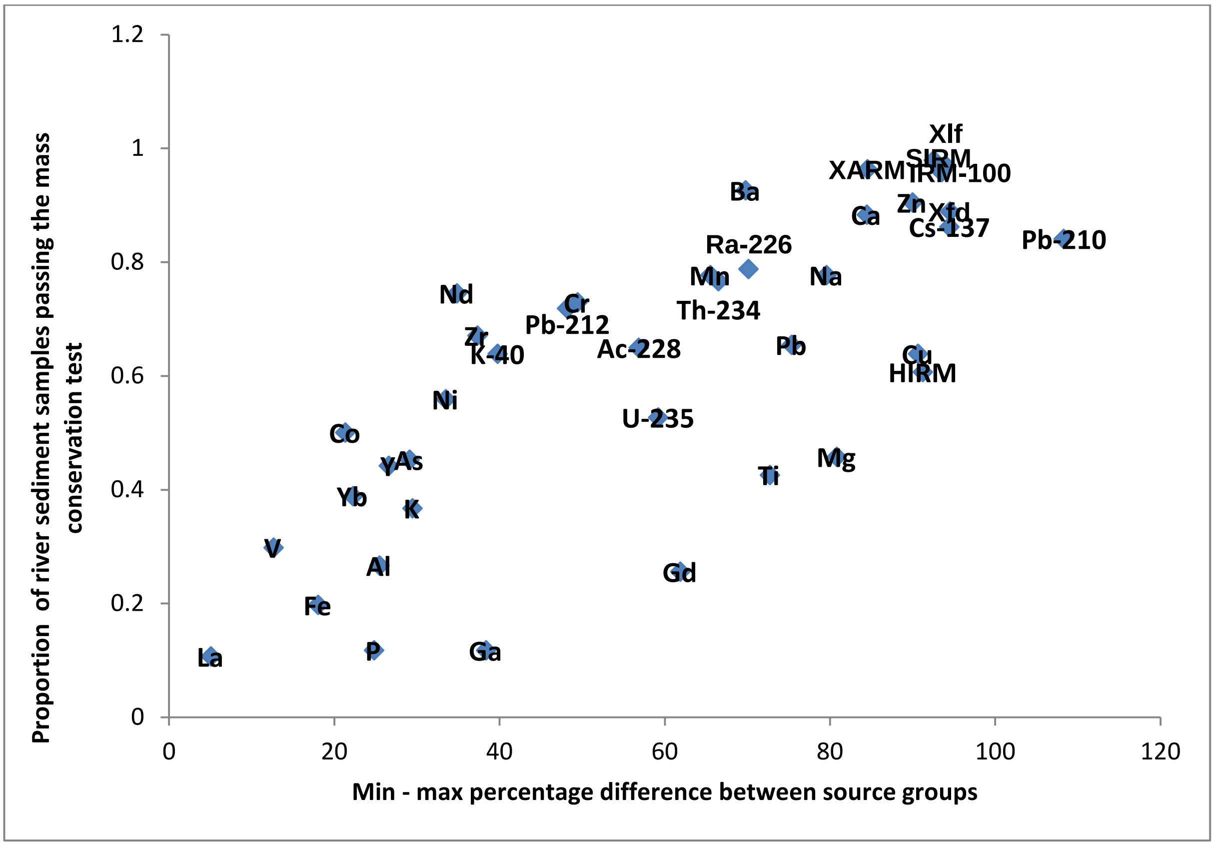


Figure 7-2: The relationship between the largest inter-source contrasts in median tracer concentrations and the proportion of river sediment samples passing the mass conservation test.

7.2.2. Kruskal-Wallace H test

A two-step statistical procedure was used to select the optimum composite fingerprint for each tracer group at each sampling location, using the tracers which passed the mass conservation test. Firstly, a Kruskal–Wallis *H* test was used to remove any tracers which did not show a significant difference in concentration between at least two of the sediment sources. Table 7-1 shows a summary of the results of the test, along with the median and median absolute deviations of each tracer in each of the source samples. Only the results for the analysis when all of the source samples were used together are shown in Table 7-1 as most other source groupings showed similar patterns to that of Table 7-1. It was found that most tracers were significantly different from both of the other source groups, so usually passed this test.

Table 7-1: Median and median absolute deviation tracer concentrations in source groups. Colours correspond to the results of a Kruskal Wallace H-test, green = significantly different (p<0.05), from both other source groups, yellow = significantly different from one other source group, red = not significantly different from either other source.

	Surface Agricultural	Median absolute	**Channel Banks**	Median absolute	**Urban dusts**	Median absolute
LOI (%)	10.44	1.23	7.47	1.03	21.34	2.57
SSA ($m^2\ g^{-1}$)	1.18	0.10	1.16	0.08	0.90	0.07
X_{lf} ($10^{-6}\ m^3\ kg^{-1}$)	0.38	0.18	0.22	0.05	**3.73**	0.45
X_{fd} ($10^{-9}\ m^3\ kg^{-1}$)	21.41	14.19	6.81	3.39	**124.75**	20.12
Xarm ($10^{-6}\ m^3\ kg^{-1}$)	3.67	2.36	1.46	0.66	**9.44**	0.91
IRM1T ($10^{-5}\ m^3\ kg^{-1}$)	4.50	2.18	2.53	0.96	**34.11**	2.62
IRM_{-100} ($10^{-5}\ m^3\ kg^{-1}$)	-3.49	1.85	-1.68	0.74	**-25.98**	3.08
HIRM ($10^{-5}\ m^3\ kg^{-1}$)	0.52	0.18	0.40	0.09	**4.57**	0.59
$^{210}Pb_{un}$ ($mBq\ g^{-1}$)	-1.26	9.30	-8.44	9.68	**101.62**	30.15
^{226}Ra ($mBq\ g^{-1}$)	31.25	8.30	**34.54**	9.94	10.31	2.80
^{137}Cs ($mBq\ g^{-1}$)	**2.89**	1.24	0.16	0.16	0.75	0.39
^{228}Ac ($mBq\ g^{-1}$)	32.86	6.17	**36.89**	6.19	15.91	4.71
^{40}K ($mBq\ g^{-1}$)	612.58	84.17	**645.74**	91.08	388.96	51.66
^{234}Th ($mBq\ g^{-1}$)	**20.27**	5.55	18.16	4.90	6.79	1.28
^{235}U ($mBq\ g^{-1}$)	**2.28**	0.96	2.23	0.95	0.93	0.28
^{212}Pb ($mBq\ g^{-1}$)	34.25	6.05	**38.40**	5.33	19.89	2.18
Al ($mg\ kg^{-1}$)	9488.73	1463.34	8841.46	1974.21	**11868.20**	693.92
As ($mg\ kg^{-1}$)	22.62	9.23	**24.95**	9.44	17.68	1.64
Ba ($mg\ kg^{-1}$)	59.02	12.61	64.29	15.81	**195.50**	19.56
Ca ($mg\ kg^{-1}$)	5570.06	1877.22	8284.87	4270.21	**35837.93**	10581.46
Co ($mg\ kg^{-1}$)	9.46	2.80	**10.82**	2.52	8.51	1.03
Cr ($mg\ kg^{-1}$)	42.62	17.36	37.49	9.20	**74.19**	14.51
Cu ($mg\ kg^{-1}$)	21.62	4.20	20.75	4.52	**222.47**	49.74
Fe ($mg\ kg^{-1}$)	34929.08	11191.21	**42631.25**	12194.19	40927.50	4052.42
Ga ($mg\ kg^{-1}$)	4.77	2.55	3.13	1.97	**5.08**	0.74
Gd ($mg\ kg^{-1}$)	2.60	1.15	**2.94**	1.42	1.12	1.10
K ($mg\ kg^{-1}$)	**1343.61**	323.03	947.59	229.36	1271.75	197.28
La ($mg\ kg^{-1}$)	15.33	3.85	**15.75**	4.22	14.95	1.73
Mg ($mg\ kg^{-1}$))	1708.98	403.85	1776.62	493.32	**8917.81**	1402.17
Mn ($mg\ kg^{-1}$)	647.86	244.88	608.39	208.75	**1765.83**	242.99
Na ($mg\ kg^{-1}$)	61.04	22.72	94.92	36.56	**299.17**	87.08
Nd ($mg\ kg^{-1}$)	28.76	8.12	**38.30**	6.73	24.95	2.05
Ni ($mg\ kg^{-1}$)	25.93	9.86	24.84	4.00	**37.36**	4.95
P ($mg\ kg^{-1}$)	**1354.41**	374.61	1018.04	249.95	1319.66	160.01
Pb ($mg\ kg^{-1}$)	30.98	7.83	26.47	7.18	**107.45**	17.62
Ti ($mg\ kg^{-1}$)	23.98	10.63	21.61	8.39	**79.26**	20.57
V ($mg\ kg^{-1}$)	52.19	18.60	53.18	15.06	**59.75**	3.84
Y ($mg\ kg^{-1}$)	14.15	4.09	**17.62**	3.99	12.93	1.07
Yb ($mg\ kg^{-1}$)	1.78	0.56	**2.29**	0.52	1.88	0.14
Zn ($mg\ kg^{-1}$)	85.27	23.06	85.82	12.68	**853.82**	290.51
Zr ($mg\ kg^{-1}$)	5.84	1.51	7.43	1.54	**9.32**	1.33

7.2.3. Discriminant analysis

The discriminatory efficiency of individual tracers

The final part of the statistical composite fingerprint determination procedure was the use of a linear discriminant analysis to identify the optimum composite fingerprint for each tracer group in each sediment sample. To determine the usefulness of tracers for discriminating between the three potential sediment source groups, a linear discriminant analysis was used to calculate the percentage of source samples correctly classified into their respective source group by each individual tracer (discriminatory efficiency). The discriminatory efficiency of each individual tracer has been used as a weighting in un-mixing models by authors such as Collins *et al*. (2010a), and is used as a weighting in this thesis (Equation 5-6). The efficiency of each tracer was summarised in Figure 7-3 as an average and standard deviation, consisting of the eight regions of the Nene basin where different combinations of the source samples were used to fingerprint the sediment (Figure 5-2). A 33.3% discriminatory efficiency would be expected for each tracer if no differences in tracer concentrations existed between the three source groups. This value is exceeded for all tracers, indicating their potential for source discrimination (Figure 7-7). The average improvement in discriminatory efficiency over the expected 33.3% is 18.3% (Standard deviation 8.7). The highest discriminatory efficiencies are exhibited by $^{210}Pb_{un}$, Ba, Ca Mg and Zr, followed by mineral magnetic signatures. Rare earth elements have some of the lowest efficiencies, as do Co and Ni.

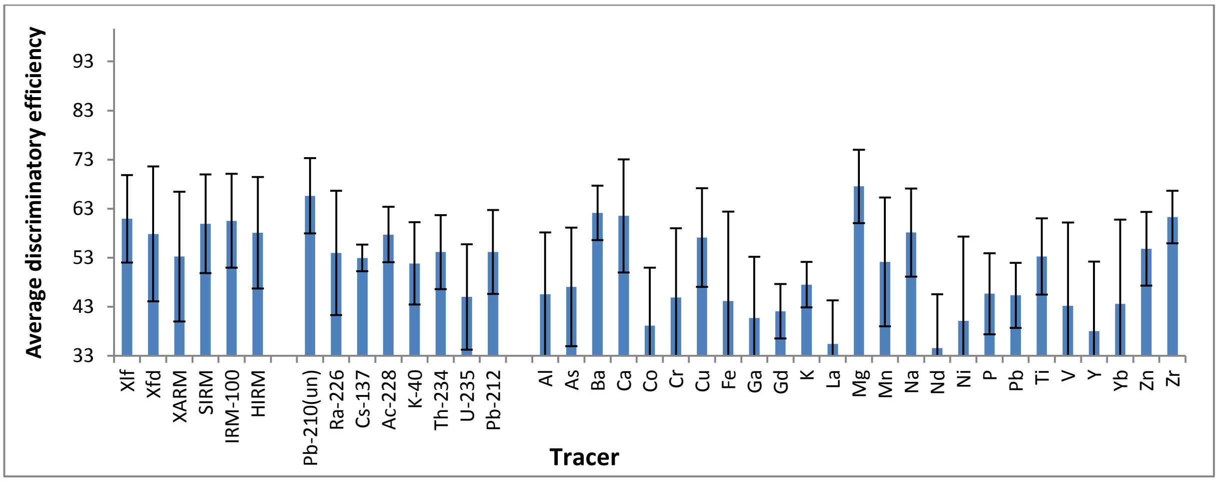


Figure 7-3: The average discriminatory efficiency of tracers used in this study when discriminating between channel banks, surface agricultural sources and urban street dusts (note Y axis starts at 33%).

Table 7-1 indicated that the median tracer concentrations in the urban street dusts sediment source group were often far higher than was found in the other source groups. Urban street dusts are seldom used as a sediment source in published fingerprinting investigations, which often are performed in rural catchments (e.g. Collins *et al*. 1997), unlike the Nene basin. Therefore, the discriminatory efficiency of the tracers when differentiating between channel banks and surface agriculture was calculated, to provide a result more applicable to many published fingerprinting studies.

Removing urban street dusts from the discriminant analysis reduces the improvement of discriminatory efficiency over the expected value of 50% to 7.2% (Figure 7-4). ^{137}Cs, K, Na and Zr have the highest discriminatory efficiencies with a ca. 15% improvement over the expected 50% efficiency. Clear differentiation between urban street dusts and the other sediment sources is therefore likely to be more successful than the discrimination between channel banks and surface agriculture.

The standard deviation error bars in Figure 7-3 and Figure 7-4 indicate a high degree of variability in the discriminatory efficiencies of each individual tracer in the different regions of the Nene, with an average coefficient of variation of 14.7% (when urban street dusts are included as a sediment source). This value is especially high when considering that, on average, tracers can each only improve on the expected discriminatory efficiency by 18.3%.

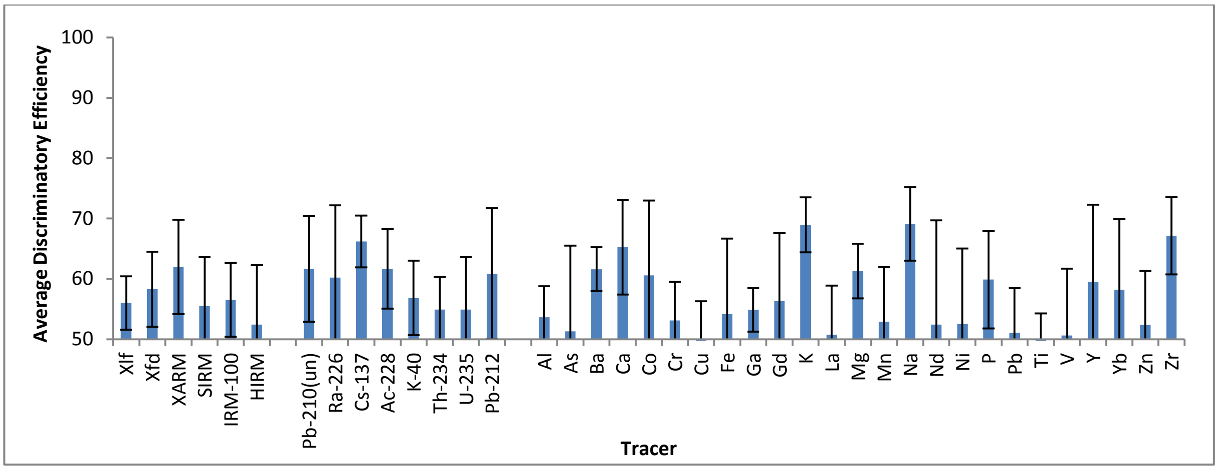


Figure 7-4: The average discriminatory efficiency of tracers used in this study when discriminating between channel banks and surface agricultural sources.

The determination of composite fingerprints of tracer groups

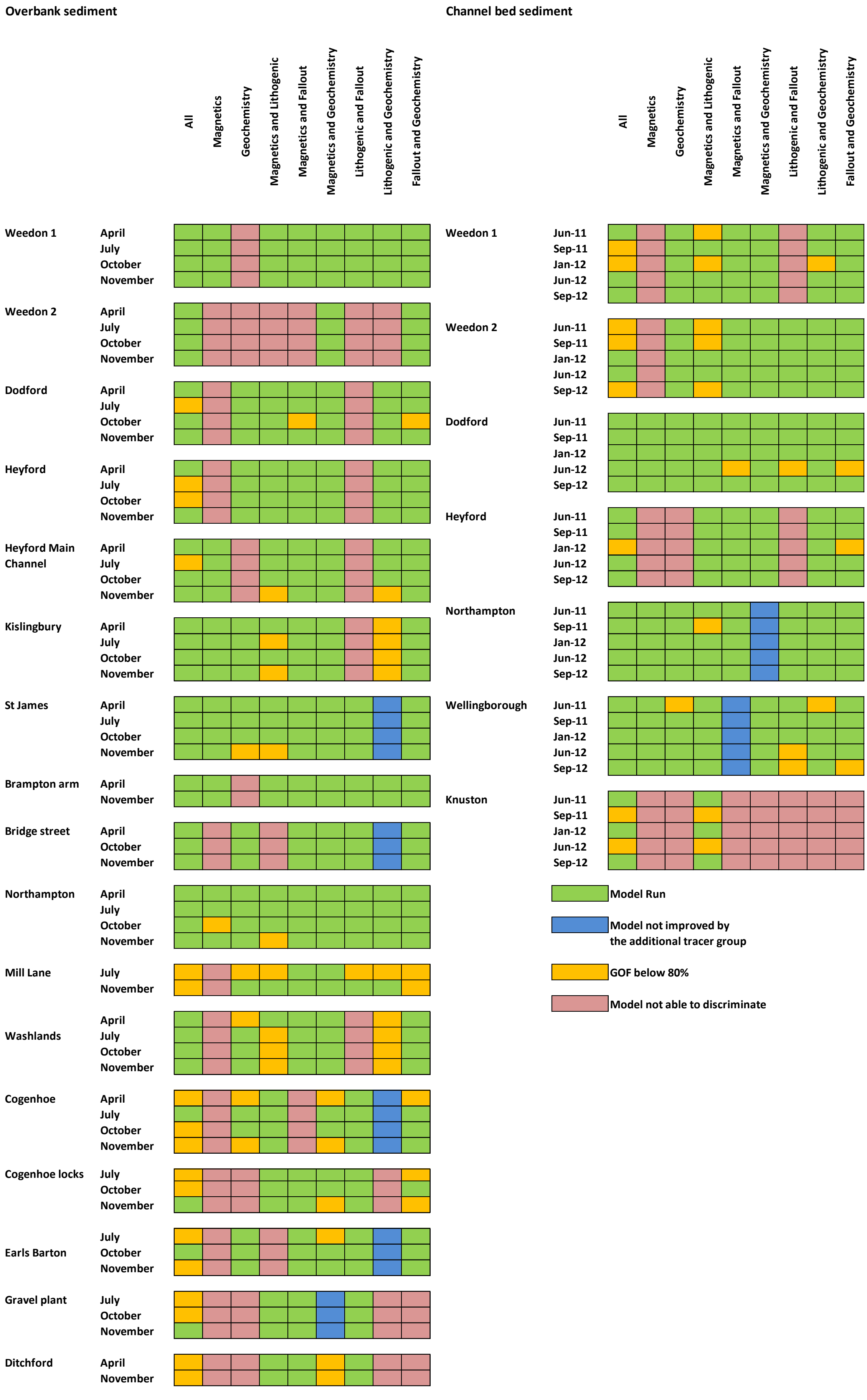
Determination of the optimum composite fingerprint of tracers, to use in the un-mixing modelling, was done using the tracers passing the mass conservation test and Kruskal–Wallis *H* test. A genetic algorithm based multiple linear discriminant analysis (GA-LDA) was used to identify the composite fingerprint for each tracer group at each sampling site. The GA-LDA was used for each of the combinations of tracer groups shown in Table 5-11 and for each river sediment sampling location shown in Figure 4-9, with the exception of channel bed sediment, where fingerprinting was only conducted for the seven sampling sites which also contained a suspended sediment trap. Where repeat sediment samples were collected in a sampling location, such as the monthly suspended sediment samples, these were all fingerprinted with the same composite fingerprint.

To minimise the uncertainty associated with the discriminatory power of the composite fingerprints on the sediment provenance predictions, only the fingerprints identified by the GA-LDA which could correctly classify in excess of 80% of source samples were judged to have passed this stage of the procedure, and were used in the un-mixing modelling. The tracer groups able and not able to form an adequate composite fingerprint are described later in this section in Figure 7-5.

7.2.4. Goodness of fit

Goodness of fit (GOF) is commonly used in published fingerprinting studies to judge how well un-mixing model predictions match the input data, and is therefore a means of judging the reliability of model results (Haddadchi *et al.* 2013). For highly correlated tracers GOF is likely to be close to 100% and problems with equifinality of goodness of fit have been highlighted by Beven, (2003). However, it provides an indication of whether or not the tracers used in a composite fingerprint are in reasonable agreement as to the outcome being predicted by the un-mixing model. It can also identify the influence of anomalous heavily altered tracers in a fingerprint which are skewing the sediment provenance predictions. On this basis any model with an average GOF falling below 80% is judged to be potentially unreliable and was not used for further analysis. As with the discriminatory efficiency, no published guidelines exist for what is an acceptable model GOF; as a result a value of 80% was chosen to ensure only the un-mixing models able to produce a goodness of fit which would be deemed acceptable in most published fingerprinting studies were used for further analysis in this chapter.

Figure 7-5 shows the results of the discriminant analysis and goodness of fit test. The ability to form an adequate composite fingerprint appeared primarily determined by the sampling location, as very few adequate composite fingerprints were produced in the Weedon 2 and Knuston sites. Most models run were found to have a goodness of fit exceeding 80%.


Overbank sediment
Channel bed sediment
All
Magnetics
Geochemistry
Magnetics and Lithogenic
Magnetics and Fallout
Magnetics and Geochemistry
Lithogenic and Fallout
Lithogenic and Geochemistry
Fallout and Geochemistry
Weedon 1
Weedon 2
Dodford
Heyford
Heyford Main Channel
Kislingbury
St James
Brampton arm
Bridge street
Northampton
Mill Lane
Washlands
Cogenhoe
Cogenhoe locks
Earls Barton
Gravel plant
Ditchford
April
July
October
November
Wellingborough
Knuston
Jun-11
Sep-11
Jan-12
Jun-12
Sep-12
Model Run
Model not improved by the additional tracer group
GOF below 80%
Model not able to discriminate

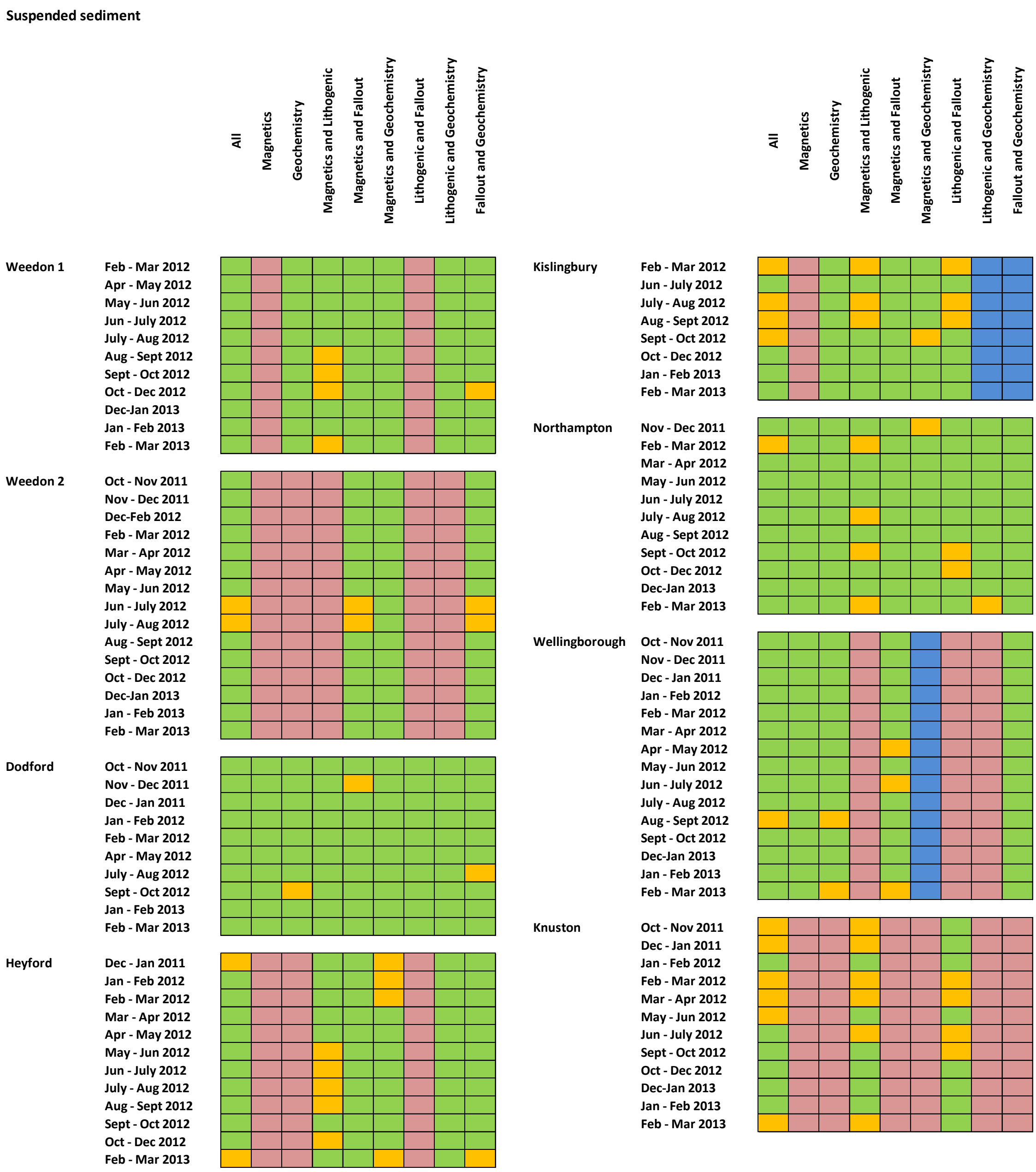


Figure 7-5: The ability of tracer groups to form a composite fingerprint able to correctly classify >80% of source samples and produce a goodness of fit in excess of 80% in an un-mixing model (when the Mag geochem group is highlighted blue its fingerprint is identical to the 'All' group).

7.2.5. Sediment provenance predictions

The following parts of this section compare the sediment provenance predictions made by the different fingerprints of the tracer groups, to determine if the same sediment provenance result was obtained with any of the tracer groups used (Objective 1). The tracer groups are first compared to determine the size of the differences between their predictions; they are then compared to determine if the trends in changing sediment provenance over the study period are consistent.

To provide context to the following results, Figure 7-6 shows an amalgamated probability density function, composed of the predicted provenance of all sediment samples in the Nene, obtained with all tracer group fingerprints. It was found that the un-mixing models predicted that channel banks are the dominant sediment source, while surface agricultural sources are much less important. The contributions of sediment from urban street dusts are much more consistently predicted by all tracer groups and in all sediment samples than channel banks or surface agriculture, with over 50% of model results predicting that between 0% and 10% of the sediment originates from street dusts.

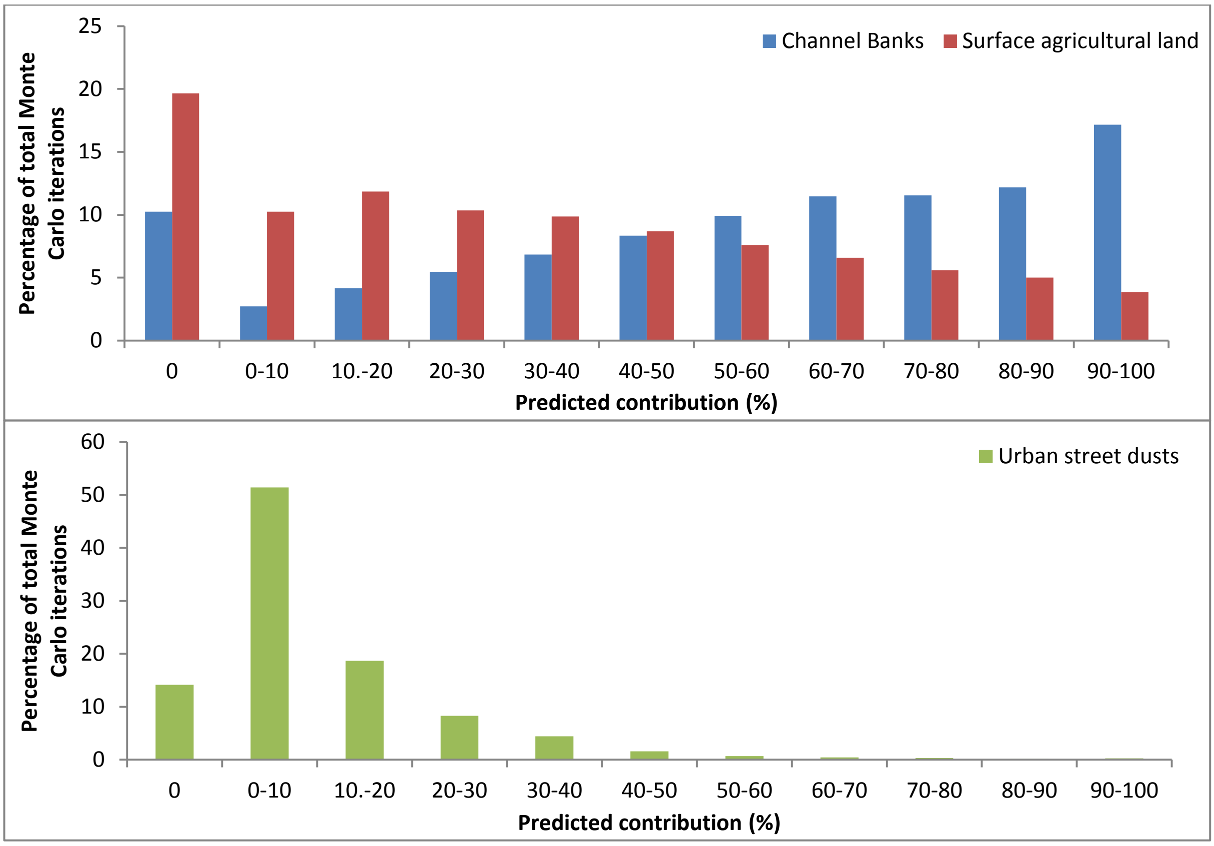


Figure 7-6: Composite probability density function of sediment source contributions to all contemporary sediment samples, produced with all tracer group combinations.

Percentage differences between tracer group provenance predictions

This sub-section quantifies the differences between the tracer group sediment provenance predictions. The fingerprinting provenance predictions were only used for the tracer groups that formed a composite fingerprint able to correctly classify over 80% of source samples into their respective groups and produce a goodness of fit in excess of 80% (Figure 7-5). To simplify the analysis of results only the predicted contributions from channel banks are discussed, as this was determined to be the dominant sediment source in the Nene (Figure 7-6), and was considered representative of the overall un-mixing model result.

The absolute difference between the predictions from two tracer group fingerprints, for each of the sediment samples, was calculated by subtracting the predicted contribution made by one tracer group, of e.g. 50%, from the predicted contribution of a second tracer group, of e.g. 70%, to produce the difference between the tracer group predictions, of e.g. 20%. This was done for each of the 2700 results between the 5^{th} and 95^{th} percentile ranked 3000 Monte Carlo iterations for each sample, to account for close to the full range of uncertainty predicted by the un-mixing model. The mean difference between the 2700 Monte Carlo results was used to quantify the differences between fingerprint predictions for each sample. The mean difference between two tracer groups in all of the sediment samples was then calculated to represent the average difference between the tracer groups' predictions.

Highly variable differences were found between the predictions of the tracer groups when fingerprinting overbank sediment (Figure 7-7); the lowest average difference of 15.3% was found between the prediction made by the Mag group compared to the prediction made by the Mag geochem group. The largest average difference of 39.4% was found when the predictions made by the Mag geochem group were compared to the predictions of the Geochem litho group. The overall average difference between the predictions of tracer groups was 26.4%. The large error bars suggest a large amount of spatial variability associated with the differences between tracer group predictions.

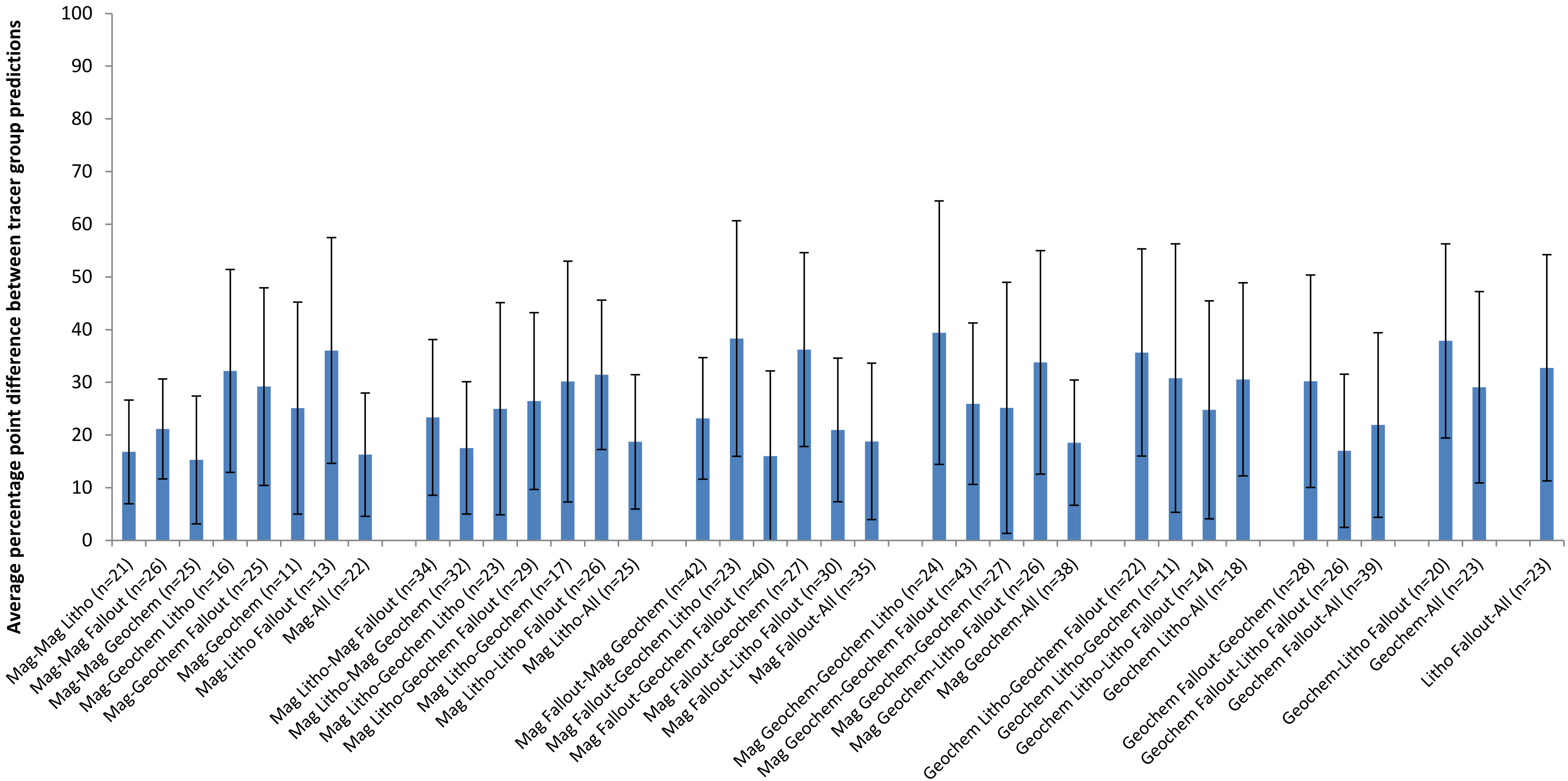


Figure 7-7: The mean absolute difference between tracer group predictions of contributions from channel banks to overbank sediment.

Figure 7-8 shows the mean differences between the predictions of each tracer group and every other tracer group when fingerprinting overbank, suspended and channel bed sediment. The mean difference between the predictions of all tracer groups in all sediment samples was 24.1% with a standard deviation of 0.12%. Little difference was observed in Figure 7-8 between the results for each individual tracer group compared to other tracer groups.

When the average difference between one tracer group and all others is compared in overbank, suspended, and channel bed sediment a mean difference of 1.41% is found between the 3 sampling locations, indicating that sediment sampling location has little effect on the consistency of provenance predictions. This similar average difference indicates that tracer conservatism is not primarily affected by processes occurring during the deposition of suspended sediment onto channel beds or riparian zones, as selective deposition of specific particle size fractions would be expected to alter tracer concentrations (Koiter *et al*., 2013). It also suggests that during the period of sediment storage on channel beds, few post-depositional alterations to the sediment are occurring. Short residence times of the sediment are a potential explanation, as processes such as the chemical alterations likely to have affected the historically deposited sediment in Chapter 6 have limited time to occur.

The size of the differences between the tracer group predictions in the Nene are higher than most of the comparisons made by Nosrati *et al*. (2011) and Evrard *et al*. (2013). However, some of the large differences between fingerprint predictions in the studies reviewed in Section 2.2, such as that by Fu *et al*. (2006) had differences between tracer group properties that exceeded those found in the Nene, suggesting that the results found in the Nene could be experienced in other catchments where the discriminating power of source signatures was relatively poor.

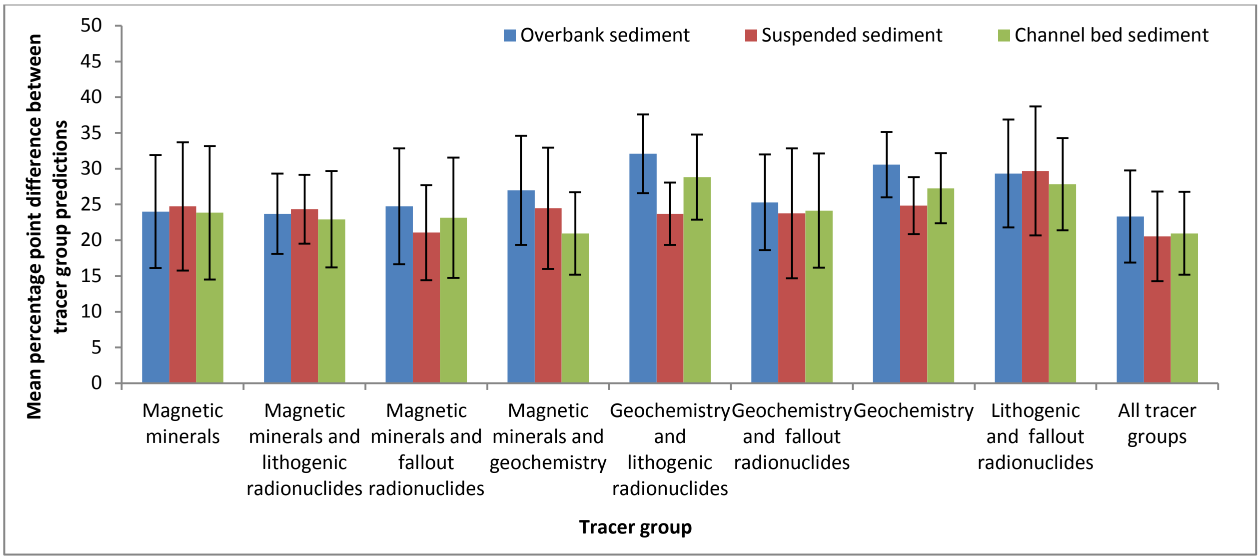


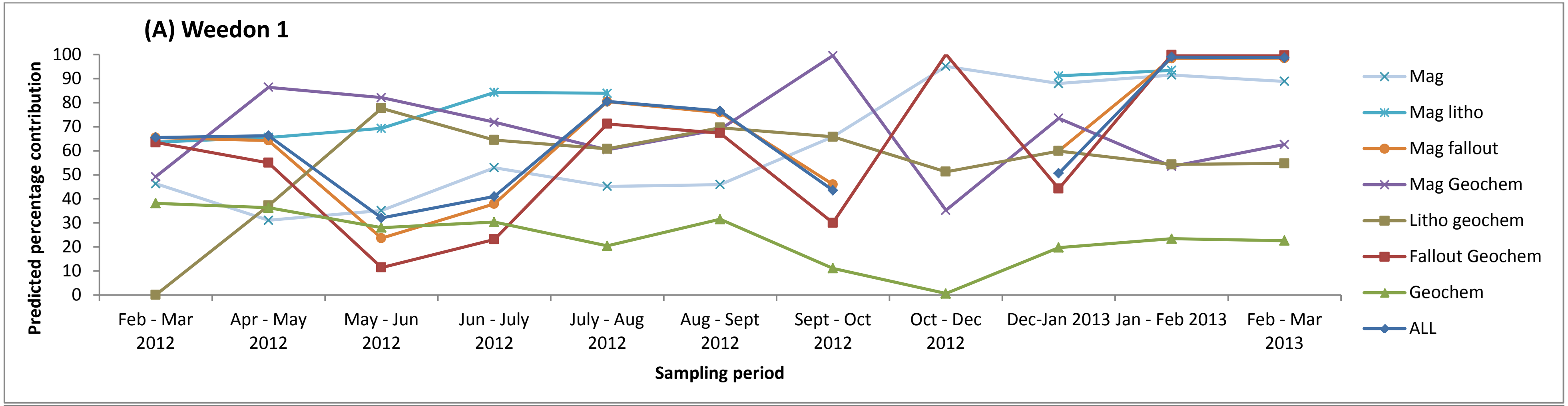
Figure 7-8: Mean differences between the predicted contribution of sediment from channel banks made by each tracer group in comparison all other tracer groups in overbank, suspended and channel bed sediment samples.

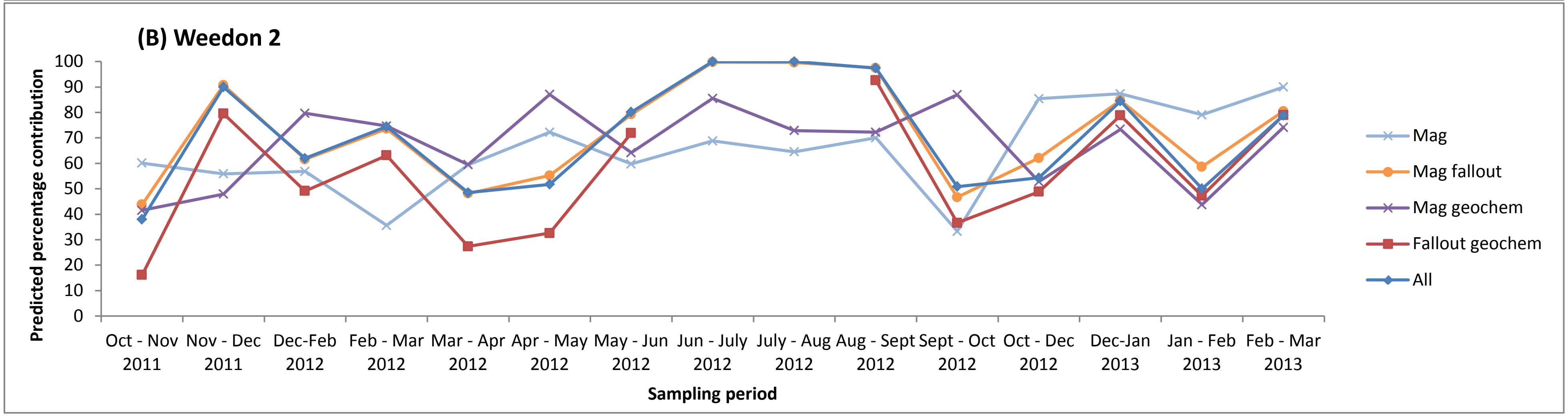
7.2.6. Trends in monthly sediment provenance

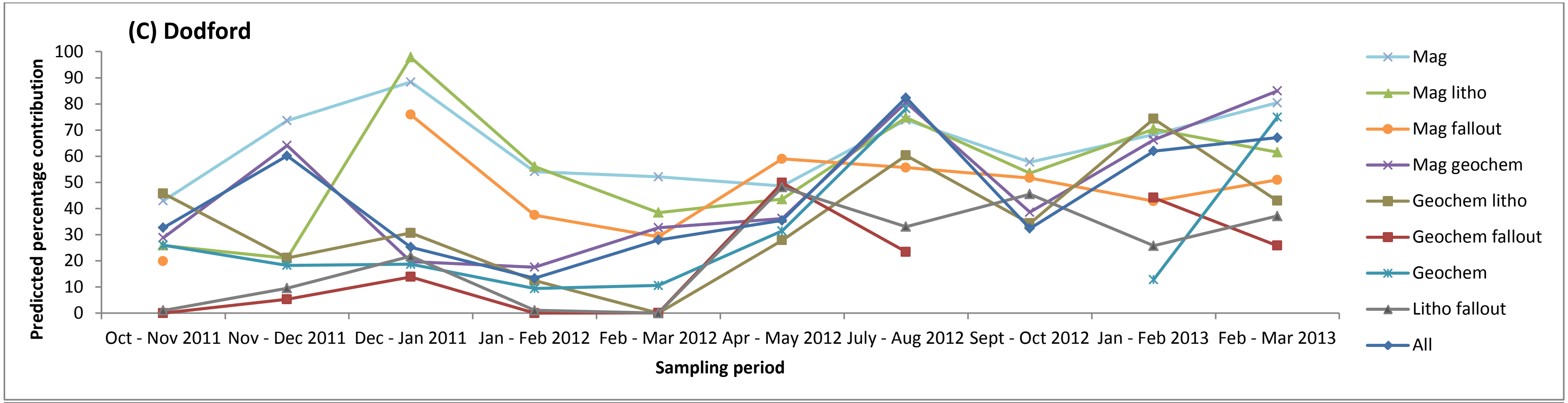
Having established that there are differences between the predictions of the different tracer group fingerprints, it was also investigated whether the trends in changing monthly suspended sediment provenance were consistent between the different fingerprints used. Trends in provenance predictions are of particular importance when assessing changes occurring after mitigation measures are applied to a catchment (Collins *et al*., 2010b), or catchment responses to different climatic conditions or changes to land utilisation (Foster *et al.,* 2012). Therefore, for a full investigation of Objective 1, the use of sediment fingerprinting to determine trends in changing sediment provenance must be considered.

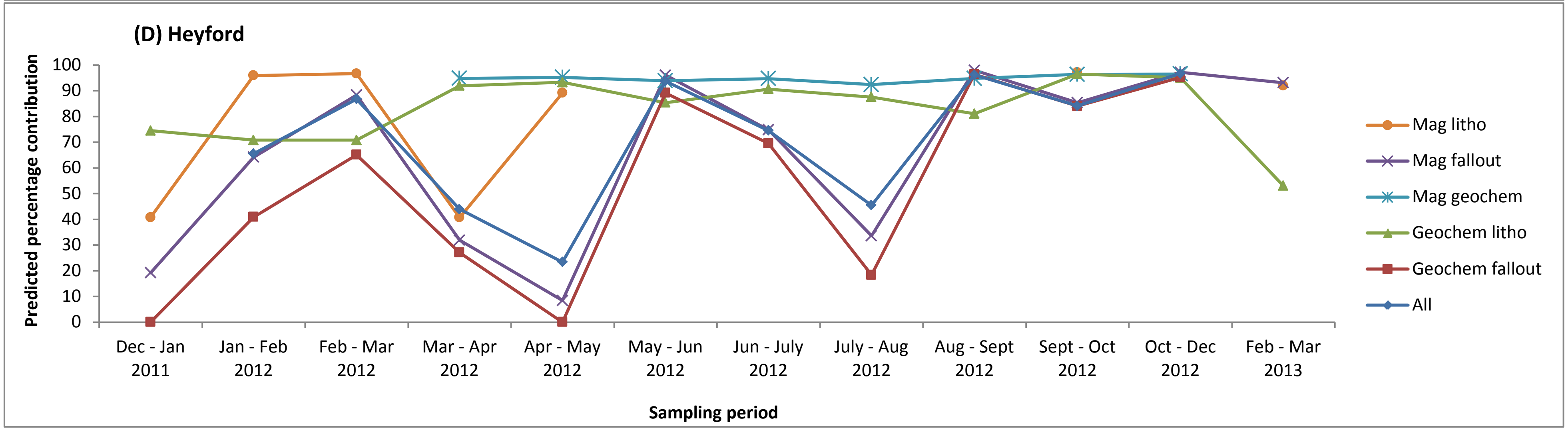
Figure 7-9 shows median predicted contributions from channel banks to suspended sediment; these were produced using the different tracer fingerprints during each month of sampling. A reasonable amount of agreement in trends can be seen in the Northampton (Figure 7-9F) and Dodford (Figure 7-9C) sampling sites, where most tracer groups predict an increasing contribution from channel banks over the duration of the sampling period. However, in the Weedon 1 sampling site (Figure 7-9A) the tracer groups often show very different trends, such as geochemical tracers predicting a decreasing contribution from channel banks and mineral magnetic signatures predicting an increasing contribution. It was, however, observed that the trends in changing sediment provenance were often comparable between composite fingerprints sharing a common tracer group (e.g. geochemical tracers).

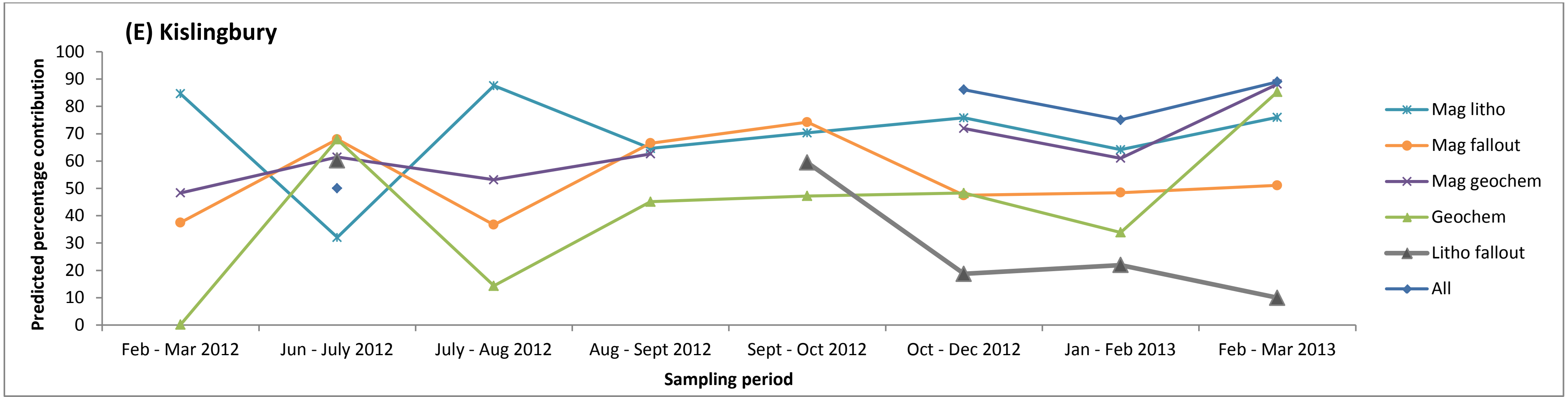
The trends in provenance predictions are often inconsistent between the tracer groups, meaning that changes in sediment provenance predictions are unlikely to be an accurate representation of changing sediment sources when a tracer group is used in isolation. An additional consideration is that many of the lines in Figure 7-9 overlap, meaning that in different months of sampling, different tracer groups can predict contributions from channel banks either above or below each other. It therefore appears that the processes causing tracer non-conservatism change in different months of sampling.

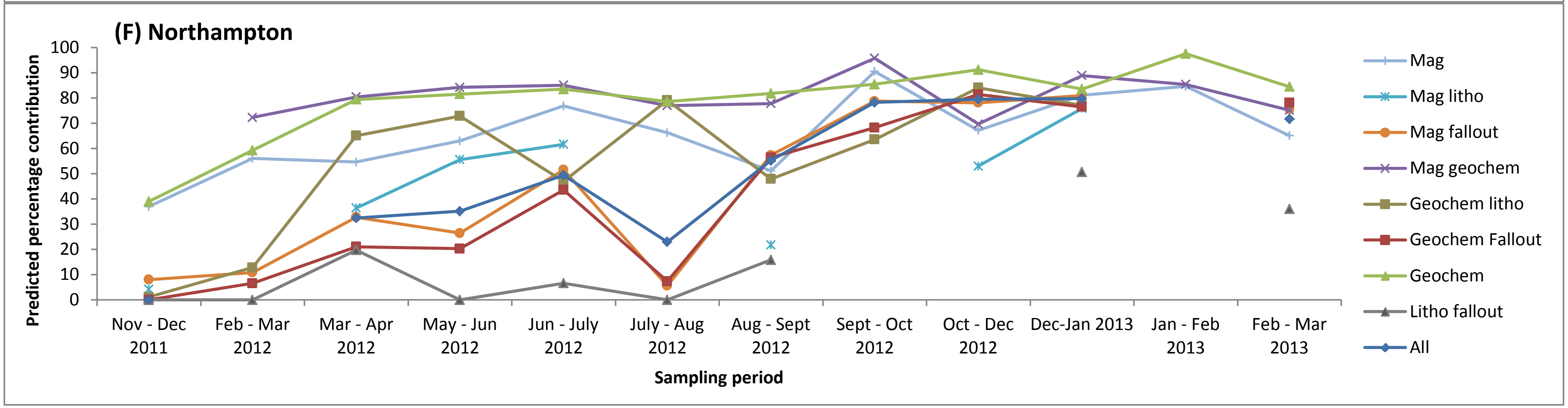

(A) Weedon 1
Predicted percentage contribution
100
90
80
70
60
50
40
30
20
10
0
Feb - Mar 2012
Apr - May 2012
May - Jun 2012
Jun - July 2012
July - Aug 2012
Aug - Sept 2012
Sept - Oct 2012
Oct - Dec 2012
Dec-Jan 2013
Jan - Feb 2013
Feb - Mar 2013
Sampling period
Mag
Mag litho
Mag fallout
Mag Geochem
Litho geochem
Fallout Geochem
Geochem
ALL


(B) Weedon 2
Predicted percentage contribution
100
90
80
70
60
50
40
30
20
10
0
Oct - Nov 2011
Nov - Dec 2011
Dec-Feb 2012
Feb - Mar 2012
Mar - Apr 2012
Apr - May 2012
May - Jun 2012
Jun - July 2012
July - Aug 2012
Aug - Sept 2012
Sept - Oct 2012
Oct - Dec 2012
Dec-Jan 2013
Jan - Feb 2013
Feb - Mar 2013
Sampling period
Mag
Mag fallout
Mag geochem
Fallout geochem
All


(C) Dodford
Predicted percentage contribution
100
90
80
70
60
50
40
30
20
10
0
Oct - Nov 2011
Nov - Dec 2011
Dec - Jan 2011
Jan - Feb 2012
Feb - Mar 2012
Apr - May 2012
July - Aug 2012
Sept - Oct 2012
Jan - Feb 2013
Feb - Mar 2013
Sampling period
Mag
Mag litho
Mag fallout
Mag geochem
Geochem litho
Geochem fallout
Geochem
Litho fallout
All


(D) Heyford
Predicted percentage contribution
100
90
80
70
60
50
40
30
20
10
0
Dec - Jan 2011
Jan - Feb 2012
Feb - Mar 2012
Mar - Apr 2012
Apr - May 2012
May - Jun 2012
Jun - July 2012
July - Aug 2012
Aug - Sept 2012
Sept - Oct 2012
Oct - Dec 2012
Feb - Mar 2013
Sampling period
Mag litho
Mag fallout
Mag geochem
Geochem litho
Geochem fallout
All


(E) Kislingbury
Predicted percentage contribution
100
90
80
70
60
50
40
30
20
10
0
Feb - Mar 2012
Jun - July 2012
July - Aug 2012
Aug - Sept 2012
Sept - Oct 2012
Oct - Dec 2012
Jan - Feb 2013
Feb - Mar 2013
Sampling period
Mag litho
Mag fallout
Mag geochem
Geochem
Litho fallout
All


(F) Northampton
Predicted percentage contribution
100
90
80
70
60
50
40
30
20
10
0
Nov - Dec 2011
Feb - Mar 2012
Mar - Apr 2012
May - Jun 2012
Jun - July 2012
July - Aug 2012
Aug - Sept 2012
Sept - Oct 2012
Oct - Dec 2012
Dec-Jan 2013
Jan - Feb 2013
Feb - Mar 2013
Sampling period
Mag
Mag litho
Mag fallout
Mag geochem
Geochem litho
Geochem Fallout
Geochem
Litho fallout
All

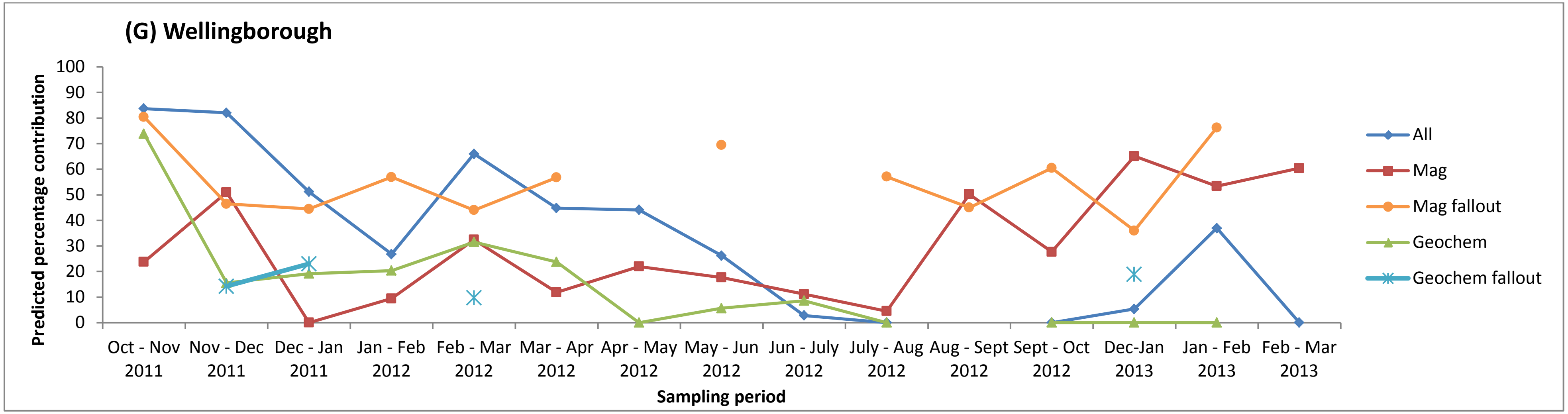


Figure 7-9: The monthly median predicted contributions from channel banks to suspended sediment, derived using different tracer groups.

Whilst mean and median predictions (used in Figure 7-9) are often used to represent data in published fingerprinting studies, the Monte Carlo analysis provides additional representation of the range of uncertainty associated with the predicted source contributions.

Table 7-2 shows the mean percentage point distance of the 25th – 75th percentile Monte Carlo predictions from the median produced by each tracer group fingerprint at each sampling site. The range of uncertainty between the 25th and 75th percentiles is between 4.87% and 53.4%. For most samples the uncertainty exceeds the differences between some tracer group medians seen in Figure 7-9, suggesting that much of the difference between tracer group medians is accounted for by the Monte Carlo analysis. However some tracer groups, such as in the October – December sampling period at Weedon 1 (Figure 7-9A), predict contributions from channel banks with up to a 100% difference, indicating that this uncertainty was not accounted for by the Monte Carlo modelling procedure. Many studies express the Monte Carlo derived uncertainty between the 5th and 95th percentile results because this would incorporate more of the different tracer group medians into the predictions of each fingerprint. However, the uncertainty in most models would have to cover a range close to 100% to fully account for all of the median values derived using the different tracer groups in Figure 7-9, meaning no determination of sediment provenance could be derived from any modelling result.

Table 7-2: The mean percentage point distance of the 25th and 75th percentile Monte Carlo predictions from the median prediction, for each tracer group fingerprint at each suspended sediment sampling location.

	T1 (%)	T2 (%)	Dodford (%)	Heyford (%)	Kislingbury (%)	Northampton (%)	Wellingborough (%)
All							
75th percentile	73.7	80.5	44.8	86.9	85.7	57.9	44.0
Median	65.9	74.4	34.1	79.3	80.6	52.3	31.9
25th percentile	54.8	65.6	21.8	67.9	73.5	44.5	20.7
Mag							
75th percentile	68.2	79.0	79.6			77.0	38.0
Median	53.0	64.6	63.1			65.7	23.7
25th percentile	36.7	50.8	43.2			53.6	10.2
Mag litho							
75th percentile	98.0		71.3	98.3	87.1	76.8	
Median	83.9		54.8	91.9	73.1	53.0	
25th percentile	61.6		34.9	72.5	29.4	23.8	
Mag fallout							
75th percentile	70.8	78.3	60.3	85.2	57.4	58.6	61.4
Median	64.9	73.6	50.9	80.1	49.8	51.5	56.8
25th percentile	56.1	66.6	38.3	72.7	39.7	43.9	51.2
Mag geochem							
75th percentile	82.3	89.1	49.0	95.8	75.5	85.2	
Median	68.9	72.9	37.4	94.8	61.5	80.4	
25th percentile	54.7	57.9	23.4	90.9	43.4	69.6	
Geochem litho							
75th percentile	78.6		43.5	90.1		79.5	
Median	59.9		32.5	86.5		64.3	
25th percentile	39.2		22.1	77.3		40.2	
Geochem fallout							
75th percentile	66.9	56.9	20.7	70.0		50.4	34.4
Median	60.5	49.1	13.9	65.1		43.6	16.6
25th percentile	51.2	38.0	8.9	58.1		35.5	0.1
Geochem							
75th percentile	54.3		30.8		65.3	89.4	39.7
Median	23.8		18.7		46.2	82.7	8.6
25th percentile	0.9		5.5		27.3	58.5	-4.6
Litho Fallout							
75th percentile			31.6		33.4	12.8	
Median			23.8		22.0	6.6	
25th percentile			14.1		5.0	0.0	

7.3. The effects of changes to the sediment organic matter content, particle size distribution and within-source variability on the differences between tracer group fingerprinting predictions.

Having established that some large differences between tracer group sediment provenance predictions occur in the Nene basin, in fulfillment of Objective 1; Objective 2 requires the investigation of the potential causes of these differences.

The potential causes of tracer non-conservatism which could result in changes to tracer provenance predictions were reviewed in the published research discussed in chapter 2. The effects of changes to the organic matter content or particle size distribution of the sediment were indicated to be the most important reasons for non-conservatism. It was also suggested that the way in which source sample data was used in un-mixing models was an additional source of uncertainty, indicating that there is potential for errors caused by sediment source tracer concentrations. On this basis these two factors are explored in this section.

In Chapter 6, which explored uncertainty when fingerprinting historical sediment, the effects of post-depositional alterations to the sediment were also investigated. Due to the short time (months) between sediment transport and the collection of the river sediment samples these processes were not investigated for the river sediment.

7.3.1. Changes to the organic content and particle size of the sediment

Changes to sediment particle size distribution and organic matter content are two of the most commonly cited reasons for tracer non-conservatism (Koiter *et al*., 2013). An examination of the SSA and LOI of the sediment samples, compared to the source samples, was initially conducted in Figure 7-10 to determine if any differences were present. It was found that, while the SSA of the sediment was comparable to the source samples, the LOI of the sediment was higher than the majority of channel bank and surface agricultural sources.

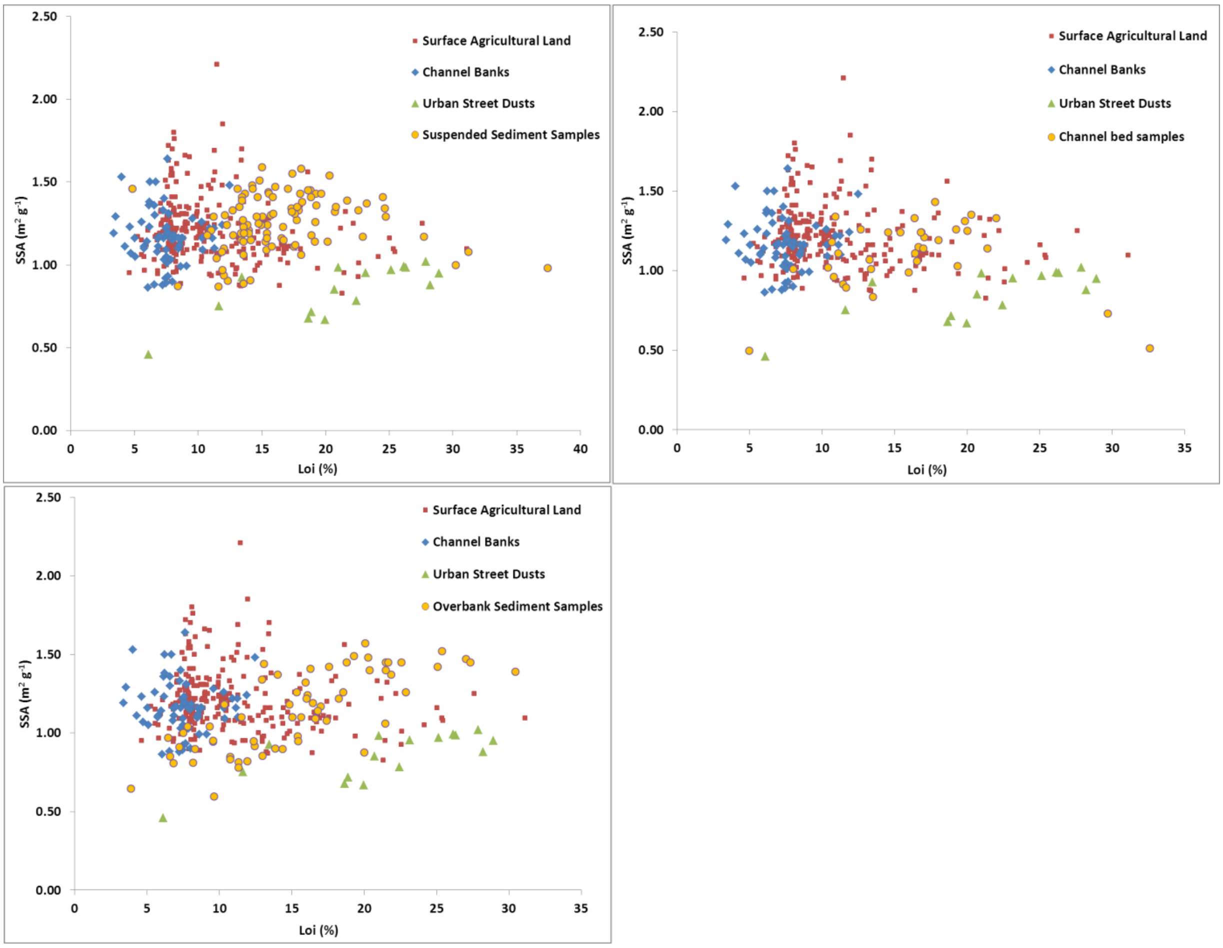


Figure 7-10: The SSA and LOI of suspended, channel bed and overbank sediment and sediment source samples.

To determine the potential impacts of LOI and SSA on the observed differences between tracer group fingerprint predictions, Pearson correlation coefficients were calculated between the differences in predicted contributions from channel banks and the calculated SSA and LOI of the sediment samples. The differences between tracer group predictions were calculated as the mean tracer 1 – tracer 2 difference between the 5th and 95th percentile Monte Carlo predictions. This is different to the absolute differences used to produce Figure 7-7 and Figure 7-8, as it was judged necessary to account for the fact that in Figure 7-9 one tracer group could predict a contribution higher or lower than another group on different months, and this variation could be a result of changes to sediment LOI and SSA.

Table 7-3A shows that of the 36 differences between tracer group predictions calculated for the overbank sediment samples, only 4 and 5 of these differences were significantly correlated with LOI and SSA respectively. This small number of significant correlations and the low correlation coefficients ranging from 0.35 to 0.66 indicate that SSA and LOI do not account for the majority of observed differences between tracer group predictions.

When the correlation analysis was performed for the fingerprinting at each suspended sediment sampling location, it was found that in only the Heyford (Table 7-3E) and Northampton (Table 7-3G) sites were more than two significant correlations found. These significant correlations were with LOI at both sites, and have moderately high correlation coefficients. These results indicate that, as with the overbank sediment fingerprinting, changes to the particle size and organic content of the sediment are unlikely to account for the majority of the observed differences between tracer group fingerprint predictions. Although, in the Heyford and Northampton suspended sediment sampling sites some effects of LOI are suggested to be occurring.

These results greatly contrast with the results found when performing this correlation analysis for the historically deposited sediment in Section 6.5, where strong correlations were found between differences in tracer group predictions and both LOI and SSA in many cores. The LOI in both the river sediment and the sediment cores was between 10% and - 20% for most samples. The SSA in sediment cores was between 1.3 m^2 g^1 and 2.5 m^2 g^1 in all cores apart from the Kingsthorpe floodplain core (Figure 6-1), exceeding the values found in most of the sediment source samples. In the river sediment samples the SSA remained comparable to the sediment source samples (Figure 7-10), explaining why SSA was likely to have comparably little impact on the river sediment fingerprinting.

An examination of the LOI of historical cores (Figure 6-1) compared to the river sediment samples (Figure 7-10), shows that values of between 10% and 20% were found in most of the cores and most of the river sediment samples. This produces a surprising result as LOI appeared to have a strong effect on the historical fingerprinting. The growth of autogenic vegetation on the floodplain is a potential explanation for this result, as tracer concentrations in autogenic matter are likely to be significantly different to the tracer concentrations of the sediment source samples. It is not possible to compare these findings with results in the published literature as no comparable studies to this have been performed; instead it is more common practice to speculate on the possible relationship between LOI, SSA and tracer concentrations prior to fingerprinting sediment sources.

Table 7-3: Pearson correlation analysis between percentage point difference between tracer groups and sample SSA and LOI in the monthly sampling period for all suspended sediment samples. Only statistically significant (p<0.05) results are displayed.

A, Overbank sediment (36 potential correlations)

	LOI			SSA		
	Sig. (2-tailed)	Correlation coefficient	N	Sig. (2-tailed)	Correlation coefficient	N
Mag - Mag geochem	0.08	-.352	25	0.02	-.457	25
Mag - Geochem litho	0.01	.659	16	0.03	.543	16
Mag litho - All	0.11	-.328	25	0.02	-.462	25
Mag Fallout - Geochem litho				0.04	.448	21
Geochem litho - All	0.05	-.472	18	0.02	-.560	18

B, Weedon 1 (21 potential correlations in each column)

Correlations	LOI			SSA		
	Sig. (2-tailed)	Correlation coefficient	N	Sig. (2-tailed)	Correlation coefficient	N
Mag Litho-Geochem	0.00	-.958	7	0.03	-.813	7
Mag geochem-Geochem Litho	0.04	.636	11	-	-	-

C, Weedon 2 (6 potential correlations in each column)

Correlations	LOI			SSA		
	Sig. (2-tailed)	Correlation coefficient	N	Sig. (2-tailed)	Correlation coefficient	N
Mag Fallout-All	0.04	-.571	13	-	-	-

D, Dodford (21 potential correlations in each column)

Correlations	LOI			SSA		
	Sig. (2-tailed)	Correlation coefficient	N	Sig. (2-tailed)	Correlation coefficient	N
Mag Litho-Mag Geochem	0.03	-.691	10	0.02	.718	10

E, Heyford (15 potential correlations in each column)

	LOI			SSA		
	Sig. (2-tailed)	Correlation coefficient	N	Sig. (2-tailed)	Correlation coefficient	N
Mag Fallout-Mag Geochem	0.05	-.707	8	-	-	-
Mag Fallout-Geochem Fallout	0.00	.906	11	-	-	-
Mag Geochem-Geochem Fallout	0.04	.724	8	-	-	-
Mag Geochem-All	0.05	.715	8	-	-	-
Geochem Fallout-All	0.03	-.672	10	-	-	-

F Kislingbury

No significant correlations found

G, Northampton (36 potential correlations in each column)

Correlations	LOI			SSA		
	Sig. (2-tailed)	Correlation coefficient	N	Sig. (2-tailed)	Correlation coefficient	N
Mag-Mag Geochem	0.00	-.840	11	-	-	-
Mag Fallout-Litho Fallout	0.05	-.674	9	-	-	-
Mag Geochem-Geochem Fallout	0.05	.632	10	-	-	-
Geochem Fallout-Litho Fallout	0.02	-.746	9	-	-	-
Geochem-Litho Fallout	0.02	-.746	9	-	-	-
Litho Fallout-All	0.02	.798	8	-	-	-

H, Wellingborough

No significant correlations found

7.3.2. The potential uncertainties associated with catchment and tracer concentration heterogeneity

It has been suggested in the previous sub-section, as part of the fulfilment of Objective 2, that the commonly cited reasons for tracer non-conservatism of organic enrichment and changes to sediment particle size were unlikely to account for most of the observed differences between the tracer groups predictions found for Objective 1. This sub-section continues to address Objective 2 by investigating the potential impacts of heterogeneity and complexity in the catchment. Including, the within-source variability of tracer concentrations, and the potential effects of sediment inputs from only small proportions of each source group. The implications of a high variability of tracer concentrations within the source groups were also considered in terms of the representativeness of the sediment source sampling.

The section begins by examining the differences between tracer group provenance predictions when fingerprinting urban street dusts. The fingerprinting of street dusts was done to determine if a greater contrast in tracer concentrations between sediment sources and low within- source variability improves the consistency of fingerprinting predictions.

The potential effects of within-source variability in tracer concentrations on the results of the sediment fingerprinting were then examined. Twenty five random sub-distributions of tracer concentrations were produced from within the 5th and 95th percentile range of the tracer concentrations found in each source group. A sediment sample was fingerprinted using each of these 25 distributions. In this way, the potential uncertainty occurring if the actual sediment sources in the environment had a different range of tracer concentrations from the collected source samples could be determined.

The relationship between the within-source variability in tracer concentration and the size of the contrasts in tracer concentration between source groups, on the uncertainty potentially present in fingerprinting results was then quantified. This allowed for the assessment of if within-source variability in tracer concentrations was sufficient to cause the differences between tracer group predictions observed as part of Objective 1.

7.3.2.1. The impacts of a low within-source variability in tracer concentrations and a high contrast in tracer concentration between source groups on the differences between tracer group predictions.

If a large amount of spatial variability in erosion and sediment delivery to the river occurred in a catchment, it could potentially result in only a small proportion of the collected sediment source samples actually being from areas which contribute sediment to the river. If this occurred when a large amount of variability in tracer concentrations was present in a source group, a different distribution of tracer concentrations would be found in the collected source samples to that of the sediment's actual sources. Therefore this would result in a change to model sediment provenance predictions, as the sediment source data no longer reflects the actual sediment sources. This sub-section explores the potential for this to be occurring and affecting the fingerprinting predictions of different tracer groups observed for Objective 1.

The potential for error associated with the heterogeneity of sediment source tracer concentrations in the Nene can be seen by examining Figure 7-3, which shows that the discriminatory efficiency of each tracer varied significantly between the different fingerprinting locations used in this study. This finding suggests that either a high spatial variability in tracer discriminatory efficiency exists, or that the source sampling was insufficient to fully represent the sediment sources in the regions. Either of these explanations highlights the potential for regional variability in tracer concentration and sediment delivery to introduce uncertainty into the sediment fingerprinting.

It can also be determined, by examining Table 7-1, that small contrasts in median source group tracer concentrations exist between channel bank and surface agricultural sediment sources, and were exploited in the discriminant analysis to form the composite fingerprints.

An examination of the within source tracer concentration coefficients of variation (COV) (Table 7-4), shows an average COV of 32.8% in the channel bank and surface agriculture source groups, indicating a significant amount of variability in tracer concentration, even within the middle 50% of source samples. There is, therefore, clear potential for the loss of the basis for source discrimination, as the COV of many tracer concentrations are often larger than the differences in tracer concentrations exploited to form the composite fingerprints. The effects of this will be most pronounced if the source samples used for modelling are not fully representative of the actual sources of the sediment in a given environment.

Table 7-4: Coefficients of variation of tracer concentrations in source groups, calculated as (median absolute deviation/median)*100).

	Surface agriculture COV (%)	Channel banks COV (%)	Urban street dusts COV (%)
LOI (%)	11.78	13.79	12.04
SSA	8.47	6.90	7.78
X_{lf}	47.37	22.73	12.06
X_{fd}	66.28	49.78	16.13
Xarm	64.31	45.21	9.64
IRM1T	48.44	37.94	7.68
IRM_{-100}	53.01	44.05	11.86
HIRM	34.62	22.50	12.91
$^{210}Pb_{un}$	-	-	29.67
^{2226}Ra	26.56	28.78	27.16
^{137}Cs	42.91	100.00	52.00
^{228}Ac	18.78	16.78	29.60
^{40}K	13.74	14.10	13.28
^{234}Th	27.38	26.98	18.85
^{235}U	42.11	42.60	30.11
^{212}Pb	17.66	13.88	10.96
Al	15.42	22.33	5.85
As	40.80	37.84	9.28
Ba	21.37	24.59	10.01
Ca	33.70	51.54	29.53
Co	29.60	23.29	12.10
Cr	40.73	24.54	19.56
Cu	19.43	21.78	22.36
Fe	32.04	28.60	9.90
Ga	53.46	62.94	14.57
Gd	44.23	48.30	98.21
K	24.04	24.20	15.51
La	25.11	26.79	11.57
Mg	23.63	27.77	15.72
Mn	37.80	34.31	13.76
Na	37.22	38.52	29.11
Nd	28.23	17.57	8.22
Ni	38.03	16.10	13.25
P	27.66	24.55	12.13
Pb	25.27	27.13	16.40
Ti	44.33	38.82	25.95
V	35.64	28.32	6.43
Y	28.90	22.64	8.28
Yb	31.46	22.71	7.45
Zn	27.04	14.78	34.02
Zr	25.86	20.73	14.27

Field based observations of the localised erosion of small areas of channel bank can be seen in a study by Henshaw *et al*. (2013), who were unable to reliably identify spatial controls on channel bank erosion using factors such as livestock stocking density or channel bank composition. Instead erosion was thought to occur in “process-intensity domains” controlled by the hydrology of the river. This means that it is unlikely that the entire range of collected sediment sources used in the fingerprinting are actually contributing sediment during each period of sediment sampling. For surface sediment sources, an examination of modelled rates of erosion in catchments such as that presented by Mutowo & Chikodzi, (2013), indicated that intense soil erosion is predicted to occur in only a small proportion of the overall catchment. Sediment delivery can also be considered as a potential major factor causing localised sediment inputs. Fryirs (2013) highlights the importance of “(Dis)connectivity” in river catchments; it was argued that dis-connectivity could result in effective catchment areas greatly reduced in size, in terms of the sediment delivery to the river channel. The effective catchment areas would also be expected to vary according to the magnitude of individual rainfall events and, over time, as the landscape within catchments changes. This represents a potential explanation for the high temporal variability in differences between provenance predictions observed in Figure 7-9. Another consideration is that, in lowland catchments such as the Nene with a lack of gulley erosion providing connectivity to channels, linear features such as roads and field drains may be of particular importance in delivering sediment to rivers. For example, Boardman (2013) highlights the importance of roads in rural catchments at increasing connectivity, and Chapman *et al*. (2003) highlights the importance of sub-surface drainage. Both of these routes of transport may result in highly localised sediment delivery from a small proportion of the surface agriculture sediment source.

It was shown in Table 7-1 that there were larger differences between the median concentrations of most tracers in urban street dusts compared to the other sediment sources, than between channel banks and surface agricultural sources (Table 7-1). It was also shown that the within source variability in most tracer concentrations was lowest in urban street dusts (Table 7-4). Both of these factors indicate that there is less potential for uncertainty to be introduced into the fingerprinting by regional variations in tracer concentration when fingerprinting urban street dusts. To test this assumption, a comparison was made between the average differences between the tracer group predictions of channel banks and the average differences between the tracer group predictions of urban street dusts, using the samples of recently deposited overbank sediment.

The results shown in Figure 7-11 indicate that average differences between most tracer group predictions range from 8.1 to 11.4% when predicting contributions from urban street dusts, indicating a reduced uncertainty from the average 24.1% difference when predicting contributions from channel banks. This result indicates that there is clearly a positive impact on the reliability of sediment fingerprinting when a robust difference between sediment source tracer concentrations is present.

However, it can also be noted that the Litho fallout group is the one tracer group where the consistency with other tracer group fingerprinting predictions is not greatly improved when predicting contributions from urban street dusts. A potential explanation for this is the non-conservatism of the tracers in this group. For example Table 7-1 shows that $^{210}Pb_{un}$ is in high concentrations in urban street dusts, providing good discrimination from the other source groups. However, Figure 7-2 indicates that fewer samples pass the mass conservation test than would be expected for this tracer, suggesting its possible non-conservative behaviour.

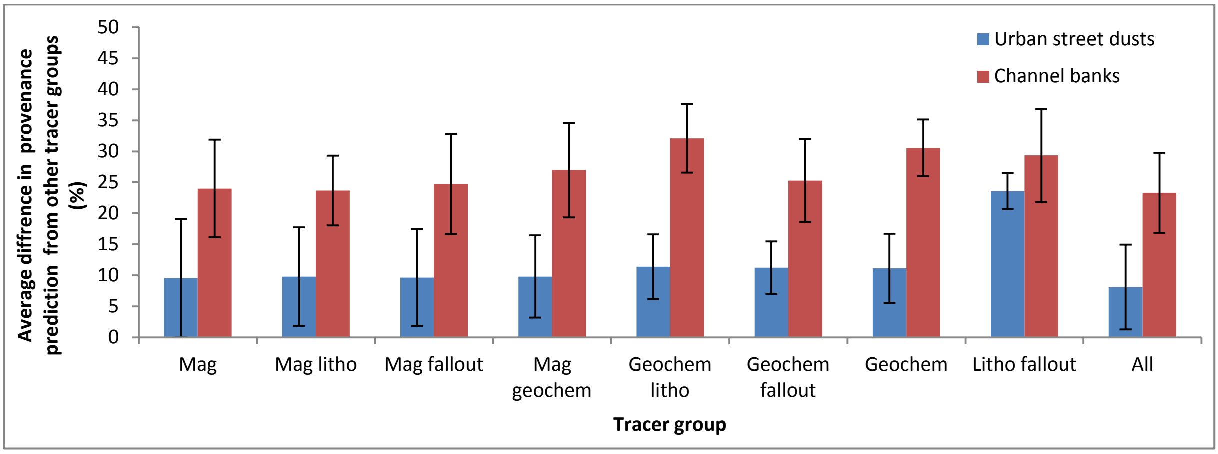


Figure 7-11: Average differences between the predictions of each tracer group and all other tracer groups, when predicting contributions of from channel banks and urban street dusts to overbank deposited sediment.

7.3.2.2 The potential uncertainty associated with within-source variability in tracer concentrations when fingerprinting contributions of sediment from channel banks.

The results in the Nene so far have indicated that small inter-source contrasts in tracer concentrations and high within source tracer concentration variability are potentially major causes of uncertainty in the un-mixing modelling in the Nene. In this sub-section the potential size of the uncertainty that could have been caused by this effect, and contribute to the differences observed between fingerprinting predictions derived for Objective 1 (Figure 7-7; Figure 7-8) is explored. To do this an additional stage was incorporated into the fingerprinting procedure outlined in Section 5.5 based upon the methods of Motha *et al.* (2003). Firstly the range between the 5th and 95th percentile tracer concentrations was calculated for each tracer in each source group. From this range, 25 randomly generated source tracer distributions were produced using the same procedure as Motha *et al*. (2003), to simulate the selective delivery of sediment from only a small proportion of the source samples. This would produce source groups with a smaller range of tracer concentrations present in each source group. The un-mixing model was run using each of these random distributions for 1000 Monte Carlo iterations.

The 25 random source distributions were used to fingerprint an individual sediment sample from the Northampton suspended sediment sampling site, collected between June and July 2012. This sample was selected on the basis that a composite fingerprint able to differentiate between 80% of source samples could be developed for every tracer group for the Northampton sampling site, and this sample was selected at random from the months of sampling available which had a GOF above 80% for all tracer group un-mixing models.

It was found that large differences in provenance predictions could be produced in the results of the 25 different randomly generated source tracer distributions when using a single composite fingerprint of tracers (Figure 7-12). The median contributions produced by the distributions ranged from 30% to 90%, indicating that the fingerprint used in this example is potentially very susceptible to effects of within-source tracer concentration variability.

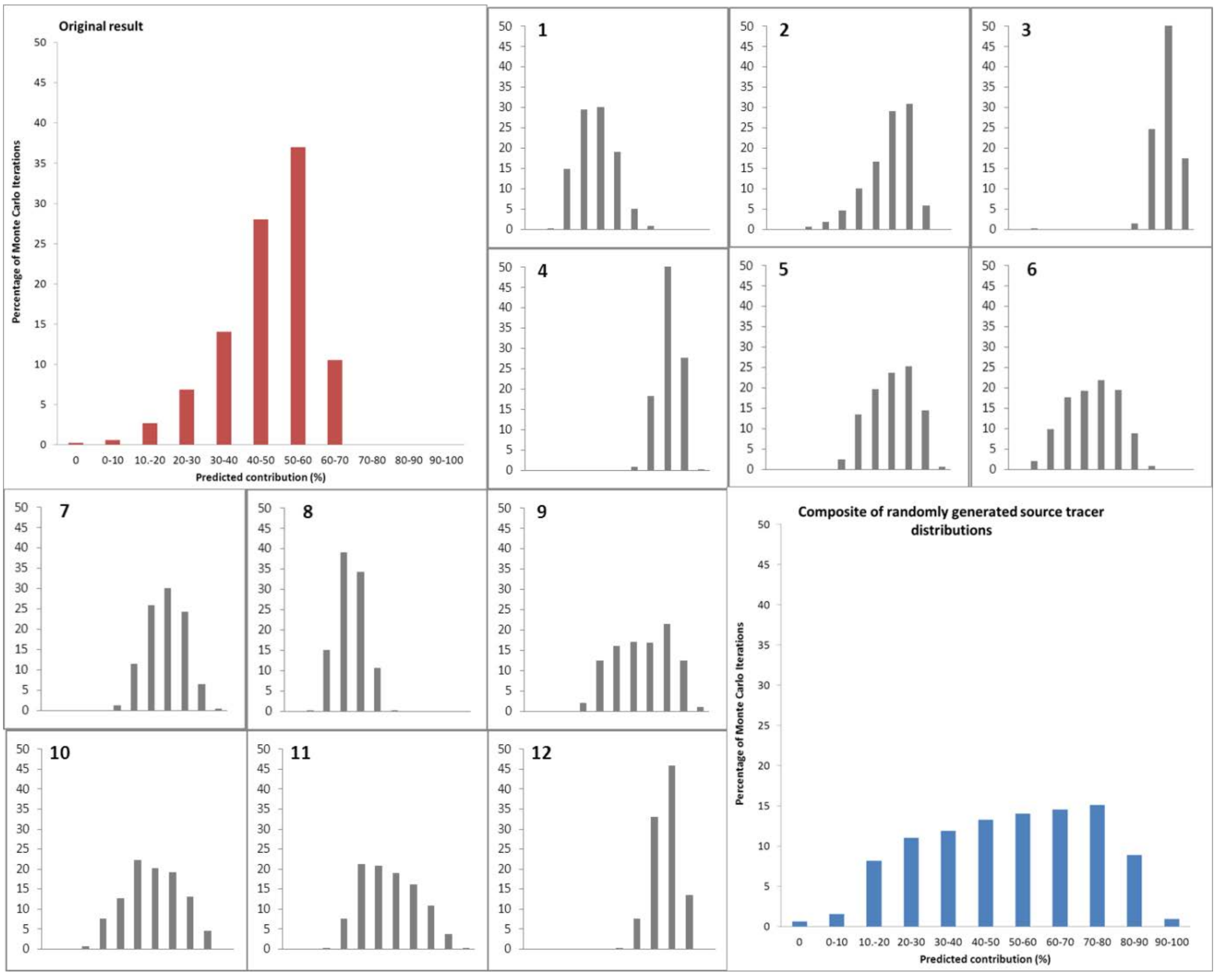


Figure 7-12: Probability density functions (PDF) of the first 12 randomly generated source tracer distributions, displayed alongside the original median and MAD distribution PDF and a composite PDF of all 25 random source tracer distributions. Results are for the "All" tracer group and predicted contribution from channel banks.

When a composite PDF composed of the 25 random source distributions were created for each of the tracer groups used to fingerprint this sediment sample (Figure 7-13), the end result was often very different to those produced using the median and median absolute deviation of each tracer group, indicating that a large potential for deviation in provenance prediction due to the tracer concentrations of the source samples exists. The selective delivery of sediment from only part of a source group must also be considered likely to produce the same magnitude of uncertainty, as the tracer concentrations of the actual sediment sources would likely be different to the collected source samples if the localised delivery of sediment to the river occurred.

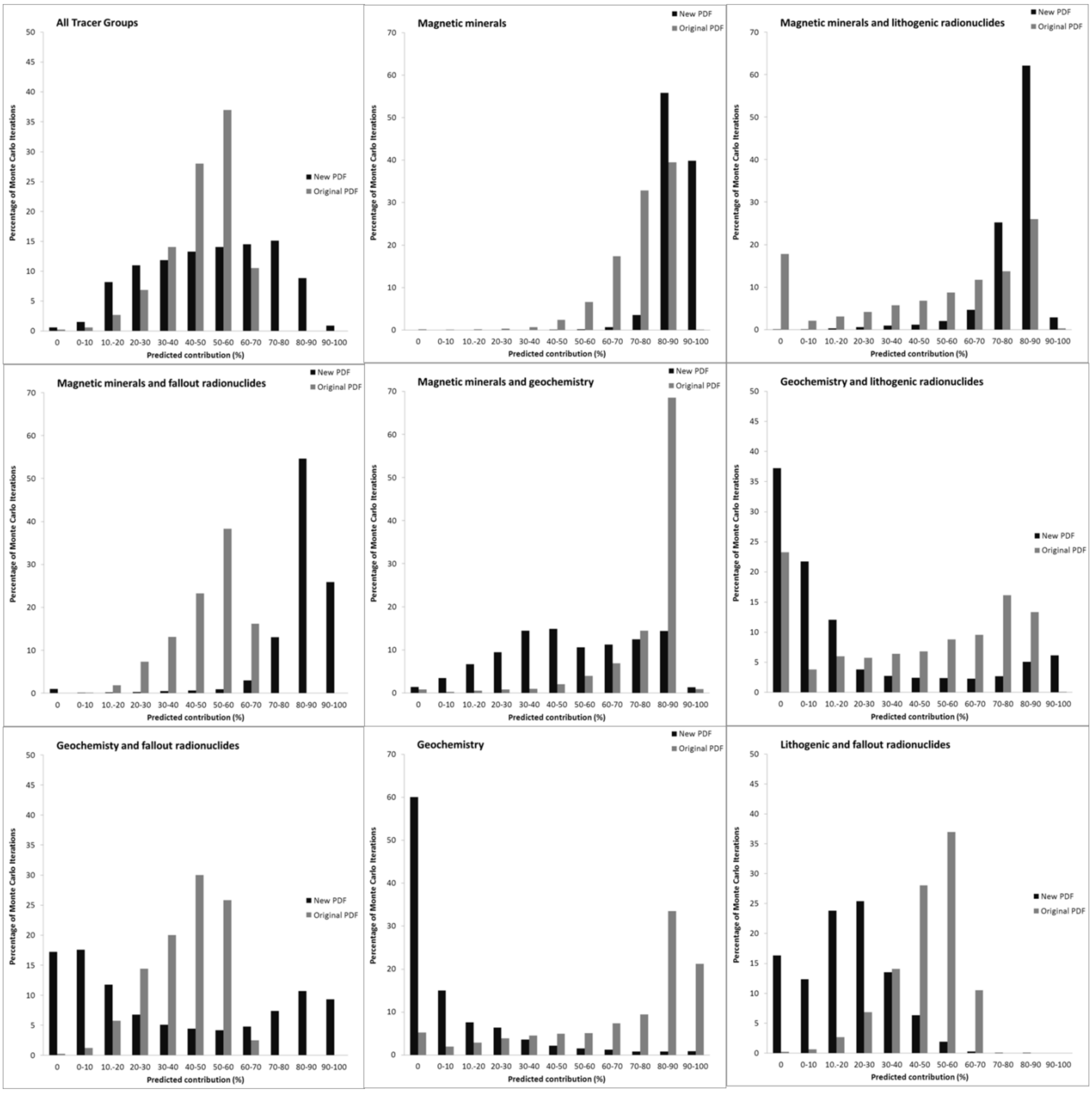


Figure 7-13: Composite PDFs of 25 randomly generated source tracer distributions in comparison to the PDFs generated using the median and MAD source groups.

A final composite PDF of the results of the random 25 random distributions of source group tracer concentrations of all the different tracer group fingerprints was produced (Figure 7-14). This composite PDF provided a representation of the potential uncertainty associated with source tracer concentration variability and the uncertainty associated with tracer selection when fingerprinting this sediment sample. The PDF indicates that the large uncertainty associated with the fingerprinting of this sample means that no conclusion as to sediment provenance can be reached. As the contrasts in tracer concentrations between channel banks and surface agriculture were found to be small in all parts of the Nene basin, it is highly likely that this amount of uncertainty is potentially present in all of the sediment samples which were fingerprinted.

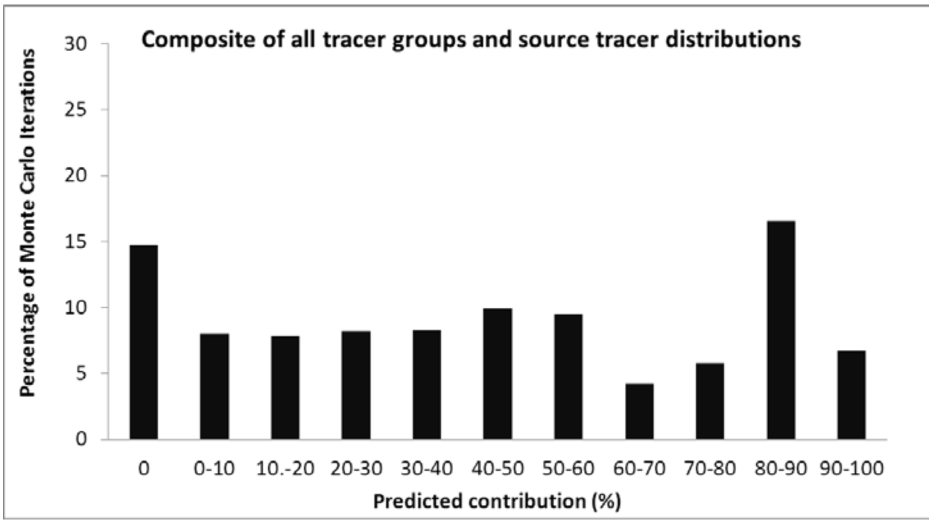


Figure 7-14: Composite probability density function of 25 randomly generated source tracer distributions of the nine tracer groups.

7.3.2.3 The relationship between inter-source contrasts in tracer concentration, within source tracer concentration variability and the uncertainty associated with un-mixing modeling.

This section has so far indicated that within-source variability in tracer concentrations is a major source of uncertainty, which could potentially have caused the differences in tracer group provenance predictions observed when investigating Objective 1 (Section 7.2). Therefore, for a fingerprinting study to have a reasonable probability of making a provenance prediction which is not masked by a large amount of uncertainty, the within-source variability must be minimised and the contrasts in source tracer concentrations must be maximised. As part of the fulfillment of Objective 2, the relationship was determined between the contrasts in source group median tracer concentrations and within-source variability of tracer concentrations and the uncertainty that can potentially occur in un-mixing model predictions, based upon the methods used by Small et al. (2002). This allowed for the possible uncertainty caused in the fingerprinting performed as part of Objective 1 to be quantified, and compared to the observed differences in tracer group sediment provenance predictions. To calculate this relationship, un-mixing models were run using a range of differences between the median tracer concentrations of two source groups and with a range of within-source tracer concentration coefficients of variation. Table 7-5 shows the differences between source group median tracer concentrations and the different mean within-source coefficient variations for the models run. The ratio of the percentage difference between median tracer concentrations in source groups and the average within source tracer concentration coefficient of variation (%) (hereafter referred to as the tracer variability ratio) was used to quantify the differences between tracer concentrations. This ratio, in essence, represents the differences in tracer concentrations between source groups divided by the variability in tracer concentrations within the source groups.

Table 7-5: The un-mixing models run to determine the impact of source tracer concentrations on the variability inherent in un-mixing model predictions.

Model number	Percentage difference between median tracer concentrations in source groups	Mean within source coefficient of variation (%)	Ratio of the percentage difference between median tracer concentrations in source groups / average within source coefficient of variation (%)
1	5	5	1.00
2	5	10	0.50
3	5	25	0.20
4	5	50	0.10
5	5	75	0.07
6	10	10	1.00
7	10	25	0.40
8	10	50	0.20
9	10	75	0.13
10	20	10	2.00
11	20	25	0.80
12	20	50	0.40
13	20	75	0.27
14	40	10	4.00
15	40	25	1.60
16	40	50	0.80
17	40	75	0.53
18	60	10	6.00
19	60	25	2.40
20	60	50	1.20
21	60	75	0.80
22	80	10	8.00
23	80	25	3.20
24	80	50	1.60
25	80	75	1.07

The un-mixing models were run for 3000 Monte Carlo iterations and the percentage point difference between the 5th and 95th percentile ranked results was extracted to provide a value close to the maximum potential range of variability for the predictions of each of the un-mixing models. This gives a value representing the uncertainty that could be produced by regional variability in sediment source concentrations and sediment inputs, or the insufficient representation of sediment sources in the source sampling.

The tracer variability ratio was calculated and plotted against the differences between the 5th and 95th percentile Monte Carlo predictions (Figure 7-15). This was done for composite fingerprints containing 3, 5, 7 and 9 tracers, to determine the additional effects of the number of tracers used in the composite fingerprints. The fingerprints used to fulfil

Objective 1 in Section 7.2 contained between 3 and 11 tracers. 76% of fingerprints used contained 4 to 7 tracers; therefore the results shown in this section for "5 tracers" are the most applicable to the fingerprinting performed in Section 7.2.

When using 5 tracers the results in Figure 7-15 show that when the source tracer variability ratio was lower than 1, the potential uncertainty associated with model predictions steeply increased. When the ratio is 1 the model uncertainty is 27%. This uncertainty decreases to 15% at a ratio of 2 and continues to decrease to 5% at a ratio of 8. When more tracers are used in the composite fingerprint the maximum uncertainty is also reduced. However, the reduction in uncertainty approximately halves with every extra 2 tracers added to the fingerprint.

It is therefore recommended that for a fingerprint to have a reasonable probability of producing meaningful provenance predictions, which are not subject to a large error associated with within–source variability, the tracer concentration variability ratio should be greater than 1. It was also shown that the model uncertainty was reduced by using larger composite fingerprints; therefore it can be recommended that the maximum number of tracers possible should be used in composite fingerprints. Model GOF was observed to decrease as more tracers were added to the fingerprints, but maximum uncertainty decreased. Common recommendations for tracer selection suggest minimising the number of tracers in a fingerprint to reduce problems of equifinality (Beven, 2003) and to use GOF as a quantification of model reliability (Haddadchi *et al.,* 2013). As Section 7.2.5 showed that GOF cannot represent the accuracy of model predictions, because different models all with a GOF above 80% can predict a very different sediment provenance, it is recommended that larger composite fingerprints are used at the detriment of GOF. Two reasons can be provided for this recommendation; first to reduce the uncertainty associated with the tracer variability ratio and, secondly, to minimise the potential impacts of the non-conservatism of individual tracers. The results shown in Figure 7-15 particularly highlight that fingerprints of only 3 tracers inherently have a large amount of uncertainty associated with their results and should be avoided.

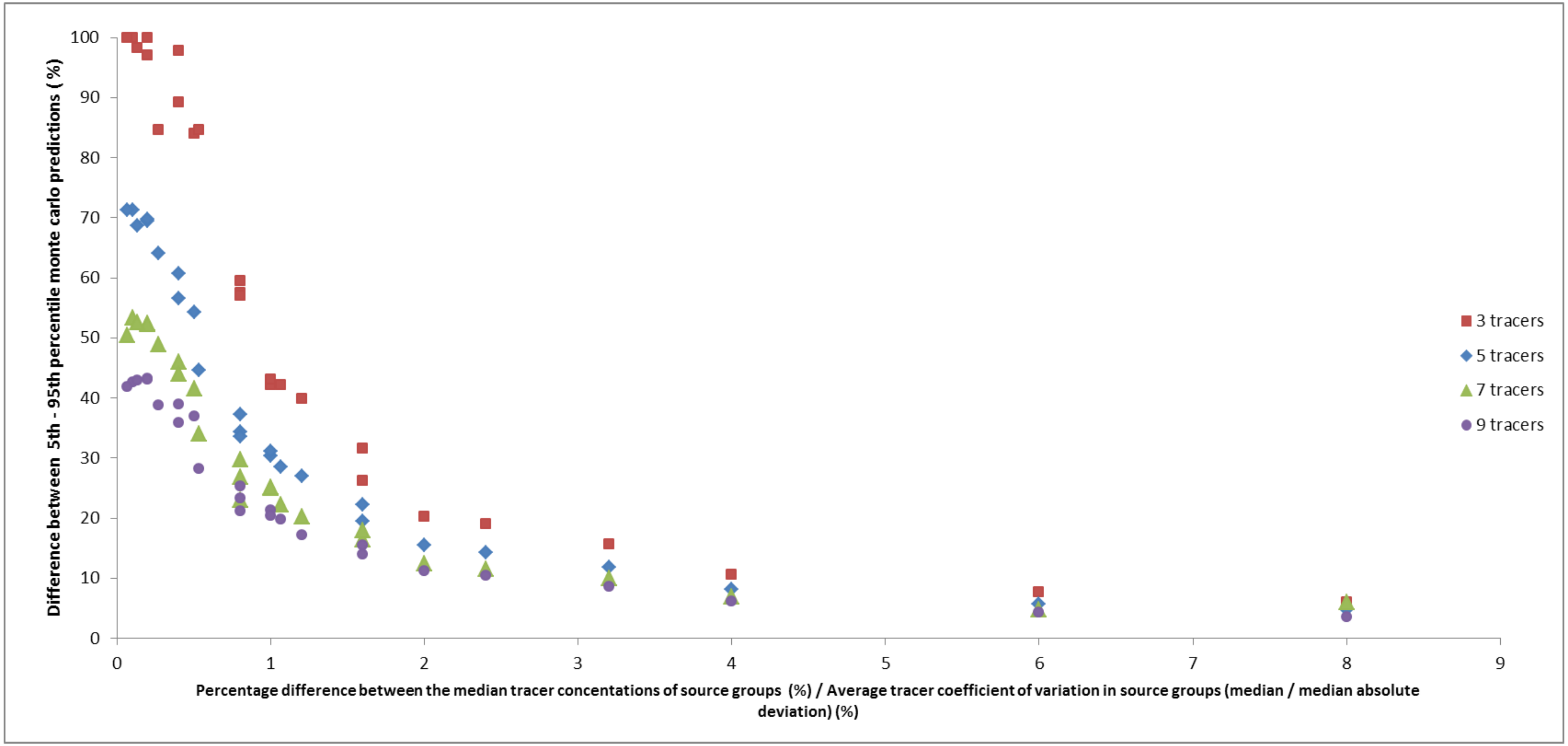


Figure 7-15: The ratio of the percentage difference between the median tracer concentrations of source groups / average tracer coefficient of variation in source groups compared to the difference between 5th - 95th percentile Monte Carlo predictions (%).

Because the relationship between the tracer variability ratio and the potential uncertainty in un-mixing models has been quantified, the potential uncertainty associated with the tracer variability ratio of the tracers used to fulfil Objective 1 can be calculated. In this way it could be determined if the tracer variability ratio can account for the differences between tracer group predictions observed as part of Objective 1 in Figure 7-7, Figure 7-8 and Figure 7-9; this will contribute to fulfilment of Objective 2.

Figure 7-16 shows the tracer variability ratio for each tracer used in this study when comparing tracers in channel banks to those in surface agriculture. The ratio is below 1 for most tracers and only Xlf, Xfd, Xarm, irm-100, ^{137}Cs, K and Nd exceed this. The maximum ratio is 1.3 for ^{137}Cs. The average ratio of 0.6 suggests from Figure 7-15 that a potential uncertainty of ~ 35% would be expected when 5- 7 tracers were used. The mean difference between tracer group provenance predictions of 24% when fingerprinting contributions from channel banks as part of Objective 1 is less than the potential uncertainty of ~35% suggested by Figure 7-15. It should also be noted that the 35% uncertainty could be doubled when comparing two tracer groups each with a 35% uncertainty. The lower uncertainty found between the tracer group predictions than is expected, according to the tracer variability ratio, suggests that the errors caused by regional variability were reduced by a range of sediment inputs more characteristic of source samples used. When comparing tracer concentrations in channel banks and urban street dusts, the ratio exceeds 1 for the majority of tracers (Figure 7-16). The average ratio of 2.3 suggests close to a 14% uncertainty would be expected to be associated with tracer variability; falling close to the average differences of 8.1 to 11.4% between the predicted contributions of sediment from urban street dusts, made by the different tracer groups (Figure 7-11).

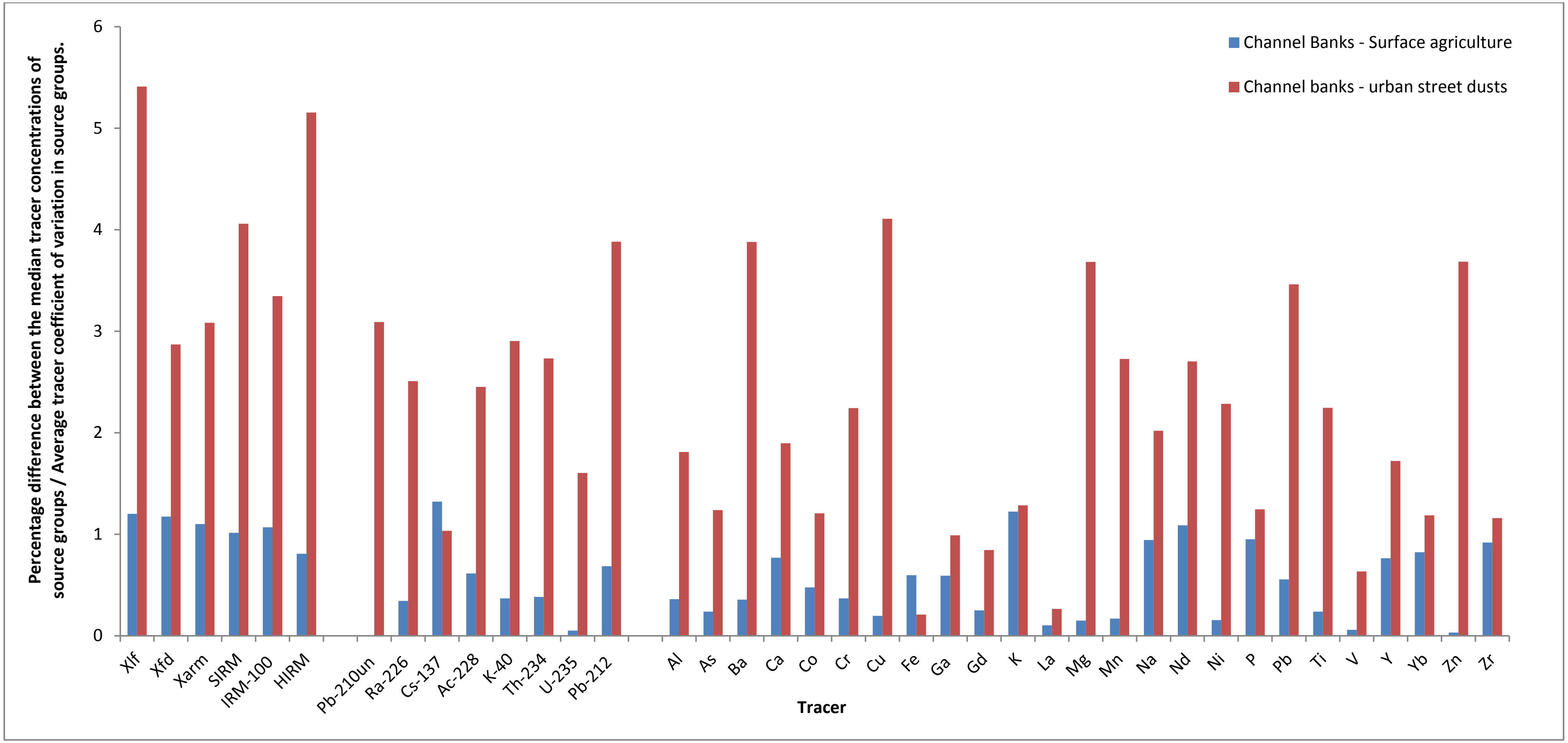
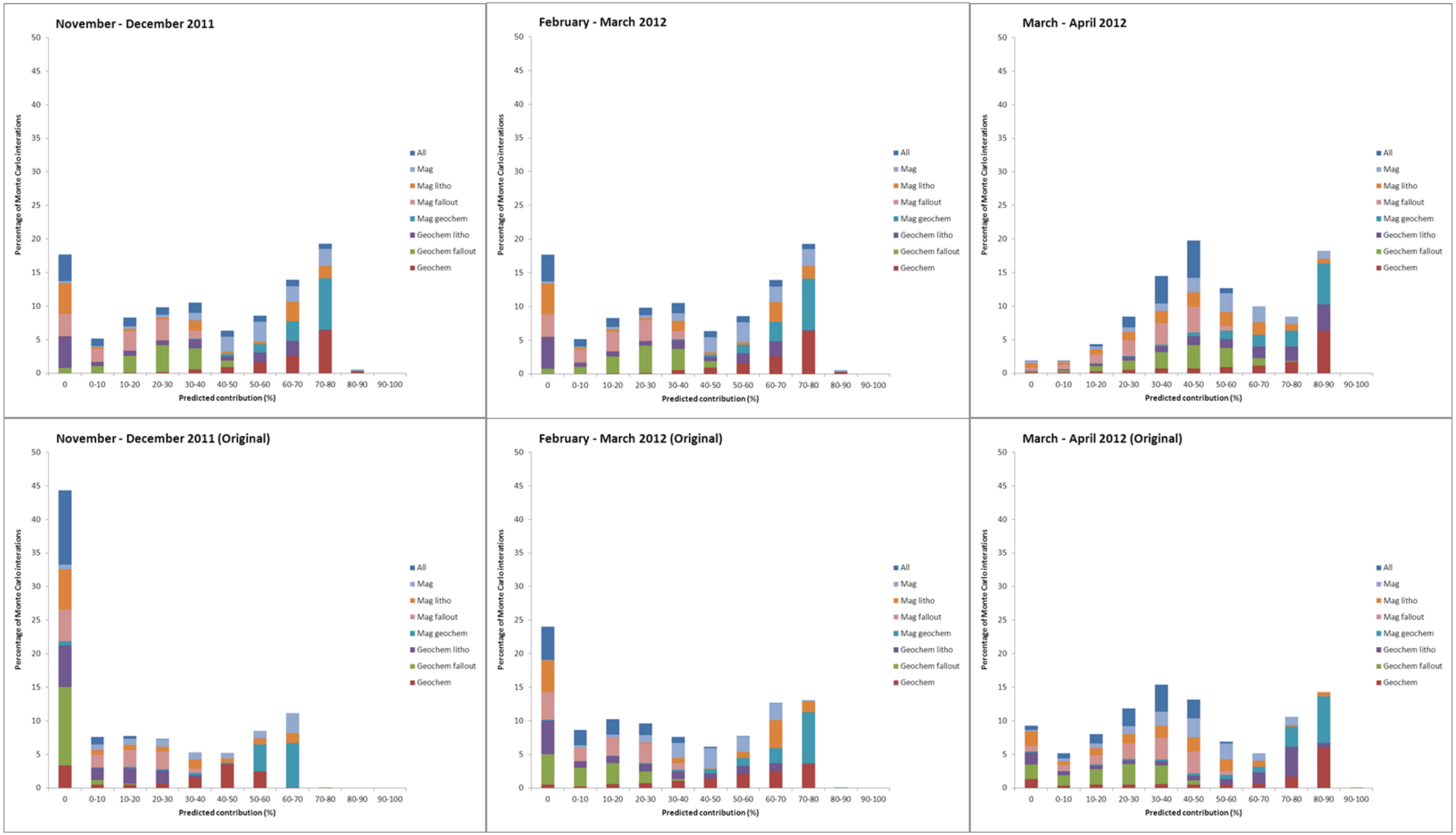


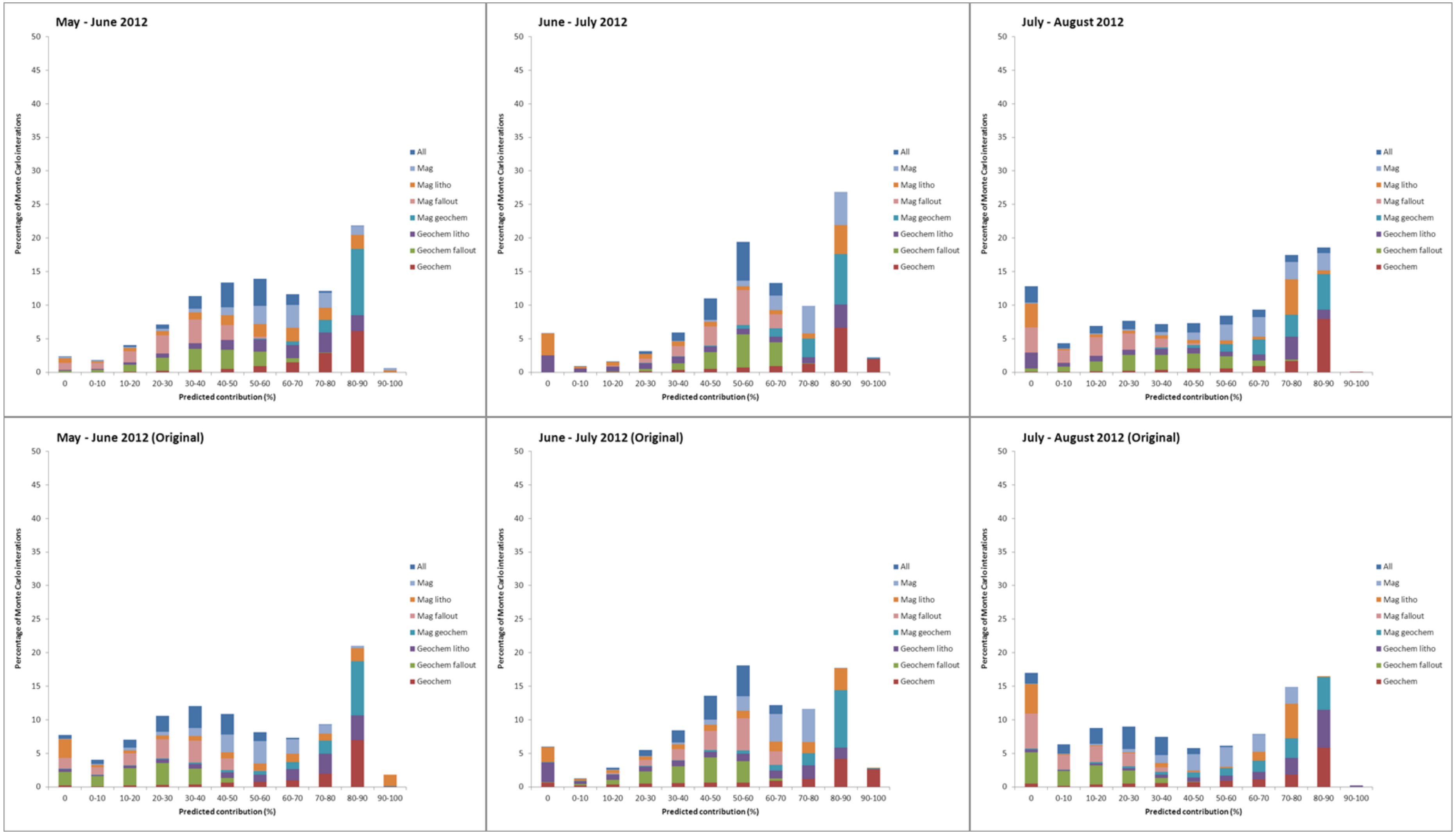
Figure 7-16: The ratio of the percentage difference between the median tracer concentrations of source groups / average tracer coefficient of variation in source groups (tracer variability ratio) for the tracers in all source samples in the Nene basin.

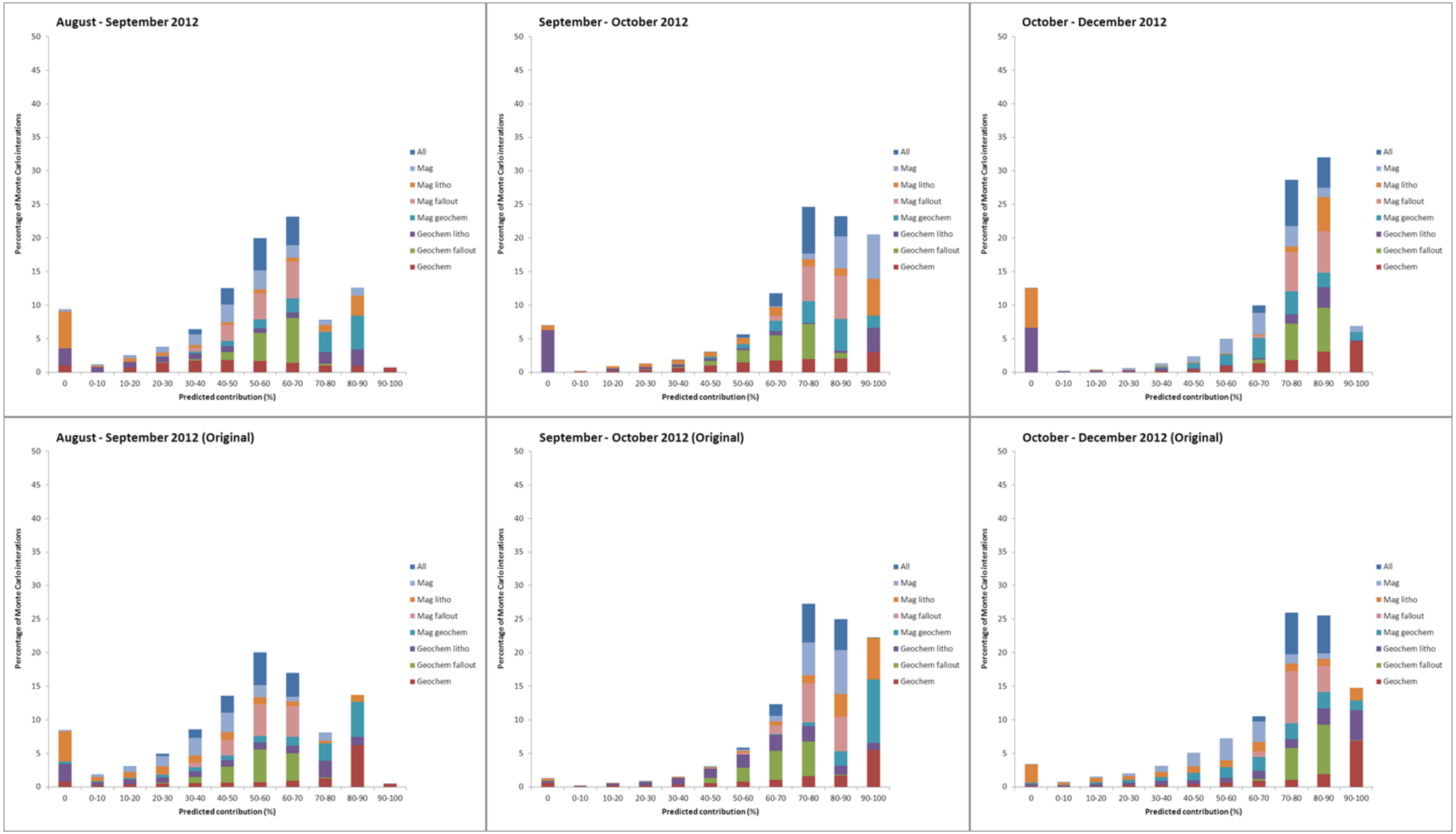
7.3.2.3 The effects of using larger composite fingerprints

The result in Figure 7-15 indicated that using larger composite fingerprints can have a beneficial effect at reducing the uncertainty associated with the tracer variability ratio. This sub-section determines if the beneficial effect of larger composite fingerprints of tracers can be seen when fingerprinting the sediment samples with the different tracer groups used to fulfil Objective 1. The fingerprinting of suspended sediment from the Northampton sampling site was repeated using the largest composite fingerprints of tracers which could be generated for each tracer group, and the differences between all of the tracer groups' predictions were compared to those found when using the original composite fingerprints which contained fewer tracers. This was done to investigate if the potential conclusions derived in the previous sub-section are likely to be valid, contributing to the fulfilment of Objective 2.

Figure 7-17 shows composite PDFs for each sediment sample generated using the different tracer groups. The result obtained with large composite fingerprints is compared to the original result which was derived as part of section 7.2. The results show that most of the PDFs retain the same general shape when the larger fingerprint is used; however there is an increase in the height of the largest peaks for most samples and a narrowing of the base of the peaks. It is therefore apparent that for the majority of samples, using the larger composite fingerprints narrows the range of uncertainty present, allowing a more precise determination of sediment provenance. However, it is clear from this result that a large amount of uncertainty still remains. Figure 7-15 indicated that fingerprints of more tracers do not remove all of the potential uncertainty; therefore differences between tracer group fingerprinting predictions would still be expected. Therefore, selecting for tracers with the highest tracer variability ratio possible remains a key recommendation of this chapter.


November - December 2011
February - March 2012
March - April 2012
November - December 2011 (Original)
February - March 2012 (Original)
March - April 2012 (Original)
Percentage of Monte Carlo interations
Predicted contribution (%)
0
0-10
10-20
20-30
30-40
40-50
50-60
60-70
70-80
80-90
90-100
All
Mag
Mag litho
Mag fallout
Mag geochem
Geochem litho
Geochem fallout
Geochem


May - June 2012
June - July 2012
July - August 2012
May - June 2012 (Original)
June - July 2012 (Original)
July - August 2012 (Original)
Percentage of Monte Carlo interations
Predicted contribution (%)
0 0-10 10-20 20-30 30-40 40-50 50-60 60-70 70-80 80-90 90-100
0 5 10 15 20 25 30 35 40 45 50
All
Mag
Mag litho
Mag fallout
Mag geochem
Geochem litho
Geochem fallout
Geochem


August - September 2012
September - October 2012
October - December 2012
August - September 2012 (Original)
September - October 2012 (Original)
October - December 2012 (Original)
Percentage of Monte Carlo interations
Predicted contribution (%)
0
0-10
10-20
20-30
30-40
40-50
50-60
60-70
70-80
80-90
90-100
All
Mag
Mag litho
Mag fallout
Mag geochem
Geochem litho
Geochem fallout
Geochem

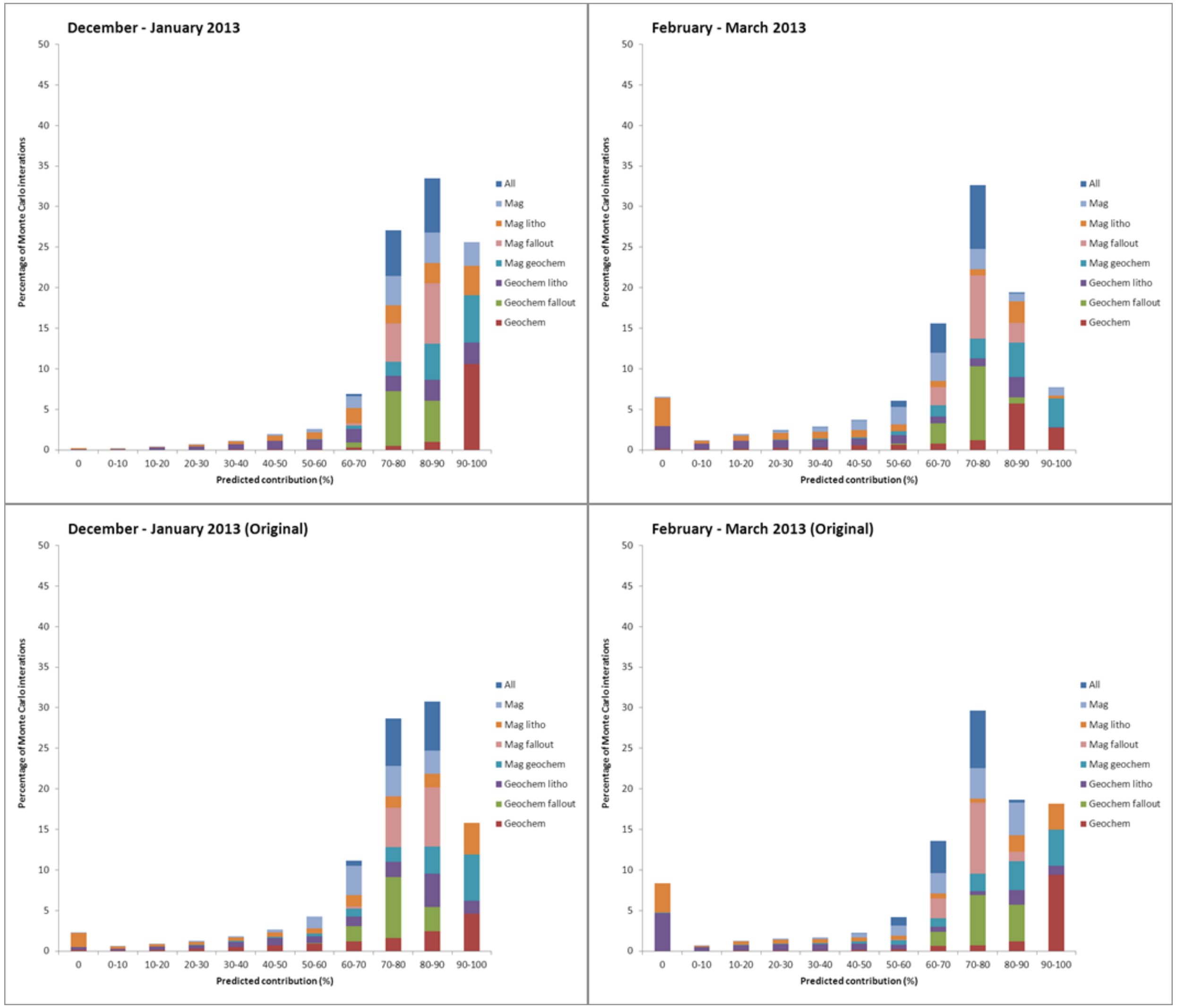


Figure 7-17: A comparison of composite PDFs of predicted contributions from channel banks derived using the different tracer groups when large composite fingerprints and the shorter original composite fingerprints are used.

7.4. Corrections for organic content and particle size distribution

Objective 3 of this thesis requires an assessment of the effectiveness of corrections for the organic matter content and particle size distribution of the sediment to tracer signatures. It was shown in Section 7.3, as part of the fulfilment of Objective 2, that the differences between the predictions of the various tracer groups were not significantly correlated with the LOI and SSA of the sediment. For this reason corrections were not applied to the composite fingerprints used in fulfilment of Objective 1 to see if they would make the predictions of any tracer group closer to another. Instead, the fingerprinting methodology (Section 5.5) was repeated from the beginning using tracer signatures which were corrected for organic matter and particle size. By doing this, if any of the discriminatory efficiency of the tracers used to form the composite fingerprints was a result of differences to the organic content and particle size distribution of the source groups, this would be accounted for by the correction. The organic matter and particle size corrections were applied using the methods described in section 5.5.3.

This section is structured into two parts. The first investigates the effects of the corrections on the statistical composite fingerprint determination procedure. Firstly, the mass conservation test was repeated for the corrected data, to determine if corrections increase the percentage of sediment samples passing the test. The linear discriminant analysis was then repeated for each tracer, to determine if the corrections increased or decreased the ability of the tracers to discriminate between sediment sources. Finally the genetic algorithm linear discriminant analysis was repeated with the corrected data to determine if a greater number of composite fingerprints, could sucessfully categorise >80% of source samples.

In the second part of this section the mean diffrences between tracer group sediment provenance predictions were compared for the fingerprints of the uncorrected and corrected tracer signatures. In this way it was determined if the different tracer groups predicted a more consistant sediment provenance when the corrections were used.

7.4.1. Statisitcal composite fingerprint determination

The mass conservation test

The mass conservation test used with uncorrected data in Section 7.2.1. was repeated with the source and sediment tracer signatures which were corrected using LOI and SSA. The results of the test shown in Figure 7-18 indicate that the corrections caused little change in the percentage of sediment samples passing the test for most tracers. More than a 5% increase in the percentage of samples passing the range test was found in 15 of the 39 tracers when at least one correction was applied. However, for 19 of the 39 tracers, at least one of the corrections reduced the percentage of samples which passed the mass conservation test. It therefore must be concluded that the corrections mostly cause only a small reduction in the ability of tracers to pass the mass conservation test.

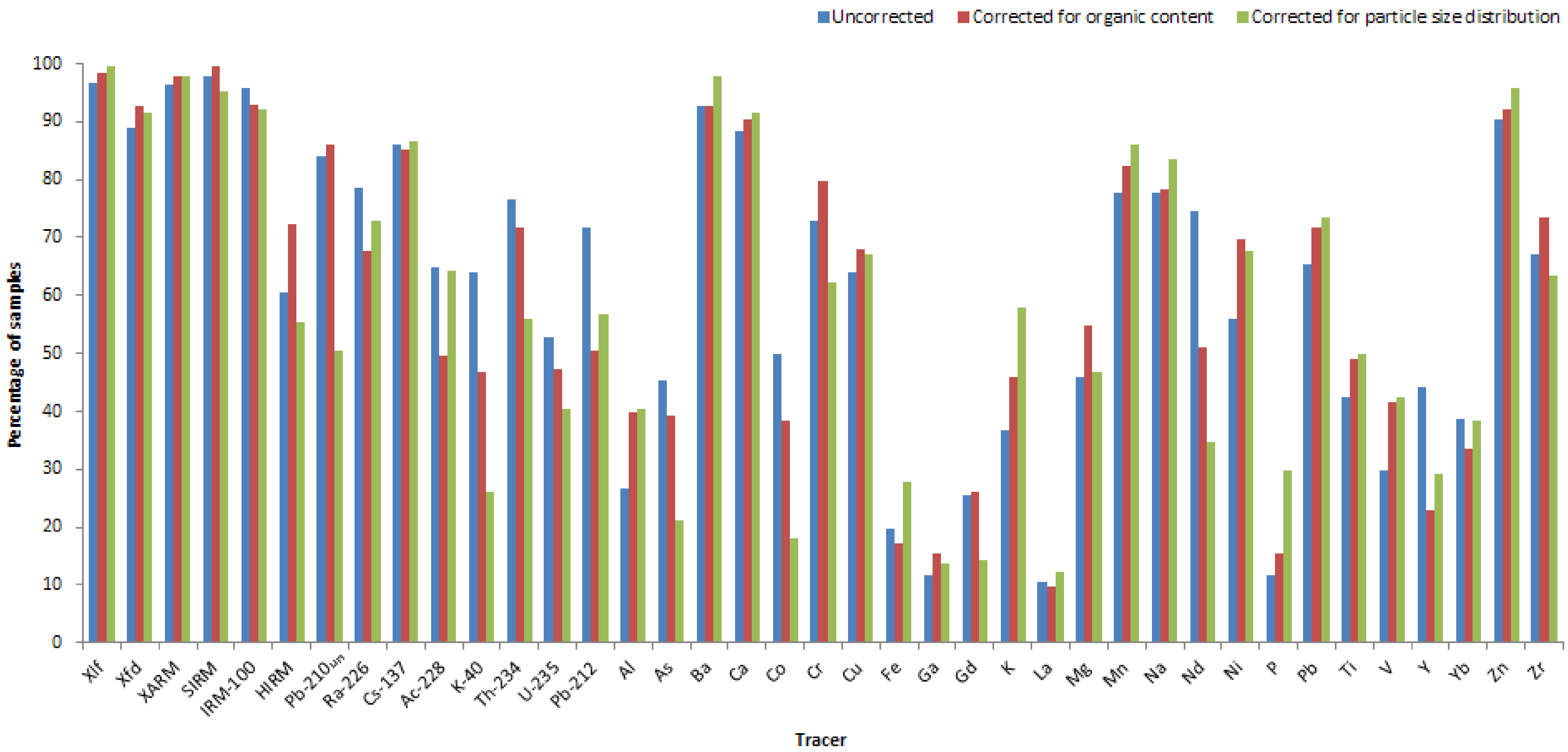


Figure 7-18: The percentage of river sediment samples where tracers pass the mass conservation test with and without data corrections.

Discriminant analysis

The linear discriminant analysis performed on the uncorrected tracer signature data in Figure 7-3 was repeated on the tracer signature data whch had been corrected using LOI and SSA. The increase of decrease in the percentage of sediment samples which can be correctly classified by each tracer are shown in this part of the section.

An organic matter correction had little impact (<+2%) on the mean discriminatory efficiency of magnetic mineral tracers, whereas particle size corrections increase the discriminatory efficiency of each tracer by between 0.5 and 4% (Figure 7-19).

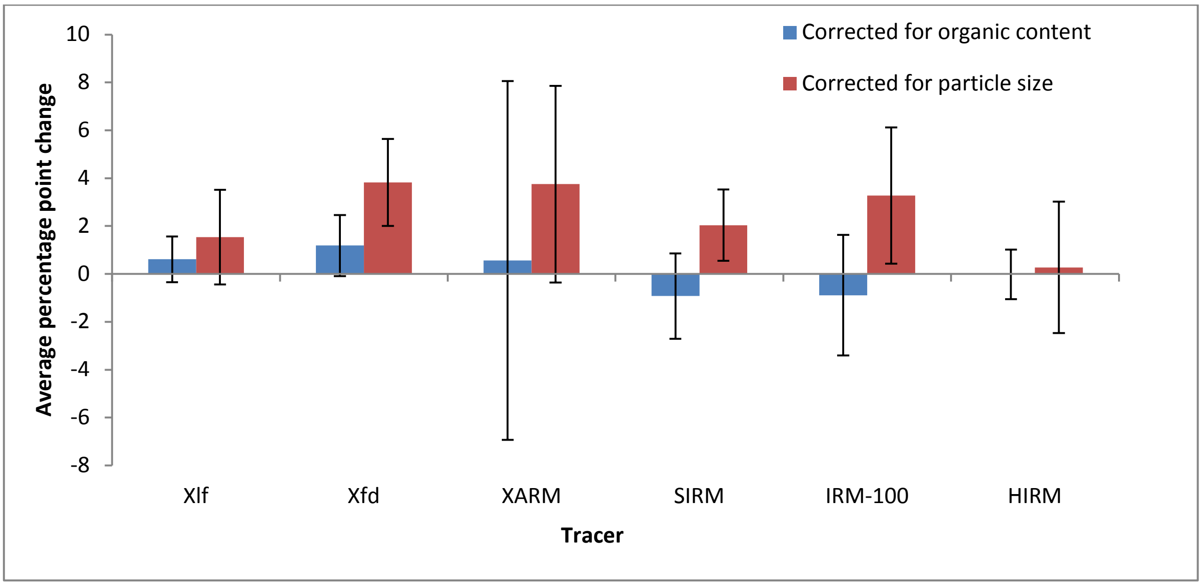


Figure 7-19: The percentage point change in the discriminatory efficiency of mineral magnetic signatures after the application of corrections.

In the case of radionuclides (Figure 7-20) an organic correction reduced the discriminatory efficiency of the tracers by 0-5%. A greater reduction of between 3-15% was found when a particle size correction was applied to the data. The fallout radionuclides $^{210}Pb_{un}$ and ^{137}Cs are impacted by corrections less than lithogenic radionuclides.

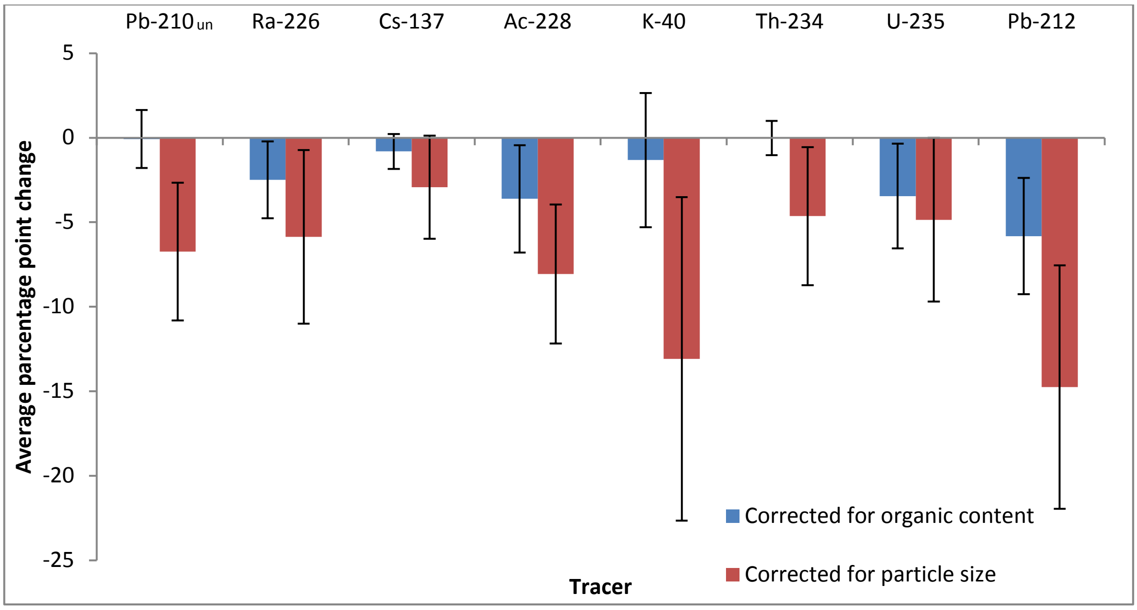


Figure 7-20: The percentage point change in the discriminatory efficiency of lithogenic and fallout radionuclides after the application of corrections.

Geochemical tracers (Figure 7-21) showed varying responses to corrections. The discriminatory efficiency of Al, La, Y and Yb increased by ~10% when a particle size correction was applied. The efficiency of As, Ga, Gd, Nd was reduced when any correction was applied.

It was observed that for almost all tracers an organic correction resulted in a smaller change in discriminatory efficiency than particle size correction did. Therefore this result indicates that the discriminatory efficiency of many tracers may in part be derived from differences in the particle size distribution of the three source groups. The implication of this is that any changes in particle size affecting the sediment would cause a loss in some of the basis for source discrimination, and therefore would cause an incorrect sediment provenance prediction. Therefore the corrected particle size data might be expected to cause some benefit to the consistency between tracer group predictions.

The standard deviation error bars in Figure 7-19, Figure 7-20 and Figure 7-21 are often larger than the average change in discriminatory efficiency affecting the tracers after correction, which indicates that a large amount of spatial variability is encountered in the change in discriminatory efficiency which occurs when corrections for organic matter or particle size are applied. Therefore, an additional source of the uncertainty associated with the regional variability in tracer concentrations discussed in Section 7.3.2. may have been introduced to the modelling by the use of the corrections. Should the corrections be applied when tracers are not related to organic matter or particle size in the sediment sources, the introduced uncertainty would be greatly increased.

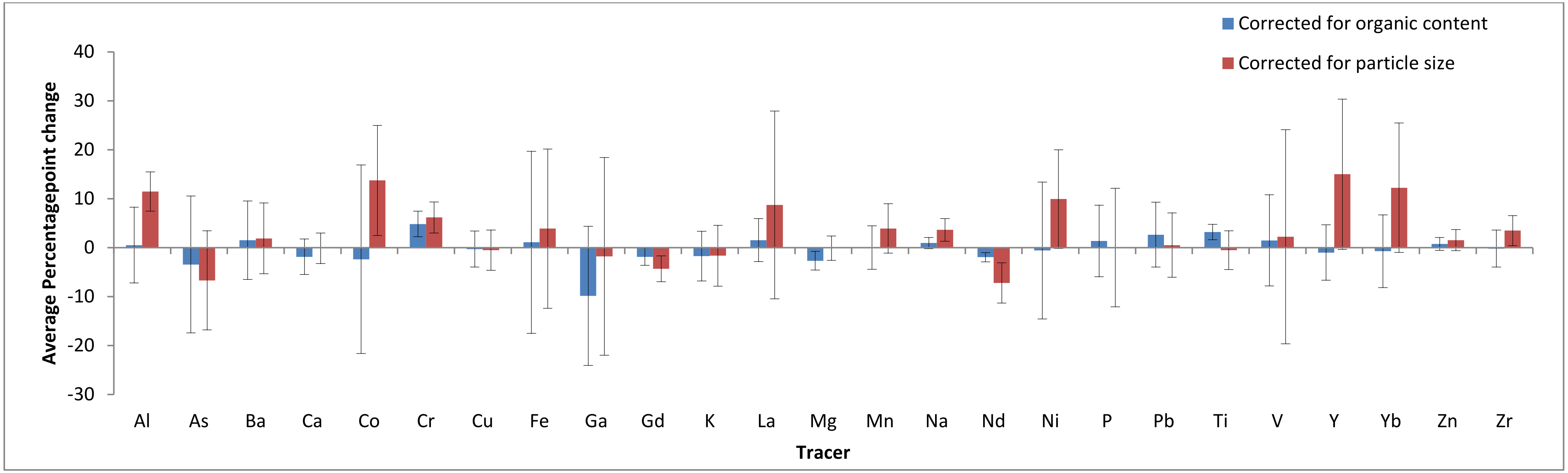


Figure 7-21: The percentage point change in the discriminatory efficiency of geochemical tracers after the application of corrections.

The final part of the statistical procedure to determine composite fingerprints for each tracer group was the genetic algorithm linear discriminant analysis. This section repeats the analysis which was originally used in Figure 7-5, on the organic corrected and particle size corrected tracer signatures.

The results shown in Figure 7-22 indicate that overall 15% fewer composite fingerprints could successfully discriminate between >80% of source samples when an organic correction was applied to the tracer signatures, and 20% fewer composite fingerprints could be used when a particle size correction was applied to the tracer signatures.

An organic correction increased the number of usable composite fingerprints for the mineral magnetic signature tracer group by 33.3%. For all other corrections, on all other tracer groups, the correction resulted in fewer composite fingerprints which could discriminate between 80% of source samples. This result therefore indicates a detrimental effect of corrections when forming composite fingerprints.

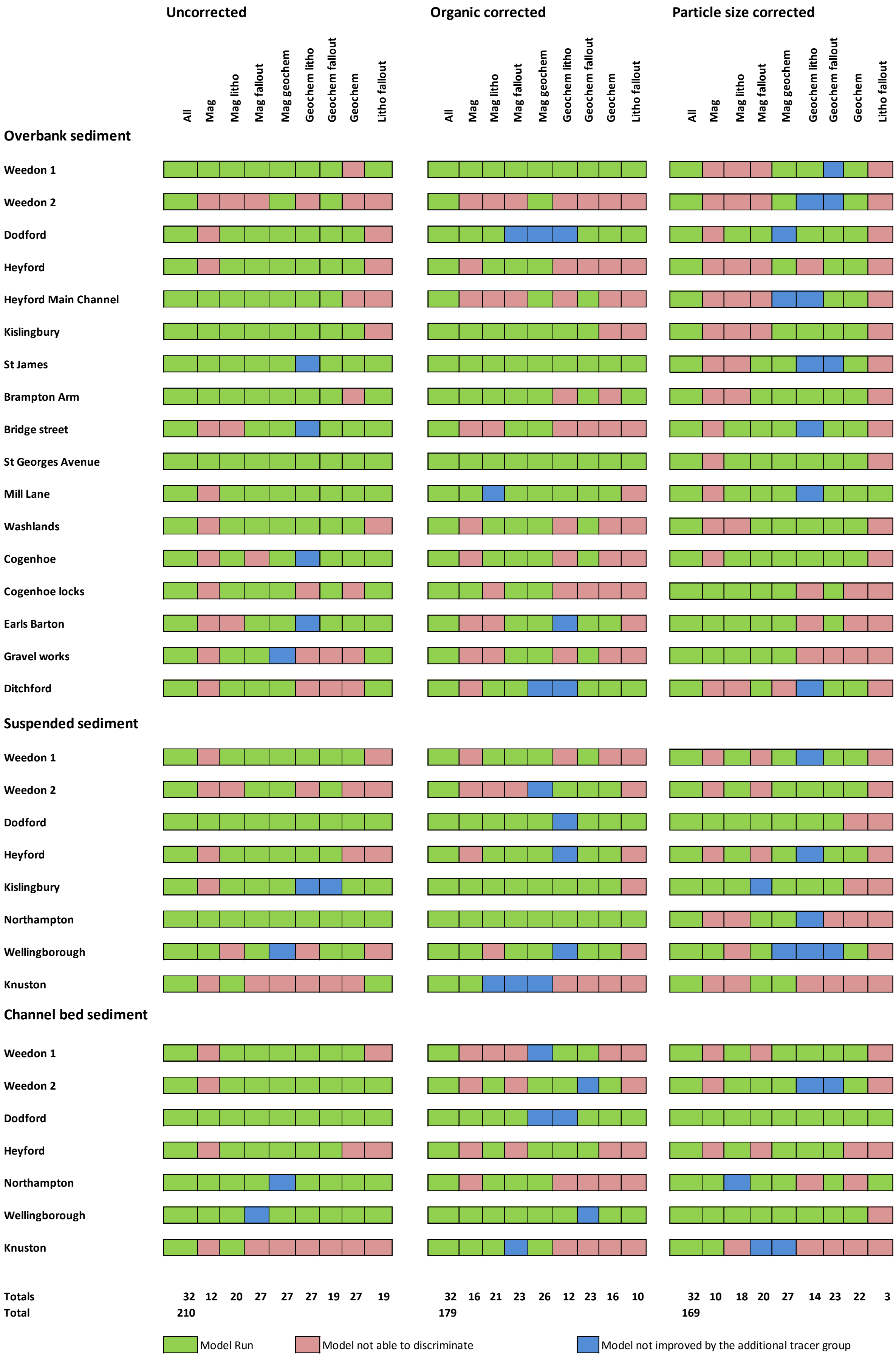


Figure 7-22: The results of the GA-DFA analysis for uncorrected and corrected tracer signatures in contemporary sediment sampling sites, where the “Mag geochem” group is blue this indicates that it is identical to the ‘All’ group.

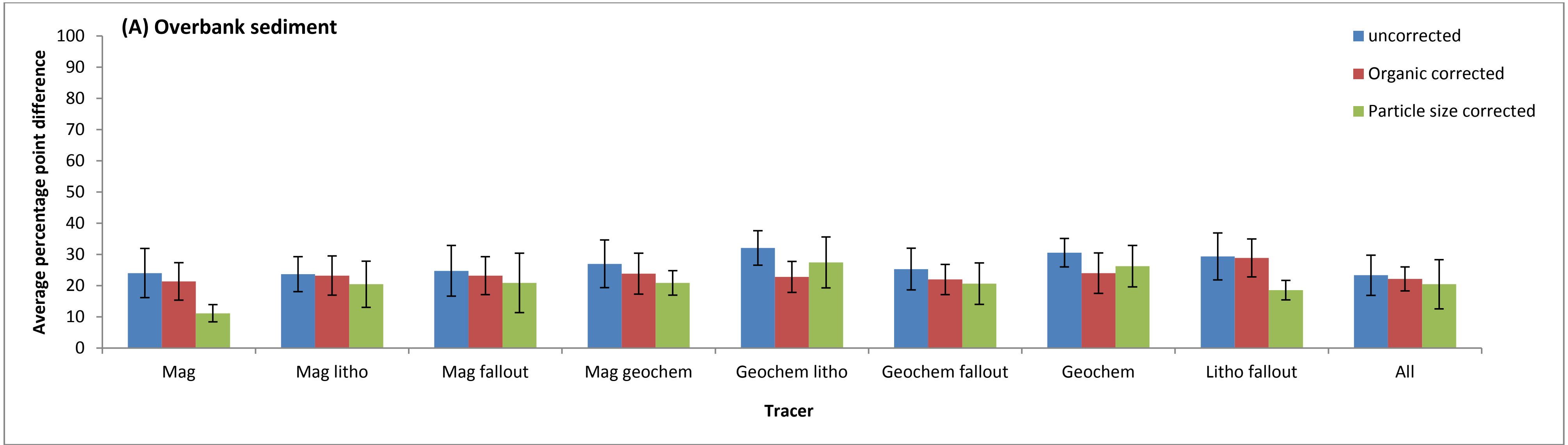
7.4.2. The differences between corrected and uncorrected tracer group provenance predictions

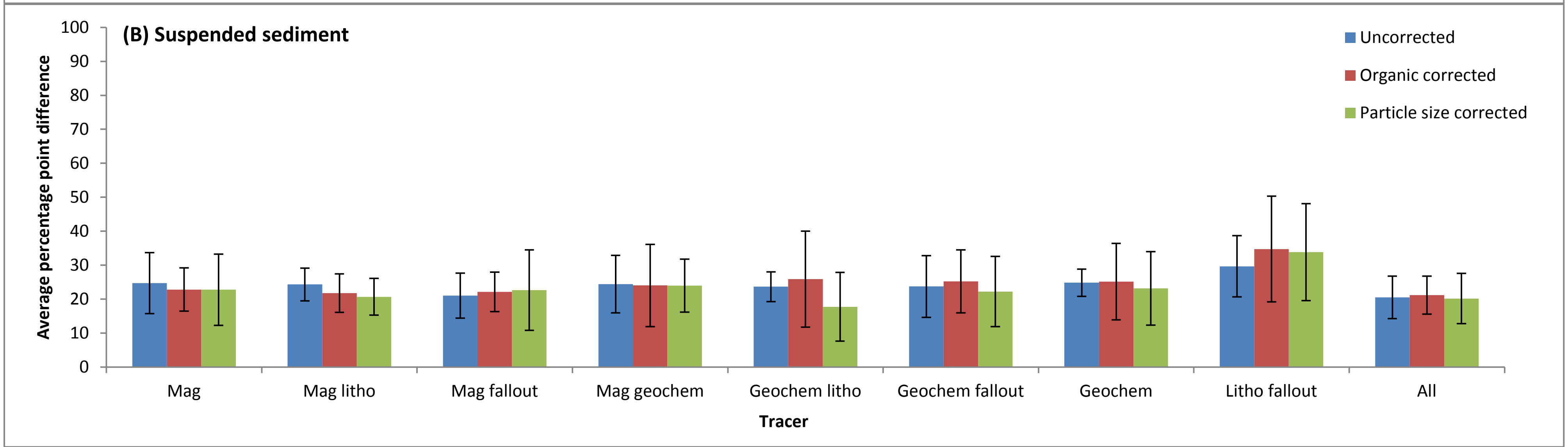
To conclude this section and complete the targets of Objective 3, un-mixing models were run for all of the tracer groups and sediment samples analysed as part of Objective 1 in Section 7.2. In this analysis the models were run using the tracer signature data which had been corrected for organic matter and particle size. The differences between tracer provenance predictions of the different tracer groups were quantified using the methods laid out in Section 7.2, and it was determined if the differences between tracer group predictions were smaller when using the corrected data.

Figure 7-23 shows the mean difference between the prediction of each tracer group and every other tracer group in the overbank, suspended and channel bed sediment samples. The mean overall difference between every tracer group produced using uncorrected tracer signatures was 24.1% (standard deviation 2.9%); using organic enrichment corrected signatures was 24.3% (standard deviation 2.1%); and using particle size corrected signatures was 30.1% (standard deviation 3.9). This indicates little effect caused by the organic correction, and a 6% increase in the mean differences when a particle size correction was applied.

Some variability exists in the effects of the corrections in the three river sediment sampling locations. For example, the mineral magnetic signature particle size correction decreases the mean differences when an organic correction is applied in the overbank sediment samples, but increases it in the channel bank samples. As a result no clear trends of greater or lesser impacts of corrections on any specific tracer groups can be determined.

Figure 7-24 shows the effects of the corrections on the tracer variability ratio, which was discussed in Section 7.3.2. The average variability ratio of all of the tracers was 0.59 for the uncorrected signatures, 0.57 for the organic corrected signatures and 0.60 for the particle size corrected signatures. It is therefore apparent that the corrections had little overall effect on the average tracer variability ratio. The increased differences between the predictions tracer groups that are particle size corrected are therefore likely to be a result of the correction being inappropriately used, rather than it causing a greater amount of within-source variability in tracer concentrations.


(A) Overbank sediment
Average percentage point difference
100
90
80
70
60
50
40
30
20
10
0
Mag
Mag litho
Mag fallout
Mag geochem
Geochem litho
Geochem fallout
Geochem
Litho fallout
All
Tracer
uncorrected
Organic corrected
Particle size corrected


(B) Suspended sediment
Average percentage point difference
100
90
80
70
60
50
40
30
20
10
0
Mag
Mag litho
Mag fallout
Mag geochem
Geochem litho
Geochem fallout
Geochem
Litho fallout
All
Tracer
Uncorrected
Organic corrected
Particle size corrected

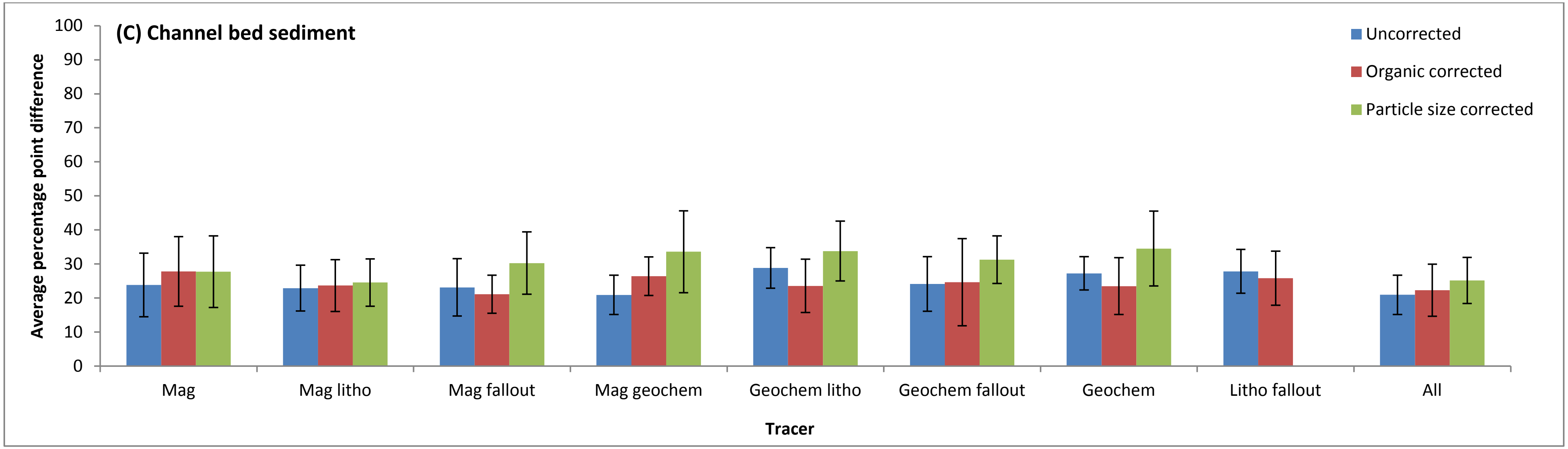


Figure 7-23: The mean differences between the sediment provenance prediction of each tracer group and all other tracer groups, with and without corrections, with standard deviation error bars.

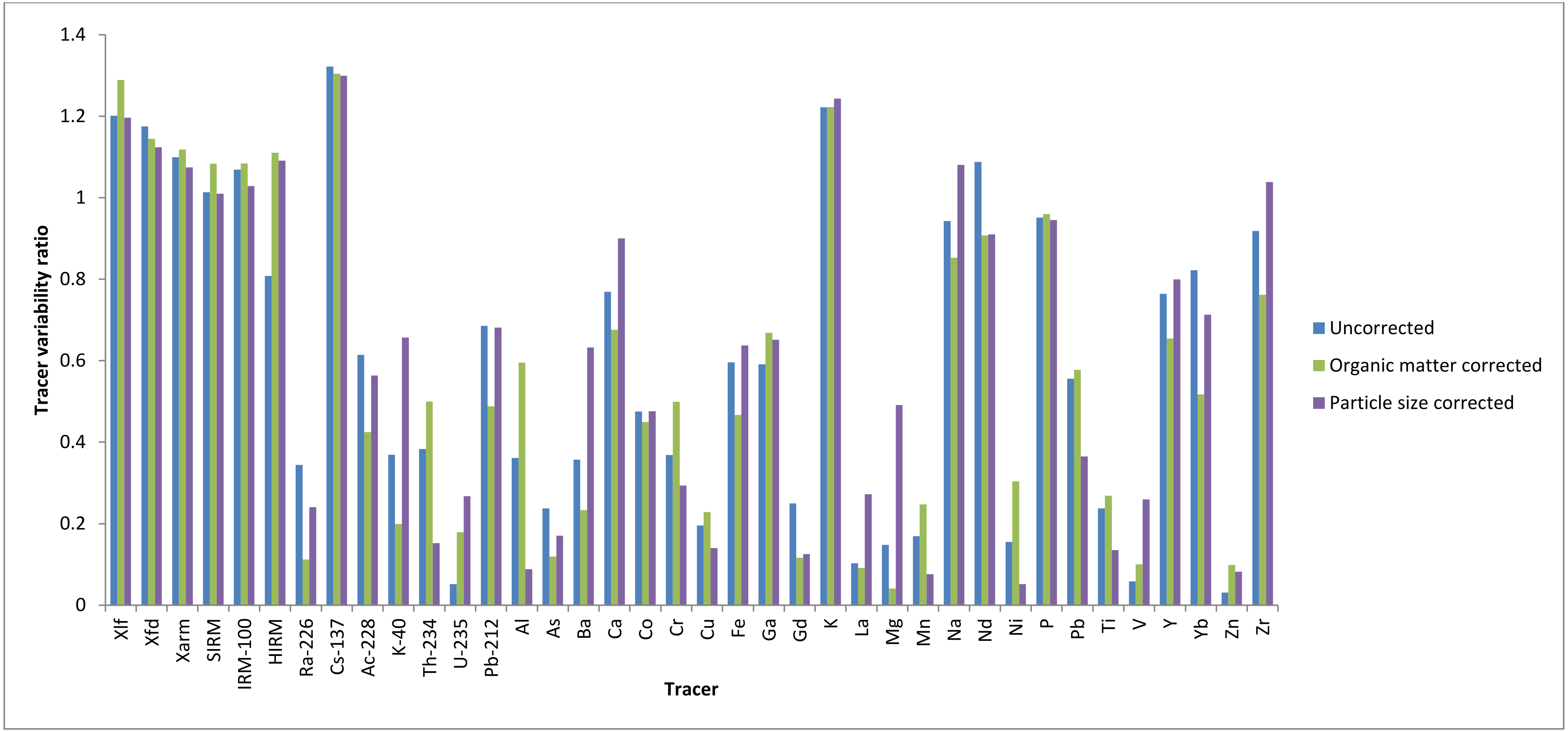


Figure 7-24: The effect of organic matter and particle size corrections on the tracer variability ratio.

8. Fine sediment dynamics in the Nene river basin.

8.1. Introduction

The results of this chapter are structured around a simplified sediment budget outline fulfilling Objective 4 of this thesis. The following sections present the results of each part of the sediment budget, and discuss them in the context of the sediment dynamics and processes found in other published fine sediment investigations.

The sediment budget consisted of the following components: sediment yield, floodplain sediment accumulation, channel bed sediment storage, sediment provenance. The results of each section were finally used to produce a sediment budget which aims to cover the past 100-150 years. The methods used to produce these results are described in Chapter 4 and Chapter 5.

8.2. Sediment Yield

8.2.1. Palaeolimnological reconstruction

^{137}Cs and $^{210}Pb_{un}$ were used to calculate the relationship between age and depth in the reservoir in a master sediment core (Figure 8-1). The peak in ^{137}Cs at 22cm was tentatively identified as the year of maximum fallout in 1963, and the initial occurrence of ^{137}Cs at 29cm was determined to be the year of the first detectable fallout at 1958, as it is now unlikely that the first occurrence will be easily identifiable in lake sediment sequences (Foster, 2006). $^{210}Pb_{un}$ dating was performed using the 'c-crs' model as the basal date of the reservoir sediments at 1906 was known (Appleby, 2001). There is some discrepancy between the ^{137}Cs peak and the 'c-crs' estimated date at 1963, although the 1958 initial occurrence of ^{137}Cs appears to be consistent with the 'c-crs' predictions. The 4 values above 30 mBq g^{-1} at 17-30 cm depth are high and follow an unusual trend in comparison to other lake profiles. They may be indicating delayed inputs of ^{137}Cs from the catchment associated with a change in sediment source, providing an explanation for the discrepancy between the two dating methods at the 1963 peak (Walling and He, 1992).

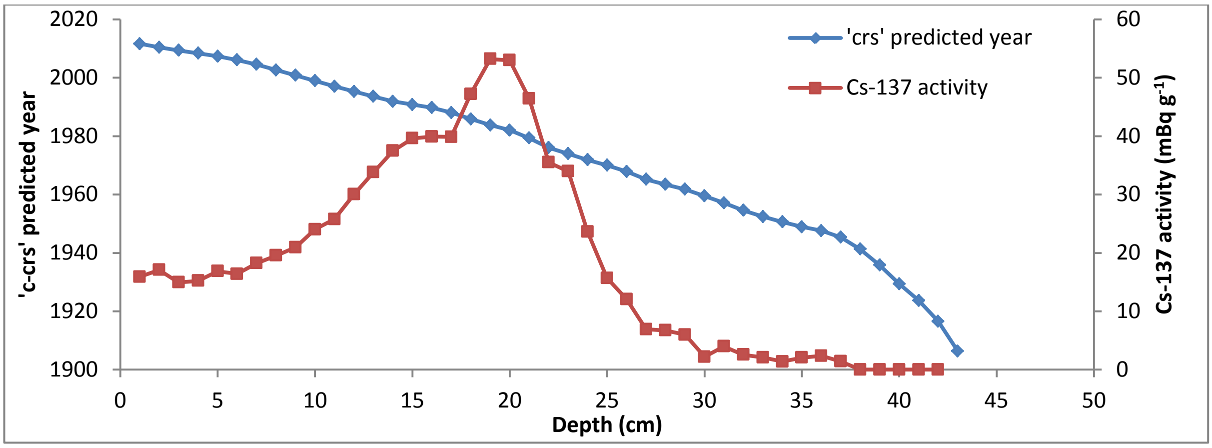


Figure 8-1: Depth-age curve calculated from the 'c-crs' model, and down-core variations in ^{137}Cs activity in Sywell reservoir.

Assuming that the 'c-crs' model represents changes in accumulation through time, it is possible to use it to calculate changes in sediment accumulation rate (Figure 8-2). Prior to the late 1940s the accumulation rate ranges from 0.03 to 0.09 g cm^{-2} yr^{-1}. At the 'c-crs' predicted year of 1948 the sediment accumulation rate increases to a baseline of between 0.11 and 0.16 g cm^{-2} yr^{-1} with a number of large peaks in excess of 0.2 g cm^{-2} yr^{-1}. On this basis a change in catchment sediment dynamics appears to have occurred at ~1948. This is entirely consistent with the findings of Rose *et al.* (2011) in a study of over 200 European lakes, where most lakes and reservoirs of the Sywell type (lake type 3121[small deep lowland lakes] of Rose *et al*. 2011) showed significant increases in sediment accumulation after 1950. Average sediment yield was therefore calculated for the period prior to 1948 and post 1948.

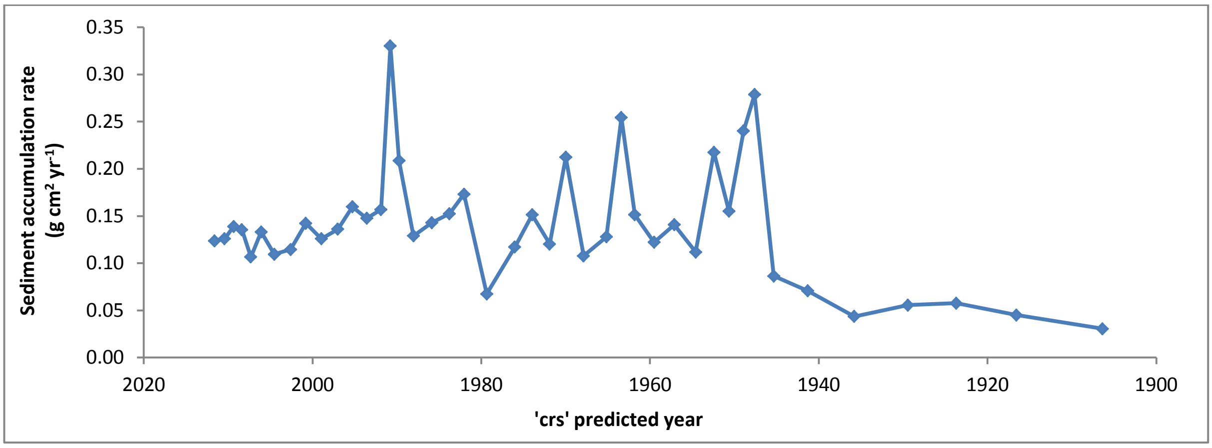


Figure 8-2: The down-core trend in sediment accumulation rate in Sywell reservoir.

The chronology determined for the master core (marked "1" in Figure 8-3) was transferred to the other cores using a core correlation using low frequency magnetic susceptibility, measured using a Bartington MS2 magnetic susceptibility meter with a MS2C core logging sensor. In this way the 1948 change in sediment accumulation rate was determined for all of the cores.

The depth of sediment was reasonably uniform in each of the 6 cores where sediment was found, and for this reason, the mean and standard deviation of the sediment depth across the entire sedimentation limit was calculated as 0.34m (Figure 8-2). The margin of error of the estimated depth of sediment was produced as an upper limit (mean + 1 standard deviation), and lower limit (mean – 1 standard deviation). The sedimentation limit was identified at the -3.9 m isobath in Figure 8-3 as no sediment was found in the core retrieved from shallower water. The depth of the sediment (+/- the upper and lower sediment depth estimates) and dry density of the sediment was multiplied by the area of the sedimentation limit, to determine the mass of sediment accumulated in the reservoir.

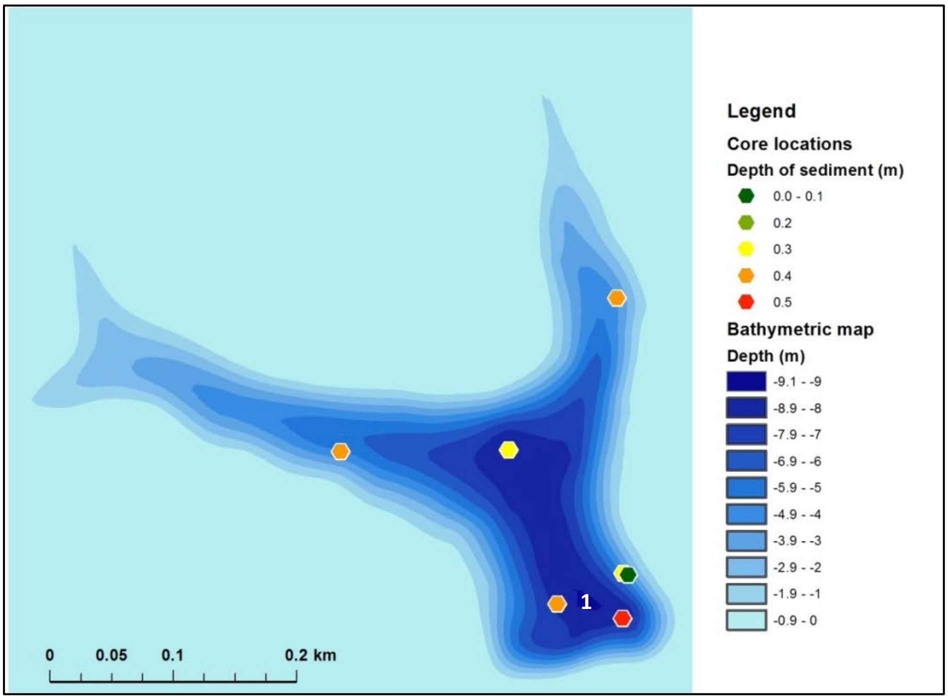


Figure 8-3: Bathymetric map, coring locations and depth of sediment in collected cores in Sywell reservoir.

Using the mass of sediment accumulated, the time of sediment accumulation (105 years), and the catchment area (8.7 km^2), the sediment yield for the catchment was determined for the pre ~1948 and post ~1948 periods. The sediment yield was calculated as the total yield with no subtraction of the quantities of organic material in the sediment. The average organic content calculated by loss on ignition in the core pre 1948 is 8% and post 1948 is 9%.

The sediment yield prior to the increase in sediment accumulation rate at 1948 was calculated at 7 t km^{-2} yr^{-1} +/- 3 t km^{-2} yr^{-1}, post 1948 this increased to 13 t.km^{-2} yr^{-1} +/- 3 t km^{-2} yr^{-1}, with an upper limit estimate of 16 t km^{-2} yr^{-1} and lower limit estimate of 10 t km^{-2} yr^{-1}.

Sediment yields are discussed in the context of contemporary monitoring and other published UK data in the conclusions to the following section.

8.2.2. Sediment yield determined from turbidity and stage measurements

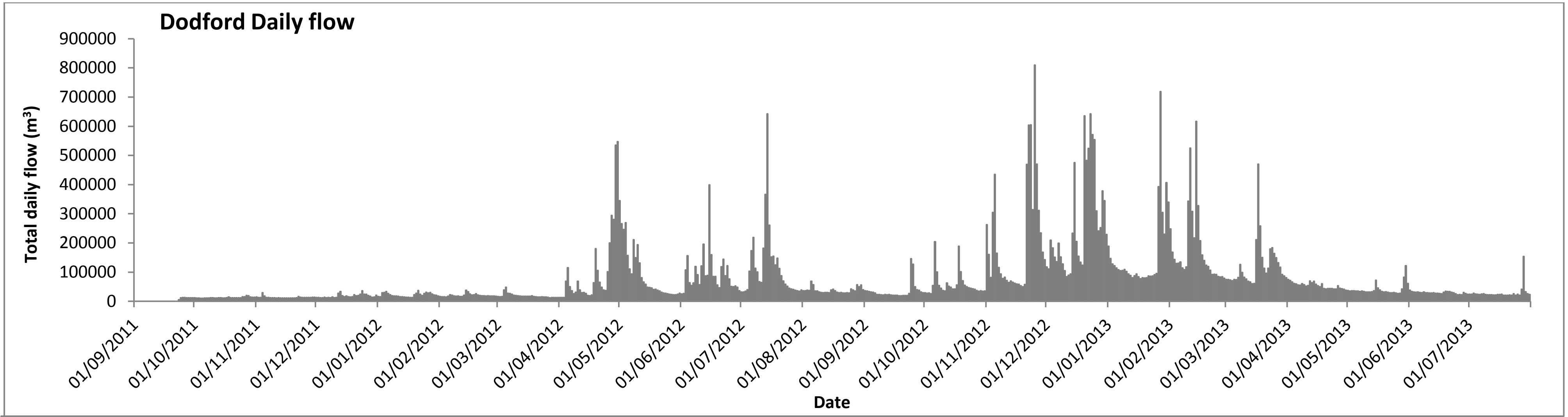
Daily sediment yield was calculated for the two tributary catchments at Dodford and Northampton, using flow values derived from Environment Agency stage monitoring and suspended sediment concentration (SSC) derived from turbidity measurement.

The monitoring period (September 2011 - August 2013 at Dodford; February 2012 -August 2013 at Northampton), was characterised by a period of drought during 2011 until April 2012 where a high flow event occurs. There is a moderately high flow in July and a series of large flood events in November and December 2012 (Figure 8-4).

Using the turbidity – SSC relationship (Figure 4-12) and the stage derived flow measurement, daily suspended sediment load was calculated for both sites and is shown in Figure 8-4.

The monitoring at the Northampton site began recording in February 2012, 5 months after the site at Dodford. As there were no high flow events during this time the average low flow sediment concentration (4 mg l^{-1}) found in the calibration samples was combined with the flow data to produce a record of sediment movement for Northampton during this 5 month period, which produced a comparable duration dataset for both sites.

Both sites have the largest peaks in suspended sediment load at the end of November and December 2012 (Figure 8-4), which also corresponds to the largest peaks in flow. The high flow events account for the majority of sediment movement; resulting in 95% of sediment moving in 17.7% of time at Dodford and 95% of sediment moving in 12.8% of time at Dodford.


Dodford Daily flow
Total daily flow (m³)
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
01/09/2011
01/10/2011
01/11/2011
01/12/2011
01/01/2012
01/02/2012
01/03/2012
01/04/2012
01/05/2012
01/06/2012
01/07/2012
01/08/2012
01/09/2012
01/10/2012
01/11/2012
01/12/2012
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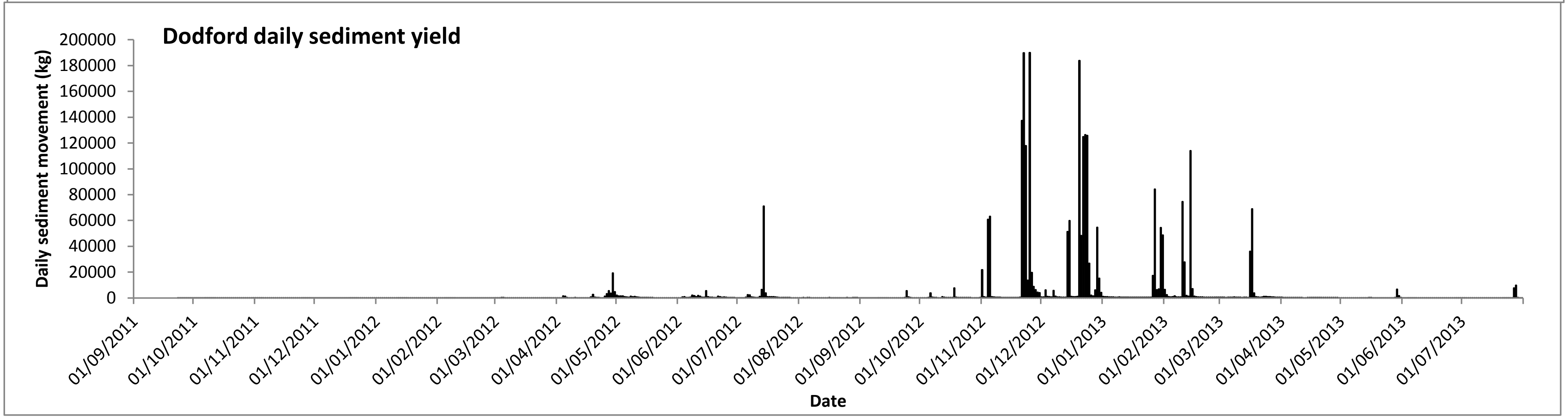
01/02/2013
01/03/2013
01/04/2013
01/05/2013
01/06/2013
01/07/2013
Date


Dodford daily sediment yield
Daily sediment movement (kg)
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
01/09/2011
01/10/2011
01/11/2011
01/12/2011
01/01/2012
01/02/2012
01/03/2012
01/04/2012
01/05/2012
01/06/2012
01/07/2012
01/08/2012
01/09/2012
01/10/2012
01/11/2012
01/12/2012
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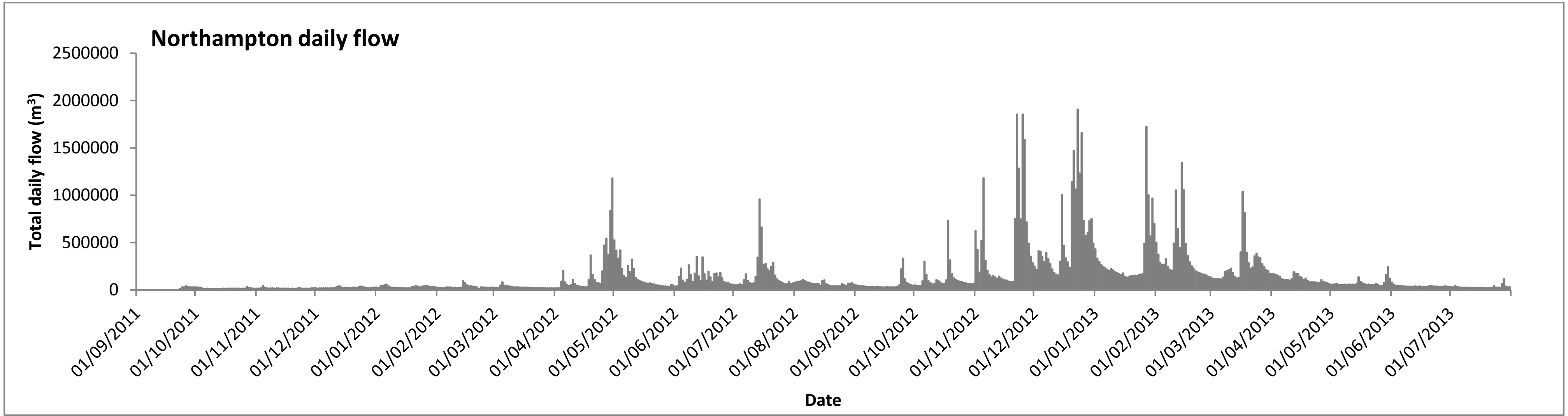
01/06/2013
01/07/2013
Date



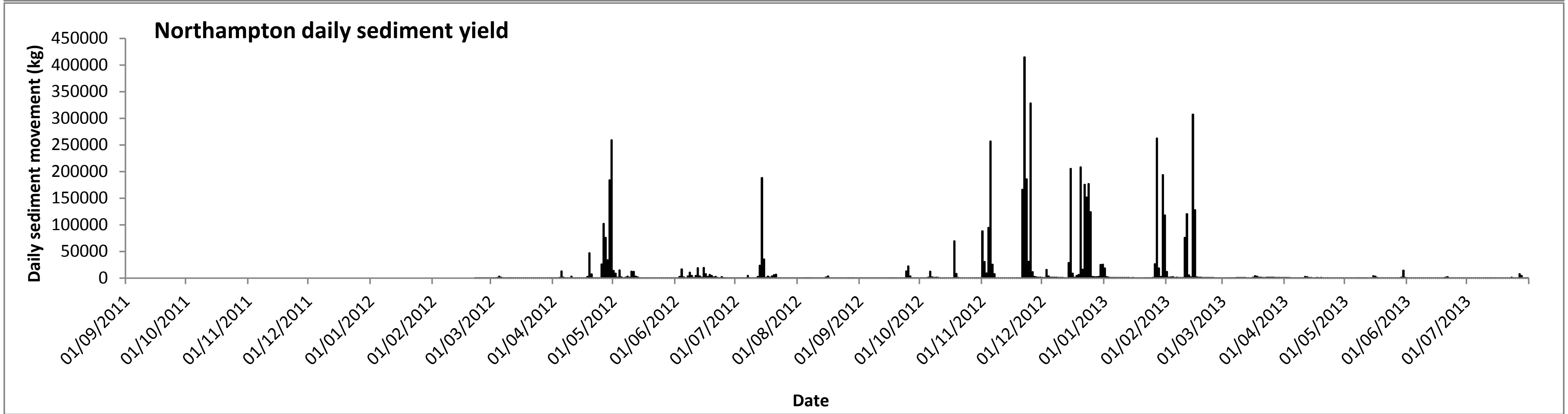


Figure 8-4: Daily flow and daily suspended sediment yield at the Northampton and Dodford sampling sites.

Using the daily sediment transport data, annual sediment yields were calculated using the area of each tributary catchment (Dodford: 105km^2, Northampton: 161km^2) and the duration of the monitoring (years). The calculated suspended sediment yields were:

Dodford (Whilton arm): 13 t km^2 yr^{-1}

Northampton (Brampton arm): 19 t km^2 yr^{-1}

Sediment yields are presented without correction for organic content. The average organic content of the suspended sediment was determined using low temperature loss on ignition, with the sediment acquired using the time-integrated suspended sediment traps. The organic content was calculated at 15.6% for Northampton and 17.9% for Dodford.

Sediment yields in UK catchments have been shown to range from 1 to 286 t km^{-2} yr^{-1} (Walling *et al*., 2007). The Nene represents a lowland agricultural catchment with a total area of between 1000 and 10,000 km^2, where a sediment yield of between 28 and 51 t km^{-2} yr^{-1} would be expected from a review of UK sediment yield data published by Walling *et al*. (2007). The sediment yields calculated in the Nene basin of 13 t km^{-2} yr^{-1} (Dodford), 19 t km^{-2} yr^{-1} (Northampton), and 13 t km^{-2} yr^{-1} (Sywell reservoir; 1948-2010), are all substantially lower than this average for lowland UK agricultural catchments. The pre 1940s sediment yield calculated for Sywell reservoir of 7 t km^{-2} yr^{-1} is comparable to the sediment yield found for lowland catchments with limited anthropogenic impact, although it should be emphasised that only one study in the River Churnet catchment provided this estimate (Walling and Webb, 2007).

It can therefore be concluded that the increase in sediment yields attributed to intensification of agricultural practices in most lowland UK catchments by Foster *et al.* (2011), occurred in the Nene, with an approximate doubling of sediment yield, although the yield remains low in comparison to other UK catchments.

A previous fine sediment investigation conducted by Wilmott and Collins, (1981) measured the sediment yield of the Nene to be between 5 t km^2 yr^{-1} and 10 t km^{-2} yr^{-1}. A rating curve methodology was used to produce this measurement. The sediment yield of 13-19 t km^{-2} yr^{-1} calculated in this thesis is considered to be in reasonable agreement with the value derived by Wilmott and Collins, (1981). Tye et al. (2013) revised the sediment yield calculated by Wilmott and Collins, (1981) to a lower value of 6.24 t km^{-2} yr^{-1} after the use of landscape evolution modelling, based upon the CAESAR model developed by Coulthard and Van De Wiel (2006). The results of this thesis suggest that this modelling approach failed to fully account for the entire sediment yield of the Nene. It is likely that the model failed to account for the large amount of sediment originating from channel banks, which was suggested by the sediment fingerprinting results presented later in this chapter. These results highlight the importance of field-based validation of modelling results.

8.3. Floodplain sediment accumulation

Using the four floodplain cores the dates of the largest peak in ^{137}Cs fallout (usually attributed to 1963) and the first occurrence of ^{137}Cs (usually attributed to 1958) (Foster, 2006), were determined using down-core plots of ^{137}Cs activity (Figure 8-5) and are listed in Table 8-1. The depth of these date markers were combined with the cross sectional area and dry density of the sediment cores to produce a floodplain sediment accumulation rate (t km^{2} yr^{-1}) between 1958 and 1963 and during the post 1963 period.

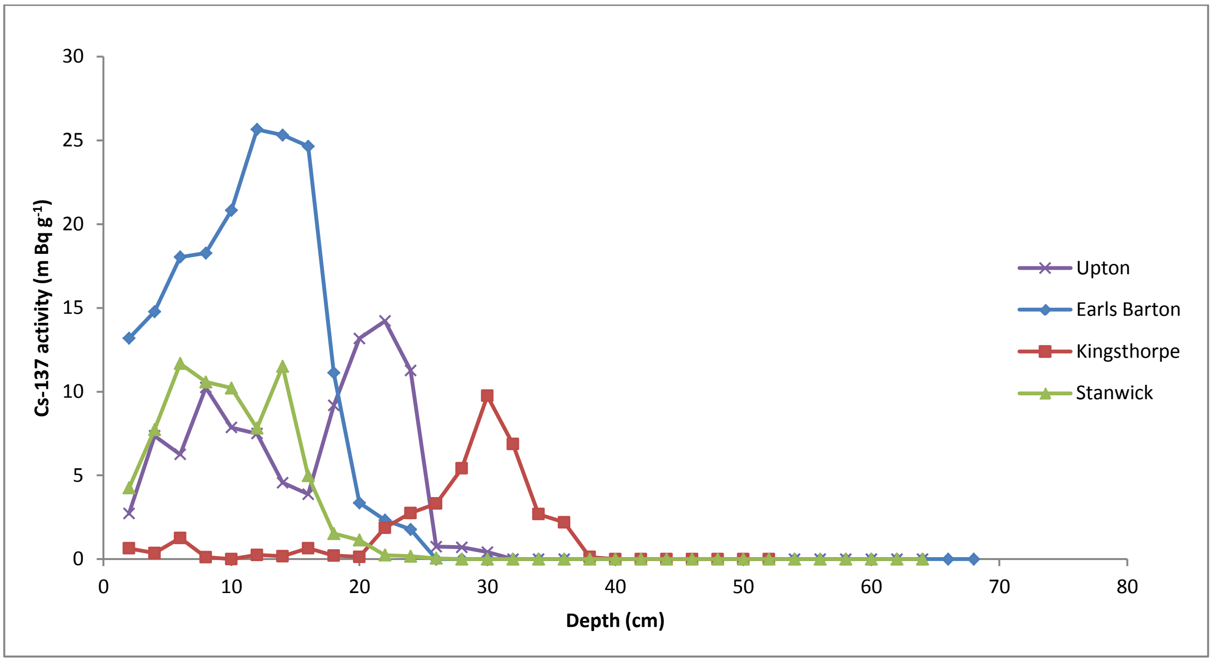


Figure 8-5: Down-core plot of floodplain core ^{137}Cs activity.

The reconstructed accumulation rates (Table 8-1) show that between 1958 and 1963 the accumulation rates ranged from 13,796 t km^{-2} yr^{-1} to 20,726 t km^{-2} yr^{-1}. After 1963 the accumulation rates have been reduced by between 65% and 93% of this rate to a range of between 924 and 7,175 t km^{-2} yr^{-1}, indicating a reduction in accumulation rate in all sampling locations.

Table 8-1: Floodplain sediment accumulation rates in the Nene basin from 1958 to 1963 and post 1963.

Core	Depth of the 1963 ^{137}Cs peak (m)	Depth of the 1958 first occurrence of ^{137}Cs (m)	Accumulation rate 1959 – 1963 (t km^{-2} yr^{-1})	Accumulation rate post 1963 (t km^{-2} yr^{-1})	Percentage change
Upton	0.22	0.32	17,440	3,400	-80%
Kingsthorpe	0.3	0.38	20,726	7,175	-65%
Earls Barton	0.14	0.26	13,796	924	-93%
Stanwick	0.16	0.22	14,998	3,581	-76%

In published studies post 1963 ^{137}Cs derived floodplain sediment accumulation rates in the UK have been shown to be highly variable. A review by Gruszowski, (2003) shows that post 1963 UK accumulation rates range from between 0 and 16,000 t km^{-2} yr^{-1} with a mean accumulation rate of 4,062 t k^{-2} yr^{1}. The value of 924 t km^{2} yr^{-1} found in the Earls Barton core is one of the lowest values found in the UK, only the River Stour, Dorset (800 t km^{-2} yr^{-1}) (Walling and He 1997b), River Teviot (900 t km^{-2} yr^{-1})(Owens *et al*., 1999a), Dorset Stour, Spetisbury (400 t km^{2} yr^{-1}) (Walling and He, 1999b), Smisby (900 t km^{-2} yr^{-1})(Walling *et al* 2002), Warwickshire Avon (900 t km^{-2} yr^{-1}) (Walling and He 1999a) and areas of the River Ouse and Tweed (~0 t km^{-2} yr^{-1})(Walling *et al* 1999b) have been calculated to have lower accumulation rates (Gruszowski, 2003). The highest rate of 7,175 t km^{-2} yr^{-1} found at Kingsthorpe is in excess of most sites in the UK with only the Lower River Ouse (9,500 t km^{2} yr^{-1}) (Owens *et al* 1999b), River Ouse (9,500 t km^{-2} yr^{-1}) (Walling and He 1999a), River Severn at Atcham (12,200 t km^{-2} yr^{-1}) (Walling and He 1999a), River Severn at Tewkesbury (8,600 t km^{-2} yr^{-1}) (Walling and He 1999a), and River Usk (8,800 t km^{-2} yr^{-1}) (Walling and He 1999a) exceeding this. The accumulation rates at Upton and Stanwick appear close to the mean value found in other UK rivers.

Between 1958 and 1963 accumulation rates in the Nene ranged from 13,700 t k m^{-2} yr^{-1} to 20,700 t km^{-2} yr^{-1} which are substantially higher than the 920 to 7,175 t km^{-2} yr^{-1} estimated to occur post 1963. The observed reductions in accumulation rates of between 63 and 93%, suggest increased dis-connectivity between the river and its floodplain. A comparable reduction in floodplain accumulation rate was observed in 24 of the 39 UK catchments cited by Gruszowski, (2003). Although in catchments such as the Ouse and Tweed in the UK accumulation rates have remained constant over the previous 100 - 150 years (Walling *et al*., 2003). The modification to the river channel as part of flood defences and the presence of locks are a potential explanation for these observed reductions in accumulation rate. For example, the Earls Barton floodplain core is closest to flood defences protecting the downstream area of Northampton and, as a result, has the largest reduction in accumulation rate. In contrast the Kingsthorpe core is situated upstream of flood defences in an area in which flood waters can be temporarily detained, resulting in its higher sediment accumulation rates.

8.4. Channel bed sediment storage

Using the channel bed sediment re-suspension method described in Section 4.4.4. , a trend of decreasing sediment storage on channel beds was observed over the study period (Figure 8-6). The highest quantities of stored sediment were found in the dry months of June 2011, September 2011 and January 2012. After the floods in April 2012 –February 2013 a reduction in the quantities of stored sediment was found, the reduction was at its greatest between the January 2012 and June 2012 sampling periods, representing the first high flow after the period of drought during 2011 and early 2012. A further reduction in stored sediment was observed after the high flows occurring between November and January 2013, after which only a negligible quantity of fine sediment remained stored within the gravel substrate.

A much greater quantity of stored sediment is present on the beds of tributaries 1, 2, 4 and 12 than on the beds of the other sampling sites. Tributary 12 is located downstream of Sywell reservoir, It is possible that buffering of high flows by the reservoir is resulting in channel aggradation, which could be leading to the excessive sedimentation observed (Wohl and Rathburn, 2003). Tributaries 1, 2, and 4 are headwater tributaries located in the westernmost part of the Nene basin, these catchments are characterised by high altitude and steeply sloped terrain in comparison to the other sampling sites.

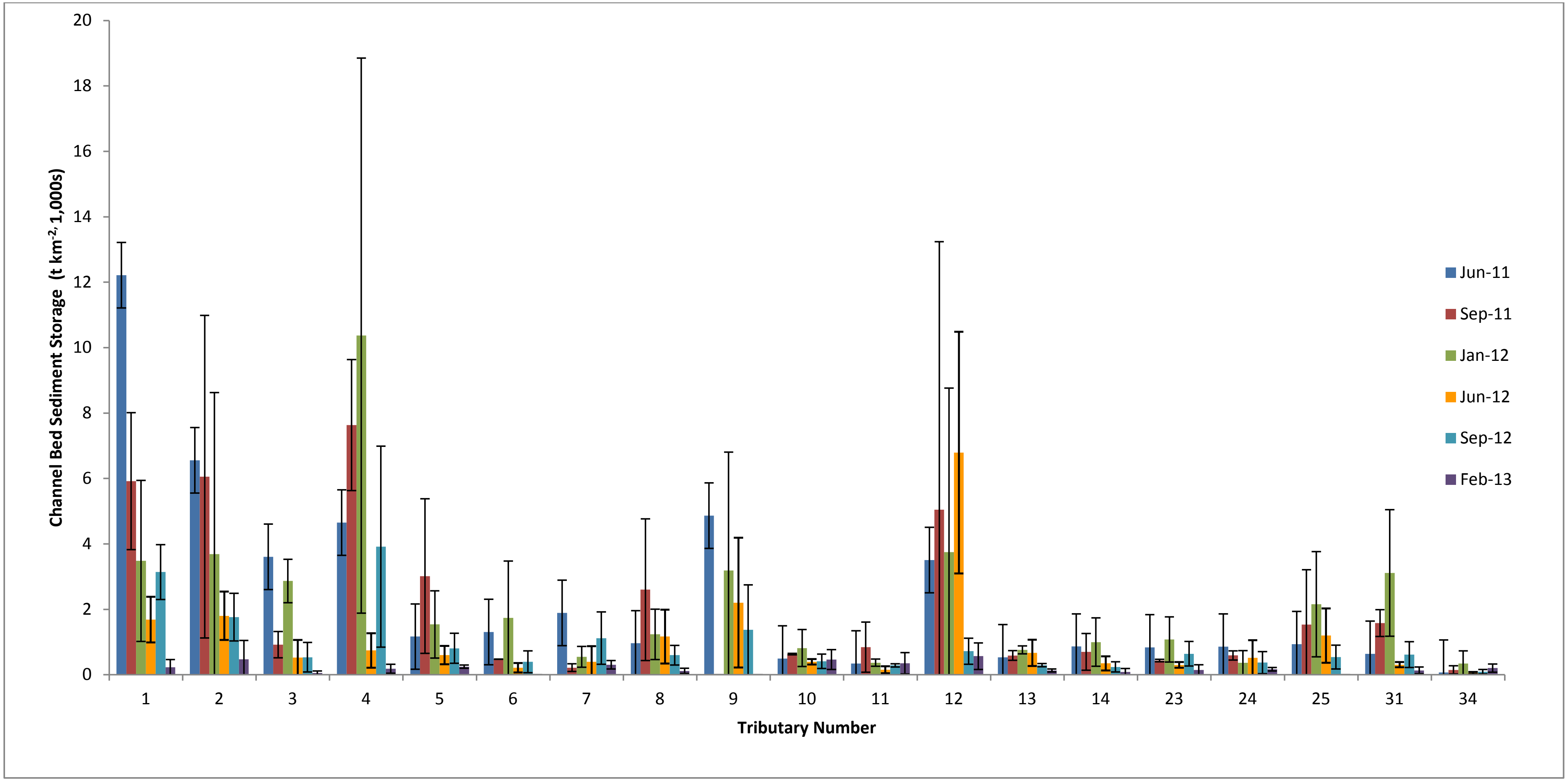


Figure 8-6: Quantities of sediment stored on the channel beds at the sediment sampling locations (tonnes per kilometer square of channel bed)(see Figure 4-9 for sampling locations).

The quantities of sediment stored on the beds of other investigated UK rivers were shown to vary from below 230 t km^{-2} to over 5,000 t km^{-2}, in a review of published studies by Gruszowski (2003). The quantities of sediment found in the Nene vary over the study period; in June 2011 the average quantity of sediment stored was 2440 t km^{-2} and the highest quantity found at any sampling location was 12,200 t km^{-2}. The average is therefore higher than was found in most UK rivers with the exception of the River Ouse / Ure (2910 t km^{-2}) (Walling *et al.,* 1998) and the river Piddle (>5,000 t km^{-2}) (Walling and Amos 1999). In February 2013 the average quantity of stored sediment in the Nene was reduced to 150 t km^{-2}, which is lower than any of the average recorded values for UK rivers, the lowest of which was 230 t km^{-2} found in the River Exe (Lambert and Walling 1986; 1988); although values in the region of 100 t km^{-2} were found after flood events in the river Piddle (Walling and Amos, 1999). From these results and the high amount of spatial variability of channel bed sediment storage it can be determined that channel bed storage in the Nene is highly variable, both spatially and temporally and seems to be at a minimum after lengthy very wet periods and highest after extended dry periods, such as was found by Walling and Amos, (1999) in the river Piddle.

The percentage of the annual sediment yield of a river stored on channel beds at any one time has been used to represent the importance of channel bed sediment storage in a sediment budget (Collins and Walling, 2007). An estimate of the percentage of the total annual suspended sediment yields stored on the channel beds were calculated in the Dodford and Northampton tributaries. Firstly, the mean quantity of sediment stored at every sampling location, during each sampling period, was calculated using the result shown in Figure 8-6. Then the total area of the channel bed in each of the two tributary catchments was calculated using Ordnance Survey (2009) Mastermap surface water vector data. Areas were calculated at 0.301 km^{-2} for the Northampton tributary, and 0.134 km^{-2} for the Dodford tributary. The average quantities of stored sediment were multiplied by the areas of channel bed to produce the total quantity sediment stored, which was calculated as a proportion of the total annual sediment yields for each site(calculated using the stage and turbidly monitoring). The site at Northampton has the highest proportions at 28.2%, 23.7% and 24.7% in June 2011, September 2011 and January 2012 respectively (Figure 8-7). The Dodford site has 12.5%, 10.5% and 10.9% stored over the same time period.

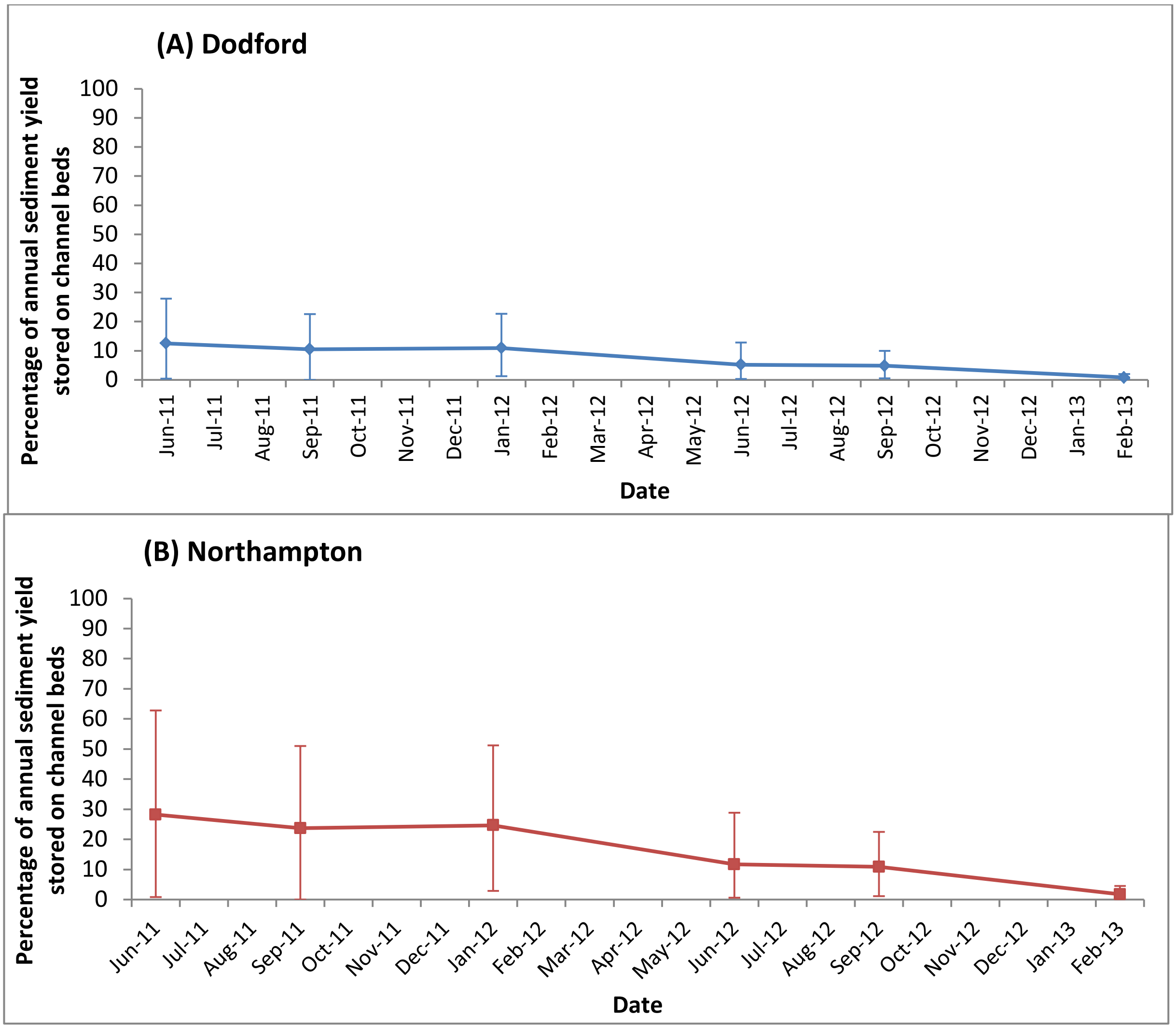


Figure 8-7: The estimated percentage of the annual suspended sediment yield stored on the channel beds of the Dodford and Northampton tributaries (Error bars were calculated using the mean + 1 standard deviation and the mean – 1 standard deviation).

Typically in UK catchments between 2% and 10% of a river's total annual suspended sediment yield resides on the channel bed at any time (López-Tarazón *et al.*, 2012). However this value can be larger, such as between 8% and 57% in the lowland groundwater fed Rivers Frome and Piddle (Collins and Walling, 2007). The proportions found in the Nene were a maximum of 12.5% (Dodford; Figure 8-7A) and 28.2% (Northampton; Figure 8-7B) in June 2011. This indicates that after the prolonged period of drought during 2011 and early 2012 the percentage of the sediment yield residing on channel beds is high in relation to other UK catchments, and is more comparable to the Frome and Piddle, which suffer from excess channel bed sedimentation (Collins and Walling, 2007). After the high flows in April 2012 the proportion of the sediment yield stored is reduced by approximately 50%, and after the floods in November and December 2012 only a negligible amount (<1%) of the total sediment yield remains.

In the River Piddle the influence of groundwater at maintaining low flows during periods of drought was highlighted as a major cause of the excessive channel bed sedimentation (Waling and Amos, 1999). Although the Nene, with a primarily clay geology, cannot be considered a particularly permeable catchment. It is likely that the influence of groundwater is also an important factor causing the sedimentation observed during the low flow sampling periods of June and September 2011 as well as in January 2012, as little rain fell during the period (a mean of 14.8mm per month; measured at the Northampton, Moulton Park climatological station, Met Office rainfall station number 160109) to provide energy for the erosion of channel bank material, or delivery of eroded surface material to the river channel.

The flushing of sediment from channel bed storage during storm events in the Nene is comparable to what has been observed in other lowland catchments (Waling and Amos, 1999; Collins and Walling, 2007b). The first major storm of the study period in April 2012 reduced the quantities of stored sediment on the channel beds. This reduction did not continue during the moderately high flows that occurred between June 2011 and September 2011; instead, it took the very large floods of November and December 2012 to remove the remaining stored sediment. The pattern of sediment removal seen here may represent the flushing of easily mobilised sediment mantling the channel bed surface in the first high flow event in April 2012, after the period of drought, and the much larger floods in November 2012 being required to flush sediment stored more deeply within the pore spaces between gravel particles on the channel beds (Lisle and Hilton, 1992).

These results therefore indicate that rather than the accumulation and redistribution of sediment on channel beds occurring during the waning periods of a flood, as shown by Lisle and Hilton (1992), the mechanism of channel bed sediment accumulation in the Nene appears to occur during low flows, and its removal occurs during the periods of high flow, as shown by Waling and Amos (1999), Collins and Walling (2007b), Walling *et al.* (1999b) and Asselman (1999).

The channel bed sediment storage results discussed indicate the importance of frequent high flow events in the Nene to limit the mantling of channel beds with sediment, and the less frequent occurrence of very high magnitude events able to flush the more deeply stored sediment from the channel beds. It is clear that without regular high flows the Nene can be affected by excessive channel bed sedimentation just as groundwater fed chalk streams, which are characterised by an absence of episodic flows, have been shown to be affected by excessive channel bed sedimentation (Collins and Walling, 2007).

8.5. Sediment provenance

The sediment fingerprinting methodology which produced the results discussed in Chapters 6 and 7 were used to provide an estimate of the sediment provenance of the suspended sediment samples and Sywell reservoir core. As historical sediment fingerprinting was determined in Chapter 6 to have a large amount of uncertainty associated with its use, conclusions were only made for Sywell reservoir where a reasonable amount of agreement in the provenance predictions made by all of the tracer groups was found. For the suspended sediment fingerprinting, conclusions were derived assuming that the 24% potential error identified in Chapter 7 was present in the predictions of channel bank and surface agriculture. The smaller uncertainty of 8% to 11% found to be associated with the predicted contributions of urban street dusts allowed for more precise conclusions to be drawn regarding sediment inputs of this sediment source.

Having identified that a change in sediment yield has occurred in Sywell reservoir after approximately 1948, the fingerprinting was used to establish if this was accompanied by a change in sediment provenance, which would indicate the impacts of changing land utilisation in the catchment. The results in Figure 8-8showed that very little changes in sediment provenance have occurred throughout the down-core profile. Channel banks are predicted to be the dominant source of sediment, typically contributing between 55% and 85% of sediment inputs. Urban street dusts are a very minor sediment source with a maximum of 7% inputs, which would be expected as the catchment is primarily agricultural land with only 2 small villages located within or at the margins of the catchment. It can therefore be concluded that the change in sediment yield was likely to be the result of a proportional increase in sediment inputs from all of the sediment source groups, perhaps driven by post Second World War agricultural intensification as reported elsewhere in the UK (e.g. Foster and Walling, 1994; Foster *et al*. 2011).

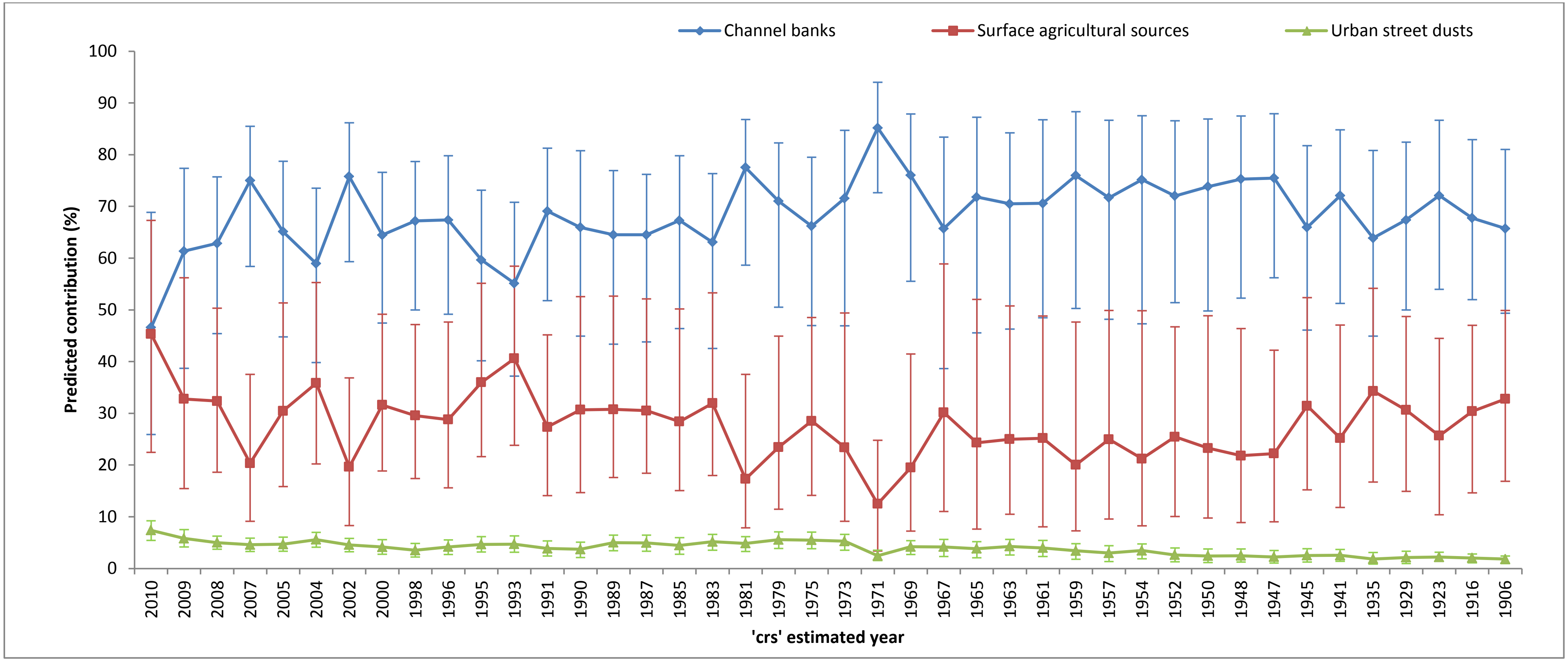
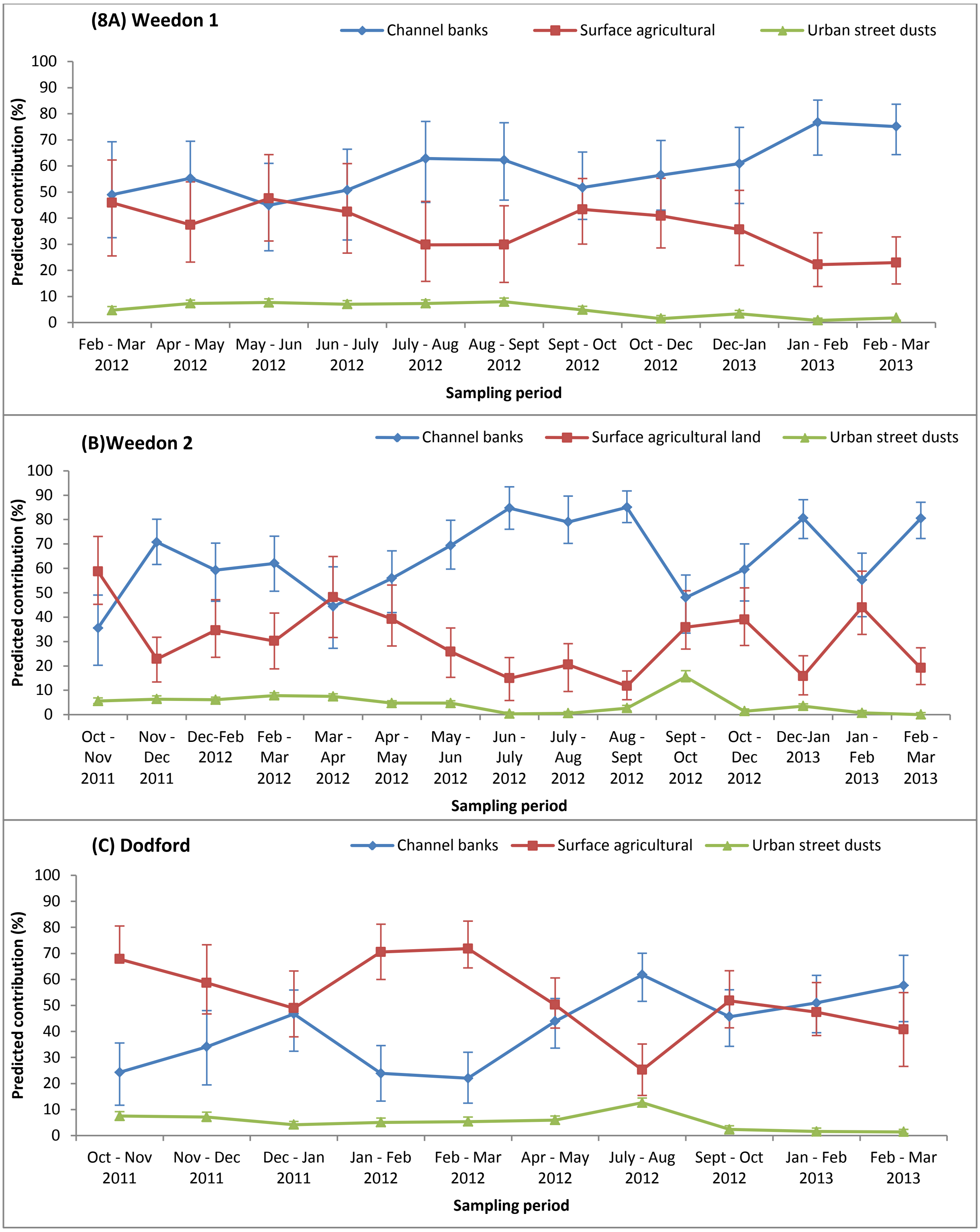
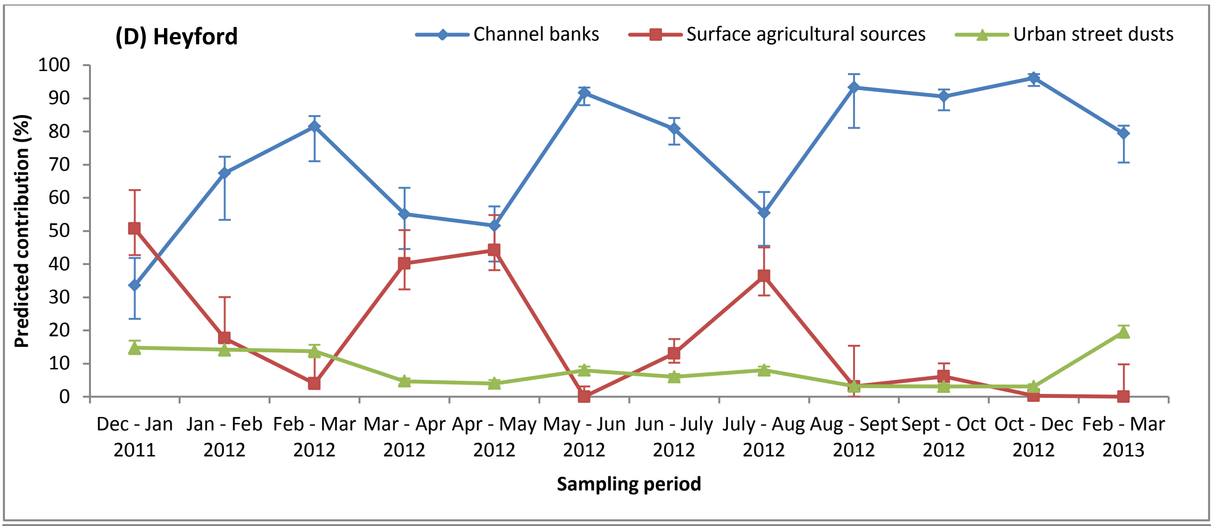
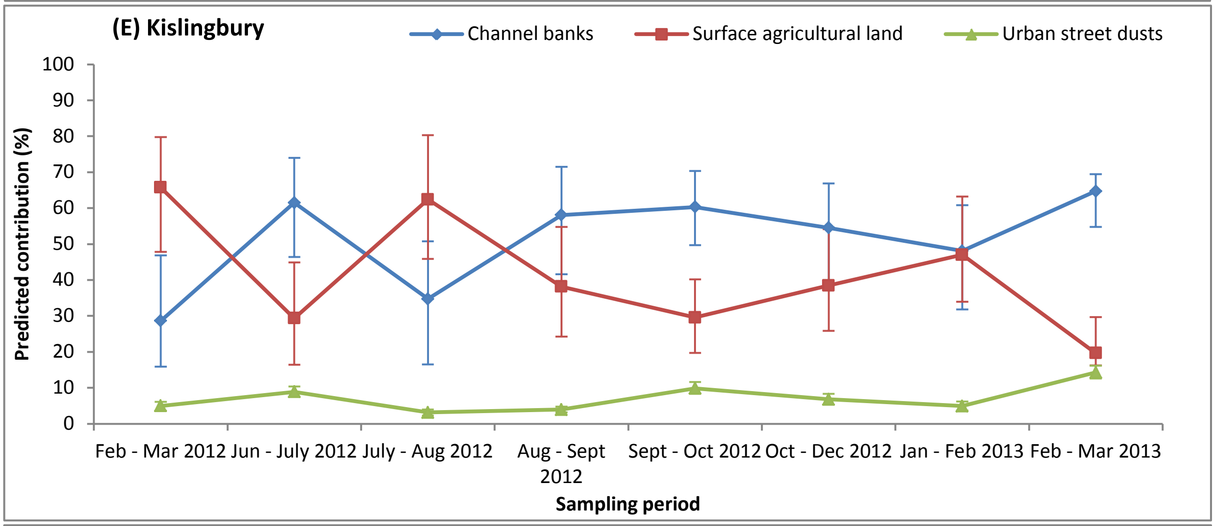


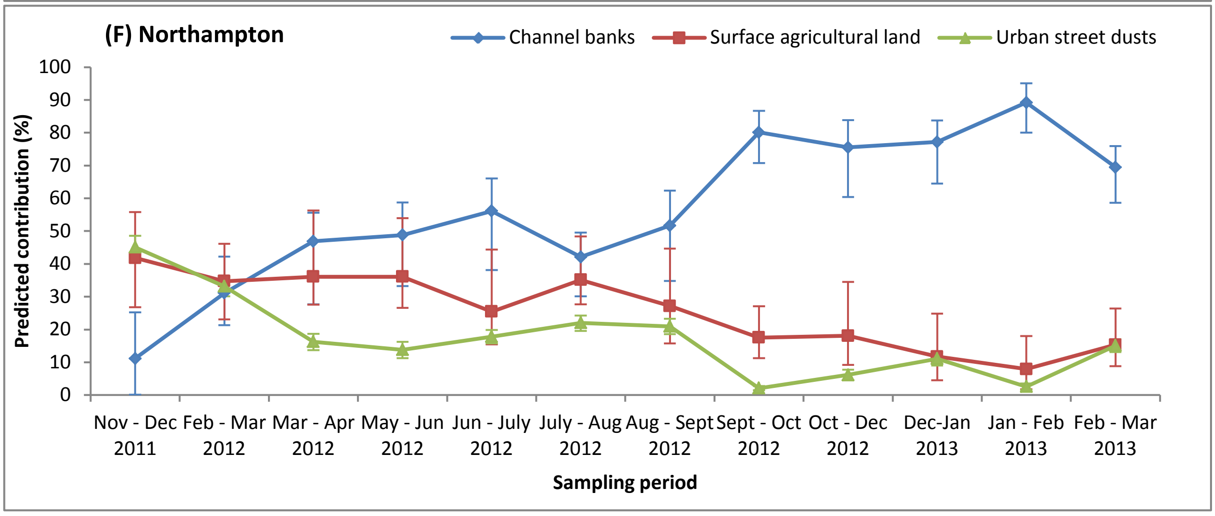
Figure 8-8: Down-core trends in the predicted contributions from channel banks, surface agriculture and urban street dusts in Sywell reservoir. Error bars are the average 25th and 75th Monte Carlo results for each tracer group used to fingerprint the sediment.

The fingerprinted suspended sediment samples also indicated that channel banks are the dominant sediment source in all sites apart from the highly urbanised catchment upstream of the Wellingborough sampling site (Figure 8-9G), and the rural catchment upstream of the Dodford sampling site, where surface sources dominate (Figure 8-9C). A trend of increasing contributions from channel banks was observed in all of the sampling sites apart from Kislingbury (Figure 8-9E) and Wellingborough (Figure 8-9G). Just as was found in Sywell reservoir, urban street dusts generally contribute less than 10% of the sediment sampled, apart from in the urbanised Wellingborough and Northampton catchments, where they contribute a maximum of 30% and 45% of the sediment respectively.


(8A) Weedon 1
Channel banks
Surface agricultural
Urban street dusts
Predicted contribution (%)
100
90
80
70
60
50
40
30
20
10
0
Feb - Mar 2012
Apr - May 2012
May - Jun 2012
Jun - July 2012
July - Aug 2012
Aug - Sept 2012
Sept - Oct 2012
Oct - Dec 2012
Dec-Jan 2013
Jan - Feb 2013
Feb - Mar 2013
Sampling period
(B)Weedon 2
Channel banks
Surface agricultural land
Urban street dusts
Predicted contribution (%)
100
90
80
70
60
50
40
30
20
10
0
Oct - Nov 2011
Nov - Dec 2011
Dec-Feb 2012
Feb - Mar 2012
Mar - Apr 2012
Apr - May 2012
May - Jun 2012
Jun - July 2012
July - Aug 2012
Aug - Sept 2012
Sept - Oct 2012
Oct - Dec 2012
Dec-Jan 2013
Jan - Feb 2013
Feb - Mar 2013
Sampling period
(C) Dodford
Channel banks
Surface agricultural
Urban street dusts
Predicted contribution (%)
100
90
80
70
60
50
40
30
20
10
0
Oct - Nov 2011
Nov - Dec 2011
Dec - Jan 2011
Jan - Feb 2012
Feb - Mar 2012
Apr - May 2012
July - Aug 2012
Sept - Oct 2012
Jan - Feb 2013
Feb - Mar 2013
Sampling period


(D) Heyford
Channel banks
Surface agricultural sources
Urban street dusts
Predicted contribution (%)
100
90
80
70
60
50
40
30
20
10
0
Dec - Jan 2011
Jan - Feb 2012
Feb - Mar 2012
Mar - Apr 2012
Apr - May 2012
May - Jun 2012
Jun - July 2012
July - Aug 2012
Aug - Sept 2012
Sept - Oct 2012
Oct - Dec 2012
Feb - Mar 2013
Sampling period


(E) Kislingbury
Channel banks
Surface agricultural land
Urban street dusts
Predicted contribution (%)
100
90
80
70
60
50
40
30
20
10
0
Feb - Mar 2012
Jun - July 2012
July - Aug 2012
Aug - Sept 2012
Sept - Oct 2012
Oct - Dec 2012
Jan - Feb 2013
Feb - Mar 2013
Sampling period


(F) Northampton
Channel banks
Surface agricultural land
Urban street dusts
Predicted contribution (%)
100
90
80
70
60
50
40
30
20
10
0
Nov - Dec 2011
Feb - Mar 2012
Mar - Apr 2012
May - Jun 2012
Jun - July 2012
July - Aug 2012
Aug - Sept 2012
Sept - Oct 2012
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Dec-Jan 2013
Jan - Feb 2013
Feb - Mar 2013
Sampling period

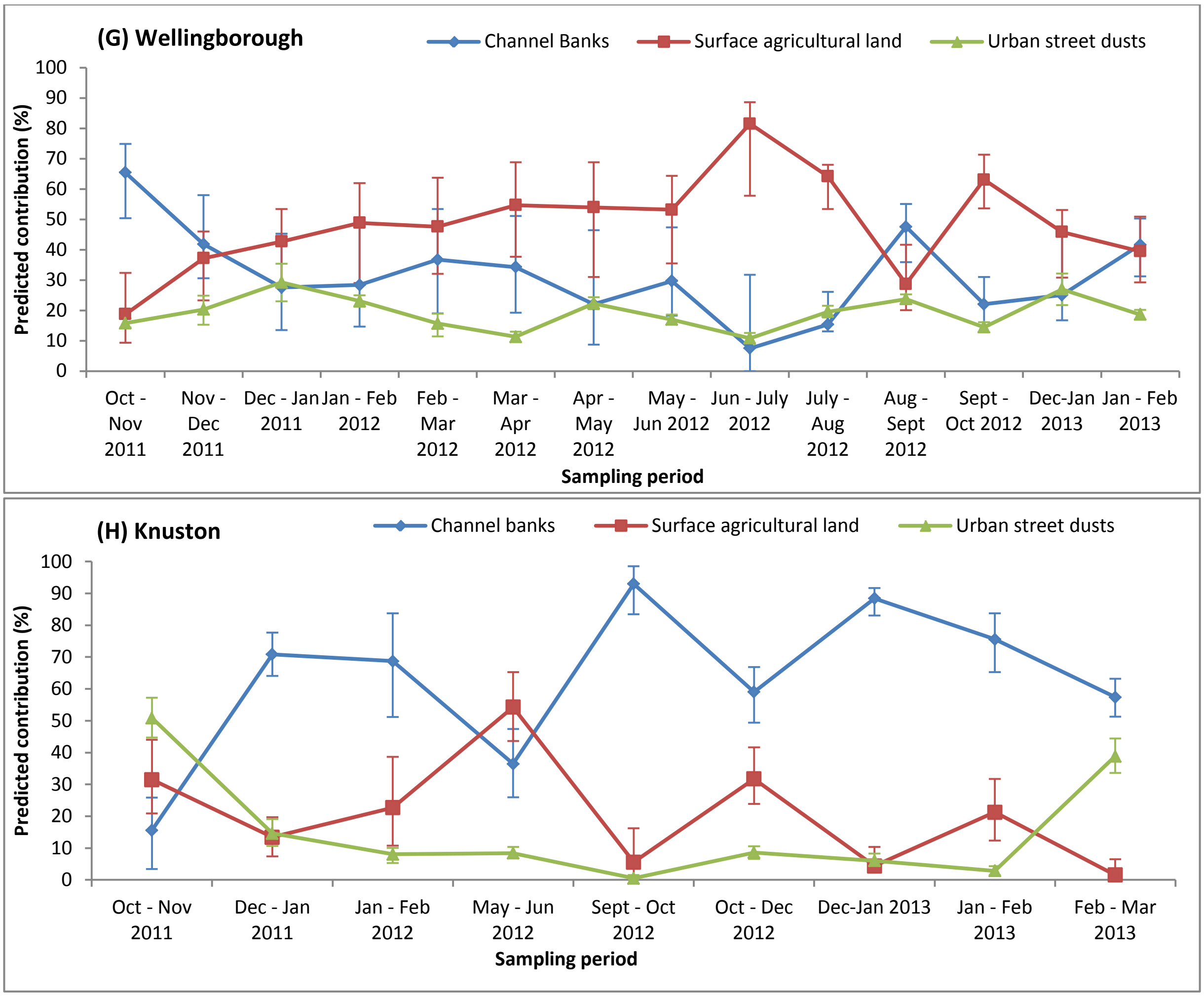

Figure 8-9: Predicted provenance of suspended sediment in eight major tributaries of the River Nene (Sampling locations are given in Figure 4-9)

A general range of sediment source contributions in published UK based sediment provenance studies is 85-95% from surface sources and 5-15% from channel banks (Walling *et al*., 2007). Channel banks are the dominant sediment source in only two catchments previously investigated in the UK, the river Aire (55% contribution) and Worm brook (55% contribution) (Walling and Collins, 2005). It is therefore clear that as the figure of 55% is exceeded in the majority of samples in the Nene, it is a highly unusual catchment in comparison to others reported in the UK. A high contribution of sediment from channel banks provides a potential explanation for the excessive channel bed sedimentation found in the Nene prior to the high flows beginning in April 2012. During the period of drought leading up to April 2012 a lack of rainfall and overland flow would be expected to severely limit the erosion of surface sediment sources and transport of sediment to the river, minimising channel bed sedimentation. Channel banks are in direct hydraulic contact with the river, so any eroded material would immediately enter channel bed storage, especially in the absence of high flows to transport the sediment downstream.

Rates of channel bank erosion in the published literature have been shown to increase after periods of sub-aerial preparation, such as freeze thaw in the winter months (Couper, 2003), waterlogging over sustained wet periods (Simon *et al.*, 2000) and desiccation during dry periods (Dietrich and Gallinatti, 1991). Most suspended sediment sampling sites show that the percentage contribution from channel banks in the Nene increases throughout the study period, indicating that desiccation during the period of drought was unlikely to have resulted in a large increase in the rates of channel bank erosion. This explains the result found that most sediment in the initial April 2012 flood of the study period originated from channel bed storage, rather than from the erosion of channel banks during the high flow event. The results in the Nene instead indicate an increase in the rates of channel bank erosion after a period of prolonged wetness, suggesting that instead of desiccation, prolonged waterlogging is an important means of sub-aerial preparation in the Nene (see Lawler, 1995). However, the accumulation of sediment on channel beds observed during periods of low flow (Figure 8-7) also highlights the importance of the erosion of channel banks during periods of low flow to overall water quality. Signal Crayfish have been shown to be in localised high populations in the Nene basin and have been shown to potentially accelerate rates of channel bank erosion (Harvey *et al*., 2011). Records obtained by the Environment Agency (Personal Communication, October 10, 2013) show that Signal Crayfish are found in high populations in tributaries 2 and 9 in Figure 8-6 which correspond to the Weedon 1 and Northampton suspended sediment sampling sites in Figure 8-9. Both of these sites are characterised by a high amount of channel bed sedimentation and a high contribution of sediment from channel banks, suggesting a potential role of crayfish at accelerating channel bank erosion. There are also unconfirmed reports of crayfish populations in the Weedon (T2) sampling site, which would provide an explanation for the high contributions of sediment from channel banks, and high quantities of channel bed sediment storage in this site. While signal crayfish were not directly investigated as part of this project, their potential role as bio-engineers could form the basis for future research.

Sub-surface land drainage has been also speculated to be a major source of sediment in the Nene basin (Tye *et al.,* 2013). During the collection of samples subsurface drainage was observed in localised areas of the Nene basin, especially within the Sywell reservoir catchment. Therefore a potential explanation exists for the increased sediment yields, which as a result of drainage could originate from both topsoil and subsurface sources, explaining the relatively consistent down-core sediment provenance (Chapman, 2001). Robinson and Armstrong (1988) showed that agricultural drainage was installed in the East Midlands region to alleviate surface water problems. The installation of drainage occurred primarily from policies enacted in 1940 to increase wartime food production, and continued until the peak rate of installation in the mid-1970s. From these dates it is possible that the increase in sediment accumulation in Sywell, estimated to occur at 1948 (Figure 8-2) is a result of the installation of field drainage. Field drainage is also a potential explanation for the high contribution of sediment originating from channel banks (sub-surface sources) in the present day suspended sediment samples (Figure 8-9).

The decreased importance of surface agricultural sources during the high flow events in the latter stages of the sampling period represents an unusual trend as the greater connectivity provided by increased surface runoff during storms would be expected to increase the effective catchment area and the delivery of surface derived sediment to the river (Fryirs, 2013). It is therefore evident that the increase in the rate of channel bank erosion is of greater magnitude than the increased rate of sediment erosion and delivery from surface sources during flood events.

The observed low sediment yields found, and low contributions of sediment from surface agricultural sources compared to other UK catchments, suggests both a combination of low erosion rates and limited connectivity with the river channel. When conducting the sampling it was observed that wide grass buffer strips and well-vegetated riparian zones often separated cultivated land from river channels throughout almost the entire Nene basin. Riparian fencing was also present between most areas of pasture and the river channel, limiting the potential for poaching. These land management practices provide an explanation for the limited connectivity of surface sediment sources with the river, and therefore the small amount of sediment reaching the river.

Slaymaker (2003) showed that rates of soil erosion in UK catchments range from 10 – 300 t km^{-2} yr^{-1}. According to Evans (1990), the soil associations present in the Nene catchment are classified as ranging from low to very low erosion risk compared to other UK catchments, so it is likely to be at the lower end of this range. Evans (1988) and Evans (1993) indicated that rates of soil erosion in nearby Cambridgeshire, which has clayey and medium loam soil, such as in the Nene, are in the region of 36 t km^{-2} yr^{-1}. The estimate was produced using aerial photography performed on an annual basis, combined with the field validation of areas which appeared to be eroding or contained erosional/depositional features too small to identify from the aerial photographs. Therefore evidence of the low erosion rates in the East Midland region of the UK has been shown in the published literature.

A rough estimation of the proportion of the ~36 t km^{-2} yr^{-1} of soil erosion indicated by Evans (1988) and Evans (1993) which is being sequestered during its transport to the river channel was produced for the Nene. The proportion of the highest recorded annual sediment yield (19 t km^{2} yr^{-1}) (Figure 8-4) which was estimated to originate from surface agriculture in the sediment fingerprinting (~30%) (Figure 7-6) was calculated. This produced a value of 5.7 t km^{2} yr^{-1} of sediment entering the river from surface agricultural sources. This represents only 14% of the ~36 t km^{-2} yr^{-1} of soil erosion expected to be occurring; indicating that in excess of 86% of eroded soil is being sequestered before reaching the river channel. In comparison Walling *et al*. (2006) report 51% and 31% is sequestered in the Pang and Lambourn catchments, Berkshire UK; and Walling *et al*. (2002) report between 14.2% and 25.7% in the Rosemaund catchment in Herefordshire and the Smisby catchment in Derbyshire respectively. Therefore the Nene represents a river with very limited connectivity between surface sediment sources and the river. However, Parsons (2012) highlights the problems of using unmeasured variables for the calculation of the sediment delivery ratio. Therefore the figure of 86% can only be considered a qualitative indicator that a high proportion of sediment is sequestered within the catchment, and not part of the overall constructed sediment budget.

Street dusts were predicted to contribute up to 10% of the sediment in the rural Weedon 1, Weedon 2, Dodford, Heyford and Knuston sediment traps and bed sediment sampling sites. Although this categorises them as a minor sediment source, it does indicate the possible role of roads as a means of connectivity between surface agriculture and the river channel as was indicated by Gruszowski (2003) and Boardman, (2013). However, the low contributions of sediment originating from the surface agriculture source group suggest that connectivity via roads is relatively unimportant in the Nene, when compared to the catchments highlighted by Boardman, (2013). For example Gascuel-Odoux *et al.* (2011) showed that 14% of the agricultural land connected to the Moulinet stream in north-western France is also connected via roads. Due to the observed limited surface – river channel connectivity in the Nene basin, roads are potentially one of the few routes by which eroded material can reach the river. There is an indication that road dusts contribute more sediment in the dry initial months of the sampling period than during the periods of high flow in its latter stages. With the absence of high intensity rainfall for erosion and sediment transport at this time, material on roads is one of the few sources of sediment that could be transported. However, it is also possible that a 'first flush' effect may be depleting finite stores of road dusts during sustained high flow periods (Deletic, 1998).

Carter *et al.* (2003) found that 19–22% of sediment inputs were from street dusts in the highly urbanised river Aire. In the urbanised Northampton and Wellingborough sampling sites urban street dusts are predicted to contribute between 2-40% of the suspended sediment at Northampton and 10-30% at Wellingborough, which are greater proportional inputs compared to the Aire. Annual sediment yields for urban areas are typically cited in the region of 0.4 to 5 t km^{-2} yr^{-1} (Taylor and Owens, 2009). When considering a sediment yield 19 t km^{-2} yr^{-1} calculated for the Northampton tributary, the average 17% contribution from urban street dusts represents a sediment yield of ~3 t km^{-2} yr^{-1} from the urban areas. However, as urban areas only cover approximately 12 % of the catchment upstream and including Northampton, these results suggest a higher sediment yield for the urban areas in the Nene than the average for UK catchments indicated by Taylor and Owens (2009).

8.5.1. A sediment budget for the Nene river basin

This paper has described the sediment dynamics in the Nene river basin and as a result a partial sediment budget can be produced, and is shown in Figure 8-10.

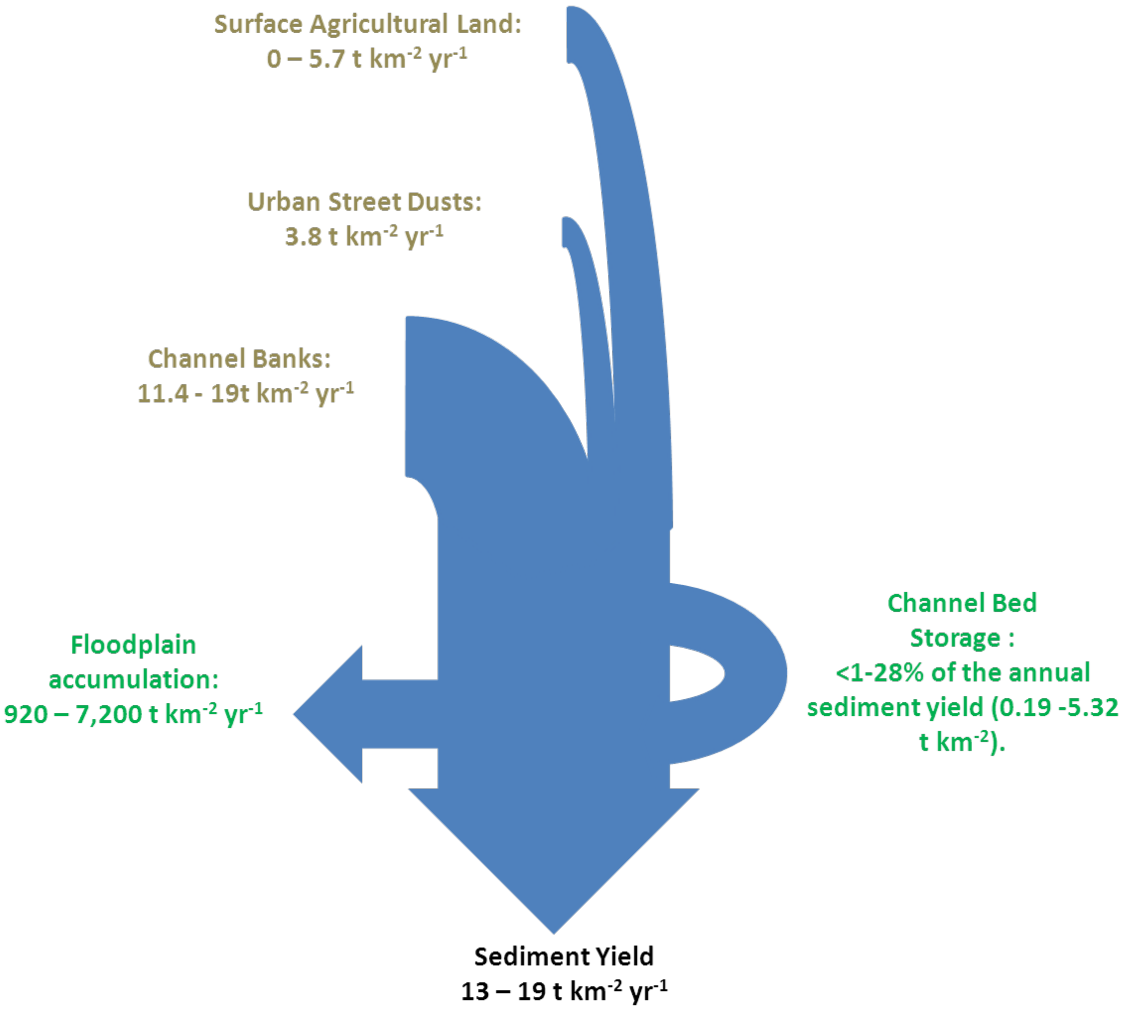

Figure 8-10: A partial sediment budget for the Nene river basin.

Parsons (2012) laid out the requirement that any sediment budget provides an indication of a timescale for which it is valid. Table 8-2 shows the timescales for which each part of the sediment budget is valid. The estimate of sediment yield of ~13 t km^{-2} yr^{-1} has been indicated by the Palaeolimnological reconstruction in Sywell reservoir to be valid since the 1940s, prior to which a sediment yield of 7 t km^{-2} yr^{-1} was likely to be typical of the Nene basin. Sediment sources also appear to have been fairly consistent throughout the entire 105 year down-core profile of Sywell reservoir, with the exception of urban street dusts, which became a more important sediment source slightly prior to ^{137}Cs peak identified for 1963. The estimates of floodplain deposition are only valid from 1963 onwards; between 1958 and 1963 rates of accumulation were substantially higher at between 13,796 t km^{-2} yr^{-1} and 20,726 t km^{-2} yr^{-1}. The contemporary monitoring of sediment yield, channel bed sediment storage and suspended sediment provenance can only be considered as valid for up to the previous 23 months. However, it is expected that the information derived will be representative of the sediment dynamics in the Nene basin until the time a significant change in catchment morphology, climate or land utilisation occurs.

Table 8-2: The timescales for which each component of the sediment budget are valid.

Method	Purpose	Time period for which the estimate is valid
Historical reconstruction		
Reservoir sediment coring	Sediment yield reconstruction and historical sediment fingerprinting	105 years
Floodplain coring	Floodplain sediment accumulation rate reconstruction	Post 1963
Contemporary monitoring		
Stage and turbidity monitoring	Quantification of sediment yield	23 months
Time integrated suspended sediment traps	Sediment fingerprinting of suspended sediment	18 months
Channel bed re-suspension	Quantification of channel bed sediment storage, fingerprinting of channel bed sediment	20 months

From a management standpoint the mitigation of fine sediment pressures in the Nene would be best achieved by the stabilisation of channel banks to reduce the overall sediment yield, re-connecting the river with its floodplain to increase the proportion of sediment yield accumulated on floodplains back to the 1958 – 1963 rate, and the removal of any obstacles to episodic high flows, able to flush fine sediment from channel beds. Urban street dusts also have been shown to contribute sediment so represent a potential target for mitigation measures.

9. Conclusions and evaluation

9.1. Chapter outline

This chapter summarises the findings of this thesis within the context of fluvial geomorphology. The key findings of this thesis are first summarised in the context of previously published research. The research design of the thesis is then critically examined, and issues of experimental design, scaling, and the importance of the validation results are explored. Finally the remaining gaps in research are highlighted and suggestions for future research to fill these gaps are explored.

9.2. Key findings

This section summarises the key findings of the thesis which relate to the two Aims laid out in Section 1.3. The key findings are first outlined and explained before the contribution of each finding to geomorphological research is explained.

9.2.1. Aim 1: Fingerprinting the sources of fine sediment

Aim 1 of this thesis required a fine sediment fingerprinting investigation to be conducted in the Nene basin, UK. The results relating to this aim were presented in two sections; a historical sediment fingerprinting study, and a study fingerprinting suspended and recently deposited sediment. Three research objectives were met for both of these sections.

Key finding

Large differences can be present between the sediment provenance predictions made by different tracer groups when fingerprinting suspended and recently deposited sediment.

Explanation

When fingerprinting river sediment, the predicted contributions of sediment from channel banks made by the nine different combinations of tracer groups were an average of 24.1%

different. The average difference between tracer group predictions was smaller when fingerprinting contributions from urban street dusts at ~8-11%.

Contribution to geomorphological research

If the fingerprinting results found for the Nene are comparable to other basins worldwide, the average ~24% difference between predictions of different tracer groups is a potentially large source of uncertainty associated with the findings of other fingerprinting studies. A review of sediment fingerprinting results in the UK by Walling et al. (2007) showed that the median predicted contribution of sediment from surface agriculture is between is 85-95%. Therefore a ~24% uncertainty due to tracer selection is unlikely to change the dominant sediment source identified in most fingerprinting studies; although, it does have the implication that sediment fingerprinting can only be used as a semi-quantitative tool. However, this study has indicated that uncertainties associated with individual tracer groups in specific sediment samples can be as high as 100%, which would produce a more uncertain result than a simple visual survey of a catchment.

The aim to use sediment fingerprinting as a management tool has been a common part of many sediment fingerprinting studies. For example, a study that uses sediment fingerprinting to determine the impact of fine sediment mitigation measures was conducted by Collins et al. (2010), who investigated sediment provenance before and after riparian fencing was installed in catchments in the south west UK . Differences in sediment contributions from channel banks before and after the installation of fences were statistically significant for only the rivers Fal and Plym, out of 12 investigated catchments. In the River Fal the difference between contributions from channel banks before and after fence installation was less than 10%; in the Plym it was greater than 50%. This thesis has indicated that if Collins et al. had conducted their study in the Nene, then to be reasonably certain that a reduction in contributions from a sediment source would be identified, regardless of the tracer group selected, a greater than the 24% difference between the predicted contribution from channel banks before and after remediation would need to be identified. Therefore, future methodologies investigating changes in sediment provenance must be aware of the potential uncertainty associated with tracer use which may mask the genuine sediment provenance.

Key finding

Changes to sediment organic matter content, particle size distribution and chemical alterations to historically deposited sediment can totally mask the signatures of sediment provenance present.

Explanation

When fingerprinting the sediment cores it was found that the differences between the predictions made by the different tracer groups were smallest in Sywell reservoir. The predicted contribution of sediment from channel banks made by the different tracer groups in this core ranged from 45% to 95%, and the down-core trend in changing sediment provenance was consistent between most of the tracer groups. In the other cores the differences between tracer group provenance predictions were very large. Differences in predictions were as high as 95% in the Kingsthorpe floodplain core, 64% in the Stanwick floodplain core, 100% in the Stanwick lake core and 89% in the Upton floodplain core. It was also found that the down-core trends in predicted sediment provenance were different for almost all tracer groups in these cores.

It was found that the organic content of the sediment was significantly correlated with an increase in the differences between tracer group predictions in the Sywell reservoir, as well as the Kingsthorpe, Upton and Stanwick floodplain cores. The particle size of the sediment was indicated to be significantly correlated with the differences between most tracer group predictions in the Upton, Earls Barton and Stanwick floodplain cores. An additional correlation analysis was performed using the differences between tracer group predictions and the Xarm / Sirm and Sirm / Xlf ratios in the sediment cores; to gain an indication of the effects of the in-growth of magnetic minerals, the selective deposition of specific grain sizes and the chemical dissolution of minerals. The in-growth of bacterial magnetite was indicated to be affecting magnetic signatures in Sywell reservoir. The dissolution of magnetic minerals was suggested to be a potential causal factor in the differences between tracer group predictions in the Upton, Earls Barton and Kingsthorpe floodplain cores. Due to this, it was also suggested that the dissolution of geochemical and lithogenic radionuclide tracers associated with the iron oxide and easily mobilised fractions of sediment would also be likely to have occurred. In the Earls Barton and Stanwick floodplain cores the effects of the selective deposition of only fine particle size fractions on the mineral magnetic signatures was confirmed by a reduction in the proportion of the magnetic signatures, accounting for large grain sizes being correlated with a difference in tracer group predictions.

Contribution to geomorphological research

The ability to identify trends of changing sediment provenance is a common objective of published fingerprinting studies conducted using historically deposited sediment. A study which used sediment fingerprinting in a historical context was Owens et al. (1999), who investigated the floodplains of the River Ouse catchment, UK. The study used a combination of mineral magnetic signatures and geochemistry to fingerprint contributions from surface and sub-surface sediment sources. As a result of tracer non-conservatism observed in the Nene, the results presented by Owens *et al.* (1999) or other similar historical studies could potentially have been found at almost any point on the 0-100% contribution scale, depending on the tracer group the author had selected, and the preservation of tracer signatures at the point of sampling. Overall the results of this thesis suggest that historical tracer use should be treated with a large amount of caution, although as Sywell reservoir shows, there is potential for historical sediment fingerprinting to become a useful tool.

Similar uncertainties to that found when using sediment fingerprinting are also likely to be present in historical sediment provenance studies which use tracers outside of a fingerprinting framework. For example, Foster *et al*. (2012) used mineral magnetic signatures as indicators of changing historical sources of sediment in the Karoo Badlands, South Africa. This is a similar approach to how tracers are used in many publications such as Oldfield *et al*. (2003). Given the significant correlations found between indicators of the alteration of mineral magnetic signatures and differences in tracer group predictions in the Nene, it is possible that changes in mineral magnetic signatures could be representative of changing chemical conditions at the point of sampling, or variability in the processes associated with erosion, sediment transport or sediment delivery, rather than a genuine change in sediment provenance. Therefore, the reliability of inferred sediment provenance data using tracers, as with sediment fingerprinting, requires the use of different tracer types to confirm that temporal trends are not due to tracer non-conservatism.

Key finding

Within source variability in tracer concentrations can be the largest source of uncertainty present in a sediment fingerprinting investigation.

Explanation

The reduced average uncertainty associated with the fingerprinting of urban street dusts (8%- 11%) suggested that sediment sources with significant contrasts between tracer groups are more accurately fingerprinted by almost all tracer groups. It was determined that the potential uncertainty present in the fingerprinting due to tracer variability could be explained using a ratio of the contrast between source group median tracer concentrations and the average within-source variability in tracer concentrations. Because the average number of tracers used in the composite fingerprints in this thesis was ~5, the ratio was used to calculate the approximate uncertainty present in the un-mixing models, assuming this number of tracers were used. When this ratio was below 1 the possible range of uncertainty steeply increased with a decreasing ratio. When the ratio was 1, the potential uncertainty in the un-mixing model was 27%, this decreased to 15% at a ratio of 2 and continued to decrease to 5% at a ratio of 8. When more tracers are used in the composite fingerprint, the potential uncertainty in the un-mixing models was reduced. However, the reduction in uncertainty approximately halves with every extra 2 tracers added to the fingerprint.

Contribution to geomorphological research

The implication of this finding is that published results, such as by Collins *et al.* (2010) and Carter *et al.* (2003), who fingerprinted contributions from distinctive road verge and urban street dust sources, are likely to be a reliable representation of sediment provenance. It is also suggested from this result,that in catchments with larger contrasts in tracer concentrations between ‘natural’ source groups, such as channel banks and surface sources, the potential uncertainty associated with tracer selection would be lower than was found in the Nene. Collins and Walling, (2002) identify the requirement that the tracers used in fingerprinting studies be selected based upon their ability to successfully differentiate between sediment source groups. Their requirement is highly supported by this key finding of the thesis.

At present, few published sediment fingerprinting investigations have quantified the potential uncertainties associated with within-source variability in tracer concentrations outside of the research conducted by Small *et al.* (2010). However, the potential for this uncertainty to be present has been recognised. For example, Haddadchi *et al*. (2013) showed that different un-mixing models could produce very different sediment provenance predictions with the same input data. The categorisation and use of the sediment source tracer concentrations was a key difference between different un-mixing model approaches used and one of the potential reasons for the differences in model predictions. Collins *et al*. (2010a) applied weightings to prioritise for tracers with the greatest contrasts in concentrations between source groups and lowest within-source variability. This thesis indicated the importance of these factors at reducing model uncertainty. However, it should be emphasised that these weightings were used in this thesis, and large differences were still found between tracer group predictions. Therefore further research is needed into the development of novel tracers to reduce the uncertainties associated with tracer variability.

This finding especially highlights the under recognised work of Small *et al.* (2002). This paper highlights that many fingerprinting papers consist of limited field campaigns and an under representation of variability in source groups. The paper also highlights a minimum number of sediment source samples is required to categorise each source group based upon the local variability in tracer properties. The findings of this thesis highly support this finding and highlight the consideration of source group variability as an important requirement for future fingerprinting research.

Key finding

The commonly cited reasons for uncertainty in sediment fingerprinting investigations of changes to the sediment's organic matter content and particle size distribution was not the most important cause of uncertainty when fingerprinting suspended and recently deposited sediment in the Nene basin.

Explanation

There was little indication that changes to the organic content of river sediment was a cause of the differences between tracer group predictions, although some small effects may have been present when fingerprinting samples from the Northampton and Heyford suspended sediment sampling sites. No evidence of effects of changing SSA on the differences between tracer group predictions was found for the river sediment fingerprinting, which was explained by the comparable particle size of the sediment and source samples.

Contribution to geomorphological research

Recent reviews of sediment fingerprinting literature by Walling (2013), Koiter *et al*. (2013) and D'Haen *et al*. (2012) highlight a need to understand the effects of changes to the organic matter content and particle size of sediment on tracers and sediment fingerprinting results. These reviews identify that much sediment fingerprinting research is aimed at understanding organic matter and particle size effects, and accounting for them in un-mixing models. The findings of this thesis have indicated that variations in sediment organic matter content and particle size distribution are not the probable causal factors of uncertainty when fingerprinting river sediment in the Nene. As a result the findings of this thesis support a careful examination of the assumption of particle size and organic effects on a catchment specific basis. Further implications of this finding are discussed as part of the following key finding.

Key finding

Simple organic enrichment and particle size corrections did not improve the consistency between different tracer group fingerprinting predictions in the Nene basin.

Explanation

When fingerprinting river sediment 15% fewer composite fingerprints able successfully categorise >80% of source samples were produced after an organic content data correction was used; and 20% fewer after a particle size correction was used. When the un-mixing models were run, no significant reduction in the average differences between tracer group predictions was found. The mean overall difference between every tracer group prediction produced using uncorrected tracer signatures was 24.1% (standard deviation 2.9%), using organic matter corrected tracer concentrations was 24.3% (standard deviation 2.1%), and using particle size corrected tracer concentrations was 30.1% (standard deviation 3.9).

Therefore the organic correction appeared to have little effect and the particle size correction appeared to increase the differences between tracer group predictions.

Particle size and organic matter data corrections were applied to tracer signatures in the sediment cores when the differences between tracer groups were indicated to be potentially caused by the differences in the organic matter content, or particle size distribution, of the sediment (Objective 2). It was found that the organic matter correction resulted in little effect on the predictions of mineral magnetic signatures in any of the sediment cores. The correction appeared to be potentially of some benefit in the Stanwick, Upton and Kingsthorpe floodplain cores when applied to fingerprints containing geochemical tracers. It was, however, difficult to determine if the correction was genuinely of benefit without an independent measurement of sediment provenance for verification.

Contribution to geomorphological research

The failure of simple data corrections to produce a clear benefit to the consistency between tracer group predictions in this thesis suggests that the routine use of data corrections may not be beneficial, even when differences exist between the organic content and particle size of source and sediment samples. Additionally, the particle size correction was shown to increase the average differences between tracer group predictions. The implications of this finding are wide reaching if the results found in the Nene are also applicable to fingerprinting performed in other catchments. For example, published works based on the methodology of Collins *et al.* (1997) and similar methodologies where organic enrichment and particle size corrections are used, could be subject to additional uncertainty introduced from the unnecessary use of corrections. The possibility for this was highlighted in a recent review by Koiter *et al*. (2013), as the use of such corrections is often included as a routine part of fingerprinting methodologies, and the unnecessary use of untested correction factors would result in inappropriate manipulation of soil and sediment property data and incorrect sediment provenance results. Smith and Blake (2014) recommend against the use of simple data corrections as it was shown in this study that corrections could result in large changes to source contribution estimates that cannot be justified. Given this key finding of the thesis it can be concluded that in the Nene basin large changes introduced to fingerprinting by corrections are also unlikely to be justifiable.

Key finding

Without an independent source of data with which to validate fingerprinting results, conclusions as to tracer behaviour and modelling accuracy can be considered greatly uncertain.

Explanation

The absence of an independent source of sediment provenance information with which to determine the most accurate tracer group predictions resulted in only qualitative conclusions being produced as to the causes of tracer non-conservatism and fingerprinting accuracy. It was also observed that without a source of independent sediment provenance information with which to verify the results of simple data corrections, it was difficult to determine their effects were positive, or detrimental to accuracy.

Contribution to geomorphological research

Almost no published sediment fingerprinting studies attempt to validate the results of sediment fingerprinting investigations. The reasons for this are the time consuming nature of alternative methods of quantifying sediment inputs to lakes and rivers. For the purpose of data validation in future research, the use of tracers can be combined with a separate proxy for changing sediment dynamics, to provide robustness to conclusions, such as the $^{210}Pb_{un}$ dating methods which were used alongside mineral magnetic signatures by Foster *et al*. (2012). However, the impacts of alterations to specific tracer groups, alterations caused by organic matter and particle size as well as tracer variability have been identified as difficult to validate from within a conventional sediment fingerprinting framework. The issues of sampling design and experimental approaches are discussed in detail in Section 9.3 and the potential for further research to overcome this limitation is explored in Section 9.4. These sections continue to discuss issues arising from this key finding.

9.4.2. Aim 2: Fine sediment dynamics in the Nene river basin

Key finding

The sediment yield of the Nene river basin is low in comparison to other UK lowland agricultural catchments.

Explanation

A sediment yield of 13 t km^{-2} yr^{-1} was calculated for the Whilton arm of the Nene at Dodford and 19 t km^{-2} yr^{-1} for the Brampton arm at Northampton, using the monitoring of stage and turbidity over a ~18 month time period. A sediment yield of 13 t km^{-2} yr^{-1} was calculated at Sywell reservoir. The sediment yield at Sywell was shown to have increased from 7 t km^{-2} yr^{-1} since a change in sediment accumulation rate occurred in approximately 1948. In comparison to other lowland agricultural UK catchments, where a sediment yield of between 28 t km^{-2} yr^{-1} and 51 t km^{-2} yr^{-1} is typical (Walling *et al.,* 2007), the sediment yield of the Nene was found to be low.

Contribution to geomorphological research

The change in catchment sediment dynamics observed at ~1948 is consistent with the findings of Rose *et al*. (2011) who in a study of over 200 European lakes, where most lakes and reservoirs of the Sywell type (lake type 3121[small deep lowland lakes]) had a significant increase in sediment accumulation after 1950. Therefore, the finding that sediment yield in a catchment typical of the East Midlands, UK is comparable to other UK catchments, can be presented.

It can also be concluded from the low sediment yield that the increase in sediment yields attributed to intensification of agricultural practices in most lowland UK catchments by Foster *et al*., (2011) occurred in the Nene, although the sediment yield remained low in comparison to other UK catchments. The observed low sediment yields found, and low contributions of sediment from surface agricultural sources, suggests both a combination of low erosion rates of agricultural land and limited connectivity with the river channel. When conducting the sampling, it was observed that wide grass buffer strips and well-vegetated riparian zones often separated cultivated land from river channels throughout almost the entire Nene basin. Riparian fencing was also present between most areas of pasture and the river channel, limiting the potential for poaching. These land management practices have the potential to indicate management practices which may potentially be of benefit in other UK catchments. These findings also provide a previously unknown insight into sediment dynamics in the East Midlands region of the UK.

Key finding

Channel banks are the dominant sediment source in the Nene river basin.

Explanation

Historical changes in Sediment provenance were determined by fingerprinting the Sywell reservoir core using the methods used to fulfil Objective 1 in Chapter 6. It was determined that channel banks were the dominant sediment source, contributing between 55% and 85% of sediment inputs. Surface agriculture was a minor source (20-30%) and inputs from street dusts were small (<7%). Very little change in sediment provenance was found throughout the down-core profile.

The provenance of suspended sediment in the Nene was determined at eight sampling locations. It was found that approximately 60-100% of sediment originated from channel banks, 0-30% of sediment originated from surface agriculture and 0-20% of sediment originated from urban street dusts. In comparison to other UK catchments, such a high contribution from channel banks is highly unusual. Contributions of sediment from channel banks typically range from 5 -15% of the annual sediment yield in UK catchments (Walling *et al*., 2007). Channel banks are the dominant sediment source in only two catchments previously investigated in the UK, the river Aire (55% contribution) and Worm brook (55% contribution) (Walling and Collins, 2005). It is therefore clear that, as the figure of 55% is exceeded in the majority of sediment samples, the Nene is a highly unusual catchment in comparison to others investigated in the UK

Contribution to geomorphological research

Channel banks were shown to be the dominant sediment source in the Nene, which contributed an atypically high proportion of sediment compared to other UK catchments (Walling *et al*., 2007). There is therefore the implication that a proper understanding of the processes of channel bank erosion in the Nene is essential for the understanding of sediment dynamics in comparable catchments in the East Midlands and worldwide. Parsons (2012) highlights that in geomorphological research far less attention is given to methods of measuring channel bank erosion than hillslope processes. Research by Couper and Maddock (2001) and Lawler *et al*. (1999) are two exceptions to this lack of attention and identify the sub-aerial preparation and fluvial erosion taking place in the investigated river catchments. The results of this thesis suggest that the relative importance of channel bank erosion to the overall sediment yield was shown to be greatest during periods of sustained high flows, indicating the water logging of channel banks accelerated erosion. The presence of sub-surface field drainage and the weakening of channel banks by Signal Crayfish were also speculated to be contributing factors to the high quantities of sub-surface sediment found in the Nene. This finding highlights the importance of the work reviewed by Harvey *et al*. (2011) which examines the role of biogenic factors on sediment dynamics. There is therefore considerable scope for the further investigation of channel bank processes, in catchments comparable to the Nene.

Another implication of this finding was demonstrated when Tye *et al*. (2013) attempted to use landscape evolution modelling in the Nene basin based upon the CAESAR model developed by Coulthard and Van De Wiel (2006). The sediment yield estimated was lower than the measured sediment yields produced in this thesis, and possibly results from an inability of the model to account for the high inputs of sediment from channel banks. The results of this thesis therefore highlight the importance of the consideration of channel banks as a potentially dominant sediment source in river catchments.

The final implication of this key finding is based upon sediment fingerprinting. Collins *et al*. (2010a) used the prior information that channel banks had not previously been shown to contribute more than 55% of sediment in UK catchments to constrain un-mixing model predictions. Had this constraint been used when fingerprinting sediment in the Nene, the results would not have shown the full contribution of sediment originating from channel banks; therefore, it is recommended that such constraints are used with caution.

Key finding

Sediment accumulates on the channel beds of the Nene basin during periods of drought and low flow before being flushed out during high flow events.

Explanation

It was found that between 150 t km^{-2} and 12,200 t km^{-2} of sediment was stored on the channel beds of the different sampling locations over the study period. This equated to a quantity of sediment of between 1-28% of the Nene's annual sediment yield. In comparison to other UK catchments the quantities of stored channel bed sediment in the Nene ranged from very high to very low. In June 2011 after a period of drought the average quantity of sediment stored was 2,440 t km^{-2}, which was higher than most UK Rivers. After high flows in April 2012 to January 2013 the average quantity of stored sediment in the Nene was reduced to 150 t km^{-2}, which was lower than any average recorded value for any of the cited UK rivers. Typically in UK catchments between 2% and 10% of a river's total annual suspended sediment yield resides on the channel bed at any time (López-Tarazón *et al.*, 2012), therefore the value of 28% is higher than would be expected. It was found that this sediment accumulated during periods of low flow causing excessive channel bed sedimentation, such as has been found in groundwater fed chalk streams (Walling and Amos, 1999). The results indicated the importance of frequent high flow events in the Nene, to limit the mantling of channel beds with sediment, and the less frequent occurrence of very high magnitude events able to flush the more deeply stored sediment from the channel beds.

Contribution to geomorphological research

Channel bed sedimentation has been identified as a major cause of the degradation of aquatic habitats, especially in groundwater fed lowland catchments. The absence of episodic flow regimes to flush out stored sediment has been identified as the cause of this sedimentation (Collins and Walling, 2007b). This key finding of the thesis identifies that in the lowland catchment of the Nene the presence of an episodic flow regime is essential for the flushing of temporarily stored sediment from channel beds. The accumulation and redistribution of sediment on channel beds has been shown to occur during the waning periods of a flood, where sediment is winnowed from riffles and deposited in pools mantling the underlying substrate (Lisle and Hilton, 1992). In opposition to this Walling *et al.* (1999b) and Assleman (1999) showed that fine channel bed deposits accumulated during low flows and subsequently discharged during the opening periods of high flows. This key finding has successfully identified that in the Nene River Basin fine sediment accumulated during a period of low flows, and a series of high flow events were required to flush out all of the stored sediment.

9.3. Study evaluation

9.3.1. Research design

A field experiment in geomorphology has previously been defined as a set of measurements conducted under controlled field conditions to formalise some general principal about the evolution of landforms (Slaymaker, 1982). Church (1984) laid out six criteria for a set of field based observations to be labelled as a scientific experiment. Whilst these criteria explicitly address issues of landscape evolution, which is not directly applicable to the fingerprinting investigation of this thesis, the work can be evaluated in the context of these requirements.

1. Specific hypotheses about the evolution of landscapes which are amenable to falsification must be formalised.
2. Definitions of explicit geomorphological properties and operational statements with respect to measurement are needed.
3. The measurements must be made in the general context of an explicit general conceptual model of landform evolution.
4. A formal schedule of measurements is required.
5. A formal scheme for analysis of measurements is necessary.
6. A data collection and management system is necessary.

The results presented in this thesis are based upon the observation of the uncertainties occurring in a structured fine sediment fingerprinting investigation and the fine sediment dynamics in the Nene river basin. Specific hypotheses were not specified and investigated, and as a result the conclusions of this thesis can be considered somewhat empirical. The fulfilment of the Aims was achieved by inductive reasoning; as a result the conclusions of the thesis provided strong evidence for the processes investigated rather than providing conclusive answers to specific hypotheses.

Aim 1: Fingerprinting the sources of fine sediment

Requirements 1, 2 and 3: formalisation of hypotheses, defining geomorphological properties and operational statements and the general context of a conceptual model.

The sediment fingerprinting investigation of this thesis (Aim 1) was conducted in the context of the current understanding (conceptual model) of the potential uncertainties associated with fine sediment fingerprinting. The approach used in this thesis is commonly used in published sediment fingerprinting studies, where an independent validation of results through controlled experiment is almost never provided. A key exception to this is research by Small *et al.* (2002) who used the controlled mixing of known quantities of sediment sources in a laboratory to explore the effects of the spatial variability in tracer concentrations. Hypotheses were not formally declared, and as a result absolute answers to research gaps in geomorphology could not be established. Therefore the experimental design of this thesis cannot be considered to conform to the requirement of Church (1984). However, the experimental approach allowed for the assessment of key questions regarding the accuracy of a sediment fingerprinting investigation and the causes of tracer conservatism outlined in previously published research.

Requirements 4, 5 and 6: The requirement for formalised measurement, data analysis and data management.

The fine sediment fingerprinting investigation conducted (Aim 1) was conducted on the basis of replicating a sediment fingerprinting methodology typical of those used in published literature, with the aim of highlighting and identifying the sources of uncertainty present. A problematic aspect of this approach is that a large amount of variability exists in published sediment fingerprinting methods, which has been shown to affect study results (Haddadchi *et al*. 2013). Therefore, the need for formalisation of fingerprinting methods is highlighted, to ensure greater comparability between the results of future fingerprinting investigations.

As is common with published research, issues of available time and resources limited the scope of the thesis. The implications of this limitation are explored in terms of the scaling of the produced results and the validation of the results which were derived primarily through field based observation in Sections 9.3.2. and 9.3.3. .

Aim 2: Fine sediment dynamics in the Nene river basin

Requirements 1, 2 and 3: formalisation of hypotheses, defining geomorphological properties and operational statements and the general context of a conceptual model.

The sediment budget (Aim 2) was not conducted with the aim of identifying and quantifying specific erosion and landscape evolution processes. Instead, the work was conducted as a comparison of the yield, sources and storage of fine sediment within the Nene basin, with other previously investigated catchments. As a result the work cannot be considered an experiment in the terms of Church (1984).

When investigating geomorphological processes the structured deductive experimental design and specific hypotheses required by Church (1984) are commonly used. It has however been recognised that many geomorphological problems cannot be resolved by the experimental method (Slaymaker, 2011). Issues of addressing specific objectives such asinvestigating fine sediment pressures for catchment management purposes can be viewed as such a situation, due to the significant time and resource requirements of large scale investigations. As a result the approach used in this thesis is often applied in published research such as by (Walling *et al*., 2006). The sampling design used had the advantages that large scale fine sediment dynamics in the Nene basin could be investigated, which would not have been possible due to the time and resource requirements of a more tightly controlled experimental design. The major disadvantage of this approach is that little indication as to the processes controlling the observed sediment dynamics could be gained, and issues of scaling and implications relating to the validation of the results are created, these are explored in Sections 9.3.2. and 9.3.3.

Requirements 4, 5 and 6: The requirement for formalised measurement, data analysis and data management.

The sediment budget framework provided a formal structure to the measurement and analysis of fine sediment dynamics in the Nene basin. However, the limited time available for work resulted in the absence of specific components of the budget, such as rates of the erosion of sediment sources and the temporary within catchment storage of sediment.

Hammond, (1978) identifies the use of quasi-experiments which, while fulfilling the six requirements laid out by Church, (1984), have the lowest level of control on environmental variables. In a quasi-experiment sampling sites are selected upon the best judgement of the geomorphologist. The sampling strategy in the Nene basin can be considered typical of a quasi-experiment. Sampling locations were selected on the judgement of the author as to the regions of the basin representative of the different topographies, lithologies and land utilisations present in the catchment. Sampling locations were also somewhat dictated by the accessibility of sampling locations. For example, sediment yield was measured where Environment Agency flow gauging was taking place, and the locations of floodplain coring sites were dictated by the extremely limited areas of the Nene's floodplain which had remained un-disturbed for the previous 100 years. The following section examines the scaling implications of the sampling design and sampling locations used.

9.3.2. Scaling and representativeness

Published fine sediment fingerprinting investigations have been conducted at local to catchment scales (D'Haen *et al*., 2012). The sampling locations used in the Nene included small tributary headwater catchments, as well as the fingerprinting of overbank sediment and floodplain cores with an upstream catchment containing the majority of the Nene basin. As a result the results obtained can be considered applicable to medium and large scale fingerprinting investigations. However, little attention was given to the effects of small scale changes to tracer signatures and small scale variability in tracer concentrations within the catchment. For example, it has been highlighted that alterations to the sediments' organic matter content and particle size distribution take place throughout the entire catchment (Hoey and Ferguson, 2010). Therefore, to fully record the uncertainties entering the fingerprinting investigation throughout the catchment, a small scale investigation of the fingerprinting would be required.

Issues of scaling are most prominent in the fingerprinting investigation of this thesis when considering the variability of source group tracer concentrations. Process domains have been defined as 'predictable areas of a landscape within which distinct suites of geomorphic processes govern physical habitat type, structure and dynamics; the disturbance regimes associated with process domains dictate the template upon which ecosystems develop'(Montgomery, 1999, pp. 402). As a result specific small areas with high rates of erosion and connectivity to the river may be contributing a disproportionally high amount of sediment to the Nene. This issue was highlighted in the analysis of the within-source variability in tracer concentrations in Section 7.3.2. It can however be considered a limitation to the sampling design of this thesis that smaller scale variability in tracer concentrations were not directly investigated in the field, specifically because there is uncertainty remaining as to the representativeness of the source sampling. The selection of channel bed sediment sampling locations was also potentially a source of uncertainty, considering localised domains of deposition processes may cause the sampling to be un-representative of the entirety of the Nene basin.

Scaling issues become more apparent when considering the sediment budget methodology used in this thesis (Aim 2). Parsons (2012) Identifies the limitation of sediment fingerprinting and the use of sediment yield, that they fail to take into account the travel distances and times of sediment through a catchment. As a result changes in the conditions of sediment mobilisation in a catchment may not be quickly realised at the catchment outlet if a significant quantity of sediment is temporarily sequestered on route to the river channel. An implication of this criticism is that changes to the Nene basin caused by factors such as the intensification of agricultural practices may not have been realised in the sediment budget produced. The quantification of within field sediment storage and the transit times of eroded material would have provided sufficient to remove this limitation, however the considerable time and resource requirements of these measurements prevented such an investigation taking place. Limiting the size of the study area used in this thesis would have allowed for this measurement and may have resulted in a more detailed study of sediment dynamics in the Nene. An argument can however be made that small scale studies can neglect major sediment sources and processes in a catchment. For example Slaymaker (2009) and Church (2010) highlight the failure of geomorphologists to consider the impacts of human agency on geomorphology. Using a large scale sampling design in the Nene allowed for the inclusion of towns and flood defences in the study area, which are an important characteristic of highly modified river catchments such as the Nene.

Scaling issues can also be identified in the selection of sampling locations within the Nene basin. Different segments of floodplain have been shown to differ in ecosystem structure and function (Bellmore and Baxter 2014). As a result the representativeness of the floodplain coring locations to the entirety of the Nene's floodplain can be questioned. The use of tributary and reservoir sub-catchments for the quantification of sediment yield also represents a potential source of uncertainty introduced in this thesis. The absence of the majority of the Nene's floodplain in the three sites investigated is likely to result in the sediment yield failing to account for the deposition of sediment on the floodplain throughout the length of the Nene's main channel. This represents a potential explanation for the higher sediment yields found in this thesis in comparison to the earlier study performed by Willmott and Collins (1981) where sampling was conducted close to the mouth of the Nene.

The most important scaling issue of this thesis is that it was conducted in a single catchment. As a result the results derived can only be considered representative of the Nene basin or catchments in the East Midlands of the UK.

Temporal scaling has also been highlighted as a potential limitation to many experimental designs. Relationships between landscape and channel morphology can only be considered to be in equilibrium (Steady time) in timescales of one year or less Schumm and Lichty (1965). Therefore, the applicability of the contemporary monitoring of sediment dynamics to future studies can be questioned. The application of palaeolimnological reconstruction provides long-term context to the results produced. However, the methods used are limited to a coarse resolution record of changing sediment provenance and sediment yield. An understanding of the processes controlling sediment dynamics in the Nene would provide robustness to the results derived in this thesis, and allow for the prediction of the impacts of future changes to the catchment.

9.3.3. The importance of independent validation of field based results

The previously highlighted limitations of the sampling design of this thesis introduce the potential for unrecognised uncertainty to be present in its results. This is most likely when investigating the accuracy of sediment fingerprinting results and utilising these results in the sediment budget. In almost all published sediment fingerprinting studies no validation of model outcomes using independently derived data is provided. This thesis used multiple tracer groups in an attempt to more completely represent the uncertainty present in the fingerprinting results. Because of this, the sediment provenance results presented in this thesis can be considered of greater reliability than is typical in published research. However, it was identified that because no independent source of accurate sediment provenance information was available, the error associated with individual tracer groups could not be quantified. As a result the possibility existed that all tracer groups produced a largely incorrect sediment provenance prediction which was interpreted as being accurate due to a high consistency between multiple tracer group predictions. This potential for uncertainty was somewhat addressed by the observation of sediment sources within the catchment during periods of intense rainfall and high flow. It was observed that almost no connectivity was present between cultivated land and the river catchment. As a result the finding that channel banks are the dominant sediment source was consistent with field based observations. The validation of results is also of importance for communicating the significance of results to non-specialist audiences (Chung and Fabbri, 2003), this may especially be of importance when conveying sediment fingerprinting outcomes which may contain a very high degree of uncertainty, such as in this thesis. As a result the absence of the thorough validation of the outcomes of this thesis can be considered a major limitation.

Validation of the effects of the organic matter content particle size and chemical alterations of the sediment were also not provided in this thesis, due to the constraints of its experimental design, leaving a gap in knowledge. The following section explores remaining gaps in research highlighted from issues of data validation, scaling and the sampling design of this thesis.

9.4. Remaining gaps in research and the need for future research

This thesis has successfully highlighted the uncertainties associated with a sediment fingerprinting investigation and has investigated fine sediment dynamics in the Nene river basin. However, the need for further research has been highlighted in particular by the limitations of the experimental design used which were identified in the previous section and the fact that this thesis only investigates a single catchment. This section describes the remaining gaps in knowledge identified in this thesis and provides suggestion for future research projects to address these gaps.

9.4.1. Aim 1: Fingerprinting the sources of fine sediment

The accuracy of fingerprinting results derived using different tracer groups.

Remaining gap in knowledge

The differences between sediment fingerprinting predictions made by different tracer groups were highlighted in this thesis. However, due to the discussed limitations of the experimental design used, no independent validation of the accuracy of individual tracer groups could be determined. The investigation of the accuracy of different tracer types represents arguably the most important need for future research. This would allow for guidelines for tracer selection to be produced, based on tracer behaviour in the environment.

Potential future research

A return to some of the earliest used geomorphological techniques such as the use of erosion pins (Davis and Gregory, 1994), profilometers (Sirvent *et al.*, 1997) and surveys of erosion features (Werrity and Ferguson, 1980) can potentially allow for the quantification of sediment inputs to lakes and rivers. On large scales such methods have been shown to be impractical (Peart and Walling, 1988), however, in a small catchment such as that of Sywell reservoir investigated in this thesis, these methods may allow for the production of an independent source of sediment provenance data with which to validate fingerprinting results derived using different tracer groups.

The effects of changes to the organic matter content and particle size distribution of the sediment

Remaining gap in knowledge

The results of this thesis have suggested that the most commonly investigated sources of uncertainty in fingerprinting studies, of the effects of organic matter and particle size on tracer signatures (Koiter *et al*. 2013), were not the most important source of uncertainty in the fingerprinting performed in the Nene basin. Therefore, a gap in knowledge remains as to ascertaining the exact effects of these factors on fingerprinting results in the Nene basin and other catchments worldwide.

Potential future research

Research by Motha *et al*. (2003) presented a study where a considerable amount of attention was given to the relationship between organic matter, particle size and tracer concentrations. The sediment source samples were fractionated into (<2, 2–20, 20–40, 40–63 µm) particle size categories and tracer concentration was measured in each fraction. The organic matter content in each fraction, and relationships of tracers with organic matter were also quantified and appropriate data corrections were applied on this basis. Using this methodology a more precise relationship between particle size, organic matter and tracer concentrations could be derived than the simple relationship assumed by the corrections which were used in this thesis. A methodology such as this, or similar methodologies used by other authors, such as Russell et al. (2001) represent a very thorough assessment of the impacts of changing sediment particle size and organic matter content to tracer signatures. Alternatively novel approaches such as the controlled mixing of known quantities of sediment sources by Lees (1997), combined with the controlled alteration of the particle size and organic matter content of the sediment, could provide a less resource intensive means of assessing the potential impacts of these factors when applied on a catchment specific basis.

The effects of within-source variability in tracer concentrations

Remaining gap in knowledge

Whilst this thesis has identified the error present in a fine fingerprinting study and the methodology strongly suggested that variability in source group tracer concentrations was a cause of the observed uncertainty, this was not able to be verified by an independent means of investigation. Therefore, a gap in research remains as to the effects of spatial variability. A study by Small *et al*. (2002) was the first to highlight this issue, which remained under investigated until this thesis. Small *et al.* (2002) also identified the uncertainty associated with the number of sediment source samples used to categorise each sediment source group.

Potential future research

The methods used by Lees (1997) present the most promising potential way to fill this gap in knowledge. Lees (1997) produced controlled mixtures of known quantities of sediment source samples to identify non-linear additivity effects associated with the use of mineral magnetic tracers. This approach was replicated by Small *et al*. (2002) for the purpose of investigating the issue of within source variability. The application of the methods of Lees (1997) and Small *et al*. (2002) provide the opportunity for the potential exploration of within source variability of specific tracer types and in specific environments to produce a set of guidelines to inform tracer selection in future research. The use of the tracer variability ratio used in this thesis also provides the potential for an additional stage in the tracer discrimination procedure, to identify if the un-mixing modelling being conducted is likely to produce an output with a suitably small uncertainty for the specific aims of future fingerprinting investigations. Alternative methods of investigation could also include detailed field based surveys of tracer concentrations in a range of sediment sources, in different catchments and at different scales. Such a database of surveys would potentially allow for researchers to make judgements of the number of source samples and types of tracers to use without extensive investigations conducted in every catchment investigated.

The ability of tracers to differentiate between sediment sources

Remaining gap in knowledge

The ability of tracers to differentiate between sediment sources has been highlighted in this thesis as an important prerequisite for a successful fine sediment fingerprinting investigation. As in this thesis, a review paper by Walling (2013), identified the current uncertainty regarding using the optimum tracer types to differentiate between sediment sources in different catchments.

Potential future research

Further work could be undertaken to develop the use of novel or under-used tracers, such as soil enzyme activity or compound specific stable isotopes by Martínez-Carreras *et al*. (2010) and Nosrati *et al*. (2011) which may display greater contrasts in concentration between sediment source groups. Alternatively, research conducted by Collins (2013) using organic isotopes provides the opportunity to potentially achieve the requirement laid out by Smith and Blake (2014) for a robust justification for tracer selection. Whilst the use of geochemical, lithogenic radionuclide tracers may exploit un-quantified variability in lithology, the presence of specific organic molecules indicative of surface vegetation provides a justification for the use of these tracers as robust as the fallout origins of ^{137}Cs, which provided robust source discrimination in this thesis. Additional to these opportunities to further explore tracer use, the use of methods such as Infrared spectroscopy by Evrard *et al.* (2013) potentially provide the ability to rapidly and inexpensively acquire a database of tracers. Such approaches could be used for the validation of, or to compliment the results derived using other tracer types.

9.4.2. Aim 2: Fine sediment dynamics

The erosion of channel banks

Remaining gap in knowledge

Channel banks were shown to be the dominant sediment source in the Nene basin, which contributed an atypically high proportion of sediment compared to other UK catchments. Therefore, it is recommended that further work could be undertaken to assess the mechanisms of channel bank erosion in the Nene basin and East Midlands region of the UK.

Potential future research

Flume based studies have shown significant potential for investigating the processes effecting channel bank erosion (Cherry and Beschta, 1989). However, research such as by Bull (1996) identified the complex nature of bank erosion in river catchments. Abernethy and Rutherfurd, (1998) and Couper and Maddock, (2001) identified the importance of so called 'process domains' where hydrology was often determined to be a major contributor to the rates of channel bank erosion. Therefore the optimum means of investigating the processes within the Nene basin may be the controlled observation of channel bank erosion during different periods of flow and after different periods of sub-aerial preparation, such as was done by Couper and Maddock, (2001) and Lawler *et al*. (1999).

Processes of soil erosion and sediment delivery

Remaining gap in knowledge

The quantification of rates and processes of soil erosion and sediment delivery were absent from the sediment budget of this thesis. This has been identified as a major limitation of the sampling design used.

Potential future research

The use of the geomorphological techniques suggested for use as an independent source of sediment provenance data for fingerprinting, such as erosion pins (Davis and Gregory, 1994), profilometers (Sirvent *et al.*, 1997) and surveys of erosion features (Werrity and Ferguson, 1980) can quantify rates of erosion. Alternative methods include computer based modelling of erosion and sediment transport. However, catchment complexity has been highlighted as a major limitation to the accuracy of such approaches (Jakeman *et al*. 1999). ^{137}Cs soil redistribution techniques have been used to quantify rates of soil erosion within a sediment budget framework (Walling and Collins, 2008). These methods could potentially be used within the Nene basin to quantify soil erosion, and the differences between erosion and sediment yield used to estimate within catchment sediment storage. However Parsons and Foster (2011) raise considerable questions as to the accuracy of the ^{137}Cs redistribution methods. Alternative methods include that of Parsons et al. (2010) who used the application of artificial magnetite grains to soils to quantify the rates of transport of eroded material, however, the 16 years used in this approach may prove impractical for most investigations. Computer based modelling has also been combined with field based measurement such as the use of SedNet coupled with a mass balance model of particle residence times based on atmospheric and fluvial fluxes of three fallout radionuclide tracers (^{7}Be, $^{210}Pb_{un}$ and ^{137}Cs) by Smith *et al*. (2014).

The role of floodplain sedimentation in the sediment budget

Remaining gap in knowledge

The results of this thesis were able to identify that rates of floodplain sedimentation in four locations in the Nene basin had reduced after 1963 using four floodplain cores. However, when the sediment deposition rates in these cores was scaled to a square kilometre scale results were clearly too high for the sediment dynamics of the Nene to make logical sense. As a result the fluvial sediment budget produced as part of Aim 2 can be considered incomplete. A study by Walling *et al*. (1999b) showed that between 39-40% of the total annual sediment yield of the River Ouse, UK, and 50% for the River Wharfe, UK was deposited on the river’s floodplains. Therefore, a significant amount of the sediment budget of the Nene may remain unaccounted for.

Potential future research

A more accurate and complete quantification of the quantities of sediment deposited onto floodplains could be produced using the methods of Walling and Owens (2002). As in this thesis, only four sampling locations were used in the 1346 km^2 catchment (comparable in size to the Nene) however, a transect of 10 cores was taken from the river across the floodplain at each sampling site. In this way the authors were able to quantify floodplain sediment storage within a sediment budget framework. The methods used for the quantification of floodplain sediment storage in the Ouse and Tweed basins used 26 such transects in a 3315 km^2 catchment (Owens and Walling, 2002). The bulk measurement of ^{137}Cs activity allowed for the rapid measurement of accumulation rates in multiple cores, as opposed to the time consuming analysis of individual segments of single floodplain cores in this thesis.

The extremely limited areas of undisturbed land adjacent to the river channel in the Nene basin restricted the use of this approach in this thesis. However, catchments elsewhere in the East Midlands region of the UK provide the potential opportunity for the expansion of the quantification of floodplain storage. Should nearby catchments be comparable to the Nene basin, the percentage of the annual sediment yield stored on the floodplains could be calculated and utilised to inform other catchments in the region, such as the Nene.

9.5. Closing statement

The results presented in this thesis have shown the significant potential for sediment fingerprinting techniques to determine sediment provenance. It has however been identified that the uncertainties present when using fingerprinting techniques can be considerable. As a result the need for the careful analysis of the uncertainty present in fingerprinting investigations due to variability in tracer concentrations, and tracer non-conservatism should be a priority for future research.

The Nene basin has been shown to have a low sediment yield in comparison to most catchments in the UK and worldwide. The most important finding about the sediment dynamics in the Nene basin is that channel banks are the dominant source of sediment, which is highly un-usual for UK rivers. The results of this thesis have identified that the mitigation of fine sediment pressures in the Nene basin would be best achieved by the stabilisation of channel banks to reduce the overall sediment yield, re-connecting the river with its floodplain to increase floodplain sedimentation back to the 1958 – 1963 accumulation rate, and the removal of any obstacles to the episodic high flows, required to flush away fine sediment accumulated on channel beds.

Appendix 1 (electronically submitted supplementary data)

The attached CD contains the raw data used in this thesis, the composite fingerprints used in Chapters 6 and 7, the raw results of the un-mixing models run and a summary of the sediment fingerprinting results.

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