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The uncertainties associated with sediment fingerprinting suspended and recently deposited fluvial sediment in the Nene river basin

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Abstract

The use of tracers within a sediment fingerprinting framework has become a commonly used technique for investigating the sources of fine sediment. However, uncertainties associated with tracer behaviour have been cited as major potential limitations to sediment fingerprinting methodologies. This paper aims to determine the differences between fingerprinting results derived using different groups of tracer properties and to determine the role of organic matter content, particle size, and within-source variability in tracer concentrations on the observed differences. A mean difference of 24.1% between the predicted contributions of sediment originating from channel banks was found when using different tracer groups. Mean differences between tracer group predictions were lower, at between 8% and 11%, when fingerprinting contributions from urban street dusts. Organic matter content and / or particle size showed little indication that they caused differences between tracer group predictions. The within-source variability in tracer concentrations and small contrasts between the tracer concentrations of different source groups were identified as

probable causes of inherent uncertainty in the fingerprinting predictions. We 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.

Keywords:

sediment fingerprinting; tracers; sediment sources; river catchments.

1. Introduction

The identification of the major sources of fine sediment in a catchment represents a key requirement for the application of targeted mitigation measures (Walling and Collins, 2008). Because the investigation of sediment inputs is time consuming when using conventional sediment source monitoring methods, such as erosion pins (Davis and Gregory, 1994) and surveys of erosion features (Werrity and Ferguson, 1980), sediment fingerprinting methodologies have gained widespread adoption in geomorphological research (Foster and Lees, 2000). The principle of sediment fingerprinting is based upon a comparison of the properties of fine sediment with 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 (tracers) and the assumption that properties of the sources reflect those of the sediment after its delivery to a river, floodplain, or lake (Collins et al., 1997a).

Over the last 2-3 decades, 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) recently deposited sediment on channel beds (Walling et al., 2006), and actively transported suspended sediment (Gruszowski et al., 2003). A wide variety of different tracers

have also been employed in the published literature which include mineral magnetic signatures (Caitcheon, 1993), lithogenic radionuclides (Gruszowski et al., 2003), fallout radionuclides (Walling et al., 1999), geochemistry (Collins et al., 1997a), particle size, shape and colour (Krein et al., 2003) in addition to a range of organic tracers (Collins et al., 2010b).

It has been recognised that the use of multiple different tracer types in composite fingerprints is important for improving discrimination between sediment sources and reducing the collinearity of the tracers used (Collins and Walling 2002). Recent work by Collins et al. (2012, 2013a,b) have expanded upon this principal by fingerprinting a sediment sample using multiple different composite fingerprints of tracers derived by different statistical procedures to increase the robustness of fingerprinting outputs. Significant potential for uncertainty associated with tracer selection has been recognised in fingerprinting studies. For example Fu et al. (2006) showed that two different composite fingerprints using geochemical tracers predicted mean contributions from sediment sources differently by an average of 35%. Very little difference was found between the predictions of geochemical tracers and tracing using soil enzyme activity by Nosrati et al. (2011). However, it was shown in this latter study that, in individual samples, the root mean square differences could be up to 48%. Evrard et al. (2013) compared fingerprinting results derived using fallout radionuclide activity and geochemical signatures and diffuse reflectance infrared Fourier transform spectroscopy measurements; in one study catchment differences between predictions were as high as ~70% for some samples.

Many processes have been identified that could alter tracers and cause differences in sediment provenance predictions such as those described above. These include changes to the

sediment particle size distribution during transport, with finer particles being carried further through a catchment than coarse particles (Walling et al., 2000). Particle size has been shown to be significantly correlated with concentrations of many different tracers, such as mineral magnetic signatures (Oldfield et al., 2009), fallout radionuclides (Ab Razak et al., 1996), and geochemical tracers (Mahler et al., 1998). Therefore, any changes in sediment particle size would also be expected to result in a change in tracer concentration and therefore a change in the sediment provenance prediction.

The organic fraction of sediment has been shown to often be carried farther in suspension through a catchment, primarily owing to its association with small particles and its lower density in comparison to the mineral fraction of sediments (Nadeu et al., 2011). In addition, the in-growth of organic material can also occur within a river or lake or on a floodplain (Kansanen and Jaakkola, 1985). The impacts of organic enrichment or depletion have been shown to vary between different tracers. For example ca. 30% of unsupported Pb-210 (Pb-210_{un*}) activity was shown to be associated with organic matter in soils in a forested catchment by Wallbrink et al. (1997). Hirner et al. (1990) showed that the elements As, Ag, B, Cd, Co, Cu, Hg, Mn, Mo, Ni, Pb, Sb, V, and Zn were all enriched by up to three orders of magnitude within the organic fraction of sediments. However, mineral magnetic signatures are generally not associated with the organic fraction of sediment as organic matter is diamagnetic (Lees, 1999).

Additional uncertainties have been shown to be associated with different mathematical unmixing models used to apportion sediment sources. An example of this was shown in a recent study by Haddadchi et al. (2013) who demonstrated that differently programmed unmixing models could produce provenance predictions up to 33% different when models used local optimisation and 95% different with global optimisation. The categorisation of tracer concentrations of the sediment source groups is a key difference between unmixing

100 modelling approaches, therefore the sensitivity of modelling to small changes in source tracer
101 concentrations is an additional potential source of uncertainty. The ability of tracers to
102 adequately categorise and differentiate between sediment source groups is a fundamental
103 requirement of sediment fingerprinting methodologies. Small et al. (2002) showed that the
104 uncertainty associated with the calculation of contributory coefficients increased when the
105 within source group tracer concentration coefficient of variation increased and when fewer
106 samples were used to categorise each source group.

107 The paper was structured to fulfil the following objectives relating to the current uncertainties
108 associated with sediment fingerprinting:

109 • To determine the difference between fallout radionuclide, lithogenic radionuclide,
110 geochemical, and mineral magnetic fingerprint predictions when fingerprinting
111 suspended sediment and recently deposited overbank and channel bed sediment.

112

113 • To determine the potential effects of particle size distribution and organic content of the
114 sediment on the difference between the tracer group fingerprinting predictions.

115
116

117 • To gain an indication of the uncertainty associated with variability of sediment source
118 tracer concentrations on a sediment fingerprinting investigation.

119

120

121 ## 2. Study catchment

122

123 The study was undertaken in the Nene basin in the east Midlands, UK (Fig 1). Sampling was
124 conducted in the middle to upper Nene basin upstream of Ditchford with a total catchment
125 area of 1060 km^2. The average annual rainfall for the previous 140 years is 638 mm, and the
126 maximum elevation is 226 m above Ordnance Datum (AOD). The catchment lithology is
127 primarily Jurassic marine sedimentary deposits, Quaternary sand and gravel, and glacial
128 diamicton. Land utilisation in the catchment is 56% cultivated, 22% pasture, and 9% urban
129 (Morton et al., 2011); and extensive flood defences follow the course of the rivers main
130 channel.

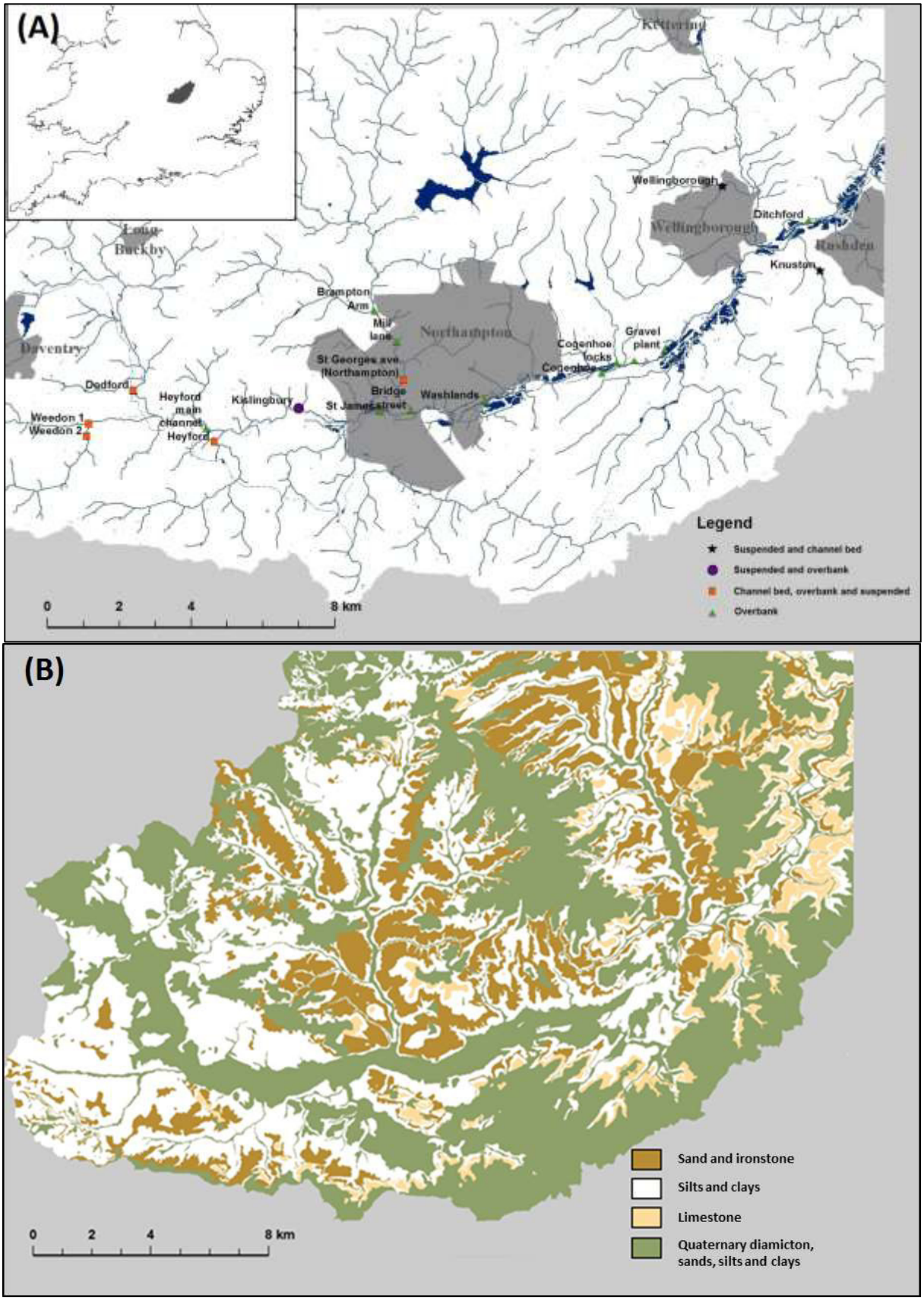


Fig 1. River Nene catchment with (A) sampling locations and (B) lithology (map based upon DiGMapGB-50, British Geological Survey).

3. Materials and Methods

3.1. Field sampling

Suspended sediment is frequently used in fingerprinting investigations (Collins et al., 2010b). For this study a total of eight time-integrated suspended sediment traps were deployed in the locations shown in Fig. 1. The sediment traps were constructed from a PVC pipe 1 m in length and 98 mm in diameter following the design of Phillips et al. (2001). A funnel with a 4 mm aperture was fixed to one end of the trap and a 4 mm hole was drilled in the other end to allow flow through the trap. The increase in diameter from the 4 mm inlet hole to the 98 mm internal diameter of the pipe results in a reduction in flow velocity and the deposition of suspended sediment within the trap. Sediment traps of this design 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). A single sediment trap was installed at each sampling location, and the traps were secured to dexion uprights using cable ties at ~0.6 of the mean water depth during the period of drought when the traps were initially installed. Each trap was emptied on a monthly basis between October 2011 and March 2013 into 10 l plastic containers and returned to the laboratory for analysis.

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). Therefore, a sample of sediment analysed during this period has the potential to be representative of sediment originating from a large spatial area of the catchment. In this study samples of sediment deposited overbank were collected from 17 locations after four high

160 flow events in April 2012, July 2012, October 2012, and November 2012 once high water
161 levels had receded to below bank full level. Sediment was washed from riparian vegetation as
162 described by Walling et al. (1997). The primary vegetation selected was common comfrey
163 (*Symphytum officinale*) and common nettle (*Urtica dioica*). The vegetation was washed with
164 native river water into a 5 l plastic container, and the resultant water and sediment was
165 transported to the laboratory for analysis in 1 l Nalgene bottles.

166 Channel beds represent an important store of recently deposited fine sediment in river
167 catchments. Not only is the degradation of channel bed habitats by fine sediment considered
168 an important ecological issue (Collins et al., 2010b), but the stored sediment often represents
169 a source of easily mobilised sediment ready to be transported when flows increase (Walling
170 and Amos, 1999). The method developed by Lambert and Walling (1988) was used to obtain
171 a sample of sediment stored on the bed of the Nene's tributaries. A total of seven sites (Fig.
172 1) were sampled on a quarterly basis from the period June 2011 to September 2012. A
173 cylinder with a surface area of ca. 0.2 m^2 was pushed into the river bed creating a seal
174 between the cylinder and river bed, and the depth of water within the cylinder was recorded.
175 The river bed within the cylinder was then disturbed to a depth of 5 cm using a wooden pole
176 for a period of 1 minute and two 0.5 l subsamples were immediately taken from the water
177 within the cylinder. Three repetitions were performed within a ca. 30 m reach of river at each
178 sampling location to provide a sufficient quantity of sediment for laboratory analysis.

179 Source samples were collected from channel banks, surface agricultural land, and urban street
180 dusts as these have been shown to be dominant sources of sediment in UK catchments (Carter
181 et al., 2003; Walling et al., 2007). Two hundred and forty seven source samples were
182 collected from surface agricultural land, 65 from channel banks, and 21 from urban street
183 dusts. Samples of agricultural soil were collected from the top 2 cm of the soil profile using a
184 nonmetallic trowel. Samples were collected from agricultural land adjacent to river channels

185 and from soils representative of the different geological units present in the basin. Urban
186 street dusts were collected using a dustpan and brush from the material deposited at the side
187 of major and minor roads. Channel bank samples were collected from the lower and middle
188 horizons of visibly eroding channel banks. All samples were composed of an amalgamation
189 of five subsamples taken from within a 15 m radius of each sampling point to further increase
190 the sample size.

191

192 *3.2. Laboratory analyses*

193

194 In the laboratory, the sediment and source samples were oven dried at 40°C and gently
195 disaggregated using a pestle and mortar. The source samples were sieved to < 63 µm to
196 achieve a particle size distribution roughly comparable to the sediment samples (Collins et
197 al., 1997a).

198 The soil and sediment samples were analysed for a range of mineral magnetic, lithogenic, and
199 fallout radionuclide and for geochemical signatures. Additionally, organic matter content and
200 particle size analysis were measured on all source samples and river sediments and deposits.

201 Mineral magnetic measurements were determined using ~10 g of the dried and sieved source
202 and sediment samples packed tightly to a depth of ~2 cm in 10 ml sample pots. Low
203 frequency susceptibility (χlf), frequency dependent susceptibility (χfd), susceptibility of
204 ARM (χarm), soft isothermal remanent magnetisation (-100 mt) (*IRM-100*), saturation
205 isothermal remanent magnetisation (1 T) (*SIRM*), and hard isothermal remanent
206 magnetisation (*HIRM*) were measured following the procedures laid out by Foster et al.
207 (2008).

To measure radionuclide activity ~3 g of both source sample and deposited sediment was packed to a depth of 4 cm in PTFE sample pots and sealed with a turnover cap and paraffin wax. All samples were left to equilibrate for a minimum of 21 days to allow for in-growth of ^{226}Ra. Sediment samples were measured for a minimum of two days (> 172,800 s) and source samples for a minimum of one day (> 86,400 s) using Ortec EG&G hyper-pure Ge γ detectors in a well configuration. Activities of ^{137}Cs, ^{210}Pb$_{un}$, ^{226}Ra, ^{234}Th, ^{235}U, ^{214}Pb, ^{228}Ac, ^{212}Pb, and ^{40}K were then determined from analysis of the resulting spectra as described by Wallbrink et al. (2003) and Foster et al. (2007).

A 0.8 g $^{+}/_{-}$ 0.05g sub-sample of each source sample and core section was weighed into tetraflouromethacrylate (TFM) vessels for *aqua regia* microwave digestion using a CEM Mars 6 digestion unit at 180°C. The digested samples were diluted to 50 ml in volumetric flasks using type 1 ultrapure water and after a period of settling for ca. 5 minutes, a subsample was decanted into 10 ml 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 the sampling sites were initially analysed with a 1 mg kg^{-1} multielement 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 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. Geochemical concentrations were then measured for the following elements Al, As, Ba, Ca, Co, Cr, Cu, Fe, Ga, Gd, K, La, Mg, Mn, Na, Nd, Ni, P, Pb, Ti, V, Y, Yb, Zn, and Zr. Particle size of samples was determined using a Malvern Instruments laser granulometer with Hydro-2000 sample injection unit. A ca. 0.1 g subsample was pretreated with 10 ml of 30% hydrogen peroxide to remove organic matter. The samples were left for 24 hours at room temperature and then

heated at 70°C for 4 hours. The samples were further dispersed using 5 ml of 3% sodium hexametaphosphate solution and 2 minutes of ultrasonic dispersion immediately prior to analysis (Gray et al., 2010). 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). Sediment specific surface area (SSA) was taken from the results file as a measure of sediment particle size distribution (Collins et al., 1997a); SSA was calculated by the Malvern® software using the diameter of the measured particles and assuming that sediment particles were spherical.

The organic content of the samples was determined using low temperature loss on ignition. A ca. 1-2 g subsample of soil or sediment was heated in a Carbolite muffle furnace set at 450°C for 4 hours. Loss on ignition (LOI) was calculated using the pre-combustion dry sample mass and the post-combustion mass (Heiri et al., 2001).

The analytical precision was calculated for each technique using repeat measurement of 10 replicate samples. The mean difference between each repeat measurement was calculated at mineral magnetic signatures: 4.96%, radionuclides: 7.09%, geochemistry: 12.44%.

4. Results and discussion

The results of this paper are displayed and discussed in three sections. In the first section (objective 1), a fine sediment fingerprinting investigation was conducted using different fingerprints of the tracer groups. The ability of tracer groups to form a composite fingerprint

able to discriminate between source groups, the predictions of the tracer groups and the trends in monthly sediment provenance made by the tracer groups were compared.

In the second section (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 between their predictions.

The final section (objective 3) examined the uncertainty associated with the within-source variability in tracer concentrations and the size of the contrasts in tracer concentration between source groups. It was determined if larger contrasts in tracer concentration between source groups decreased the differences between tracer group predictions. The relationship between variability in source group tracer concentrations and the potential uncertainty present in unmixing models was then quantified to determine if tracer variability was able to account for the differences between tracer predictions observed as part of objective 1.

4.1. Sediment fingerprinting results

4.1.1. Statistical determination of composite fingerprints for source discrimination

The sediment fingerprinting procedure used was based upon the methods used by Collins et al. (2010b). It consisted of an initial mass conservation test, followed by a two-step statistical determination of the composite fingerprint able to best differentiate between the three sediment sources. The sediment source samples collected in the upstream catchment of each core site were utilised in the fingerprinting analysis.

279 The combinations of tracer groups used to fingerprint the sediment are shown in Table 1,
280 along with the abbreviations for each group used in future figures and tables.

281

282 **Table 1.** The composite fingerprints of tracer groups used in this study and their abbreviations

Tracer group fingerprint	Abbreviation
Mineral magnetic signatures	Mag
Mineral magnetic signatures and lithogenic radionuclides	Mag litho
Mineral magnetic signatures and fallout radionculides	Mag fallout
Mineral magnetic signatures and geochemistry	Mag geochem
Geochemistry and lithogenic radionuclides	Geochem litho
Geochemistry and fallout radionuclides	Geochem fallout
Geochemistry	Geochem
Lithogenic and fallout radionuclides	Litho fallout
All tracer groups combined	All

283

284 A mass conservation test was used to identify any tracers falling outside of the medians of all
285 of the source groups (Wilkinson et al., 2012). When over 10% of samples in each core fell
286 outside of the median source values, the tracer was judged to violate the assumption that it is
287 representative of the sediment sources and was removed from further analysis. A two-step
288 statistical procedure was then used to select the optimum composite fingerprint for each
289 tracer group at each sampling location, using the tracers that passed the mass conservation
290 test. Firstly, a Kruskal–Wallis *H* test was used to remove any tracers that did not show a
291 significant difference in concentration between at least two of the sediment sources. Table 2
292 shows a summary of the results of the test, along with the median and median absolute
293 deviations of each tracer in each of the source samples. Only the result for the analysis when
294 all of the source samples were used together is shown in Table 2, as most other source
295 groupings upstream of the different sampling sites showed similar patterns to that of Table 2.

296

Table 2: Median and median absolute deviation tracer concentrations in source groups; Highlighted tracers show no significant difference in concentration between source groups ($p<0.05$) in a Kruskal-Wallis H-test

	Surface agriculture		Chanel banks		Urban street dusts	
	Median	**Median absolute deviation**	**Median**	**Median absolute deviation**	**Median**	**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
$^{210}Pb_{un}$ (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

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 unmixing models by researchers such as Collins et al. (2010a) and is used as a weighting in this paper. The efficiency of each tracer is summarised in Fig. 2 as an average and standard deviation, consisting of the different sampling locations in the Nene basin. 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. The average improvement in discriminatory efficiency over the expected 33.3% is 18.3% (standard deviation 8.7).

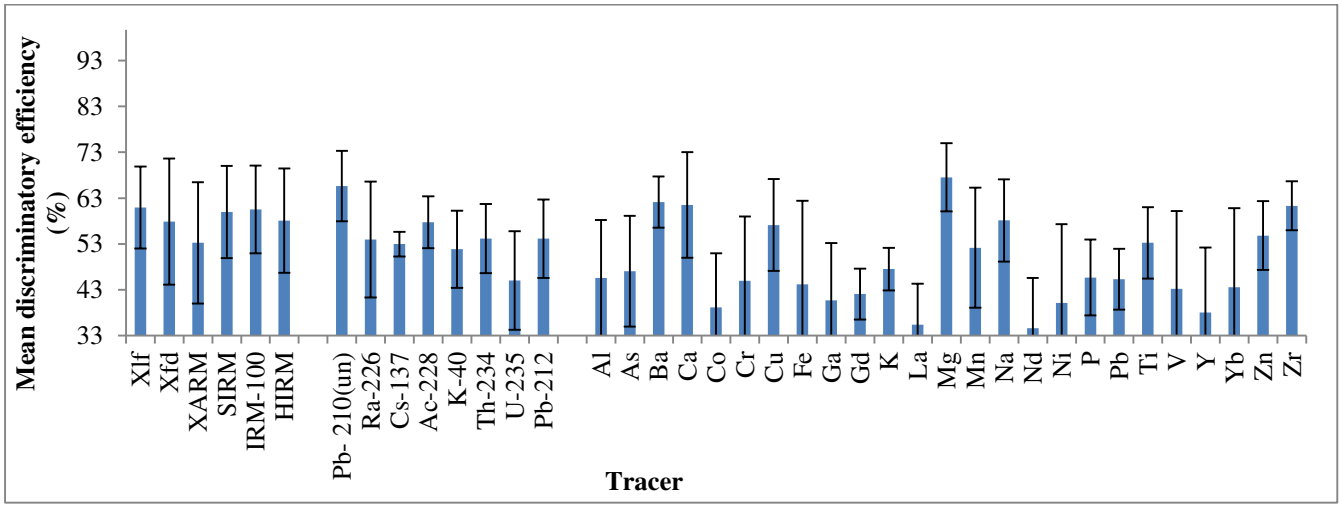
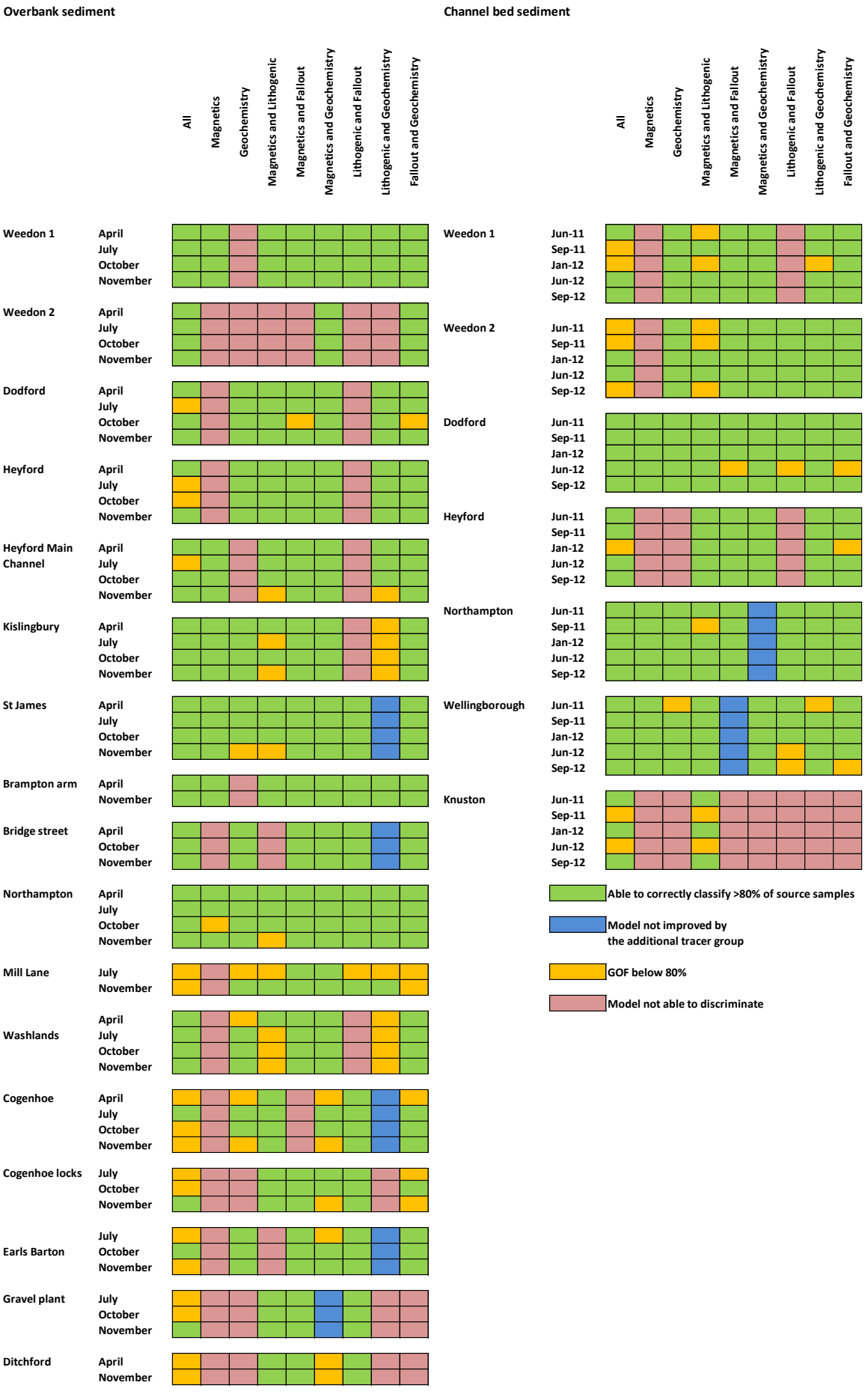


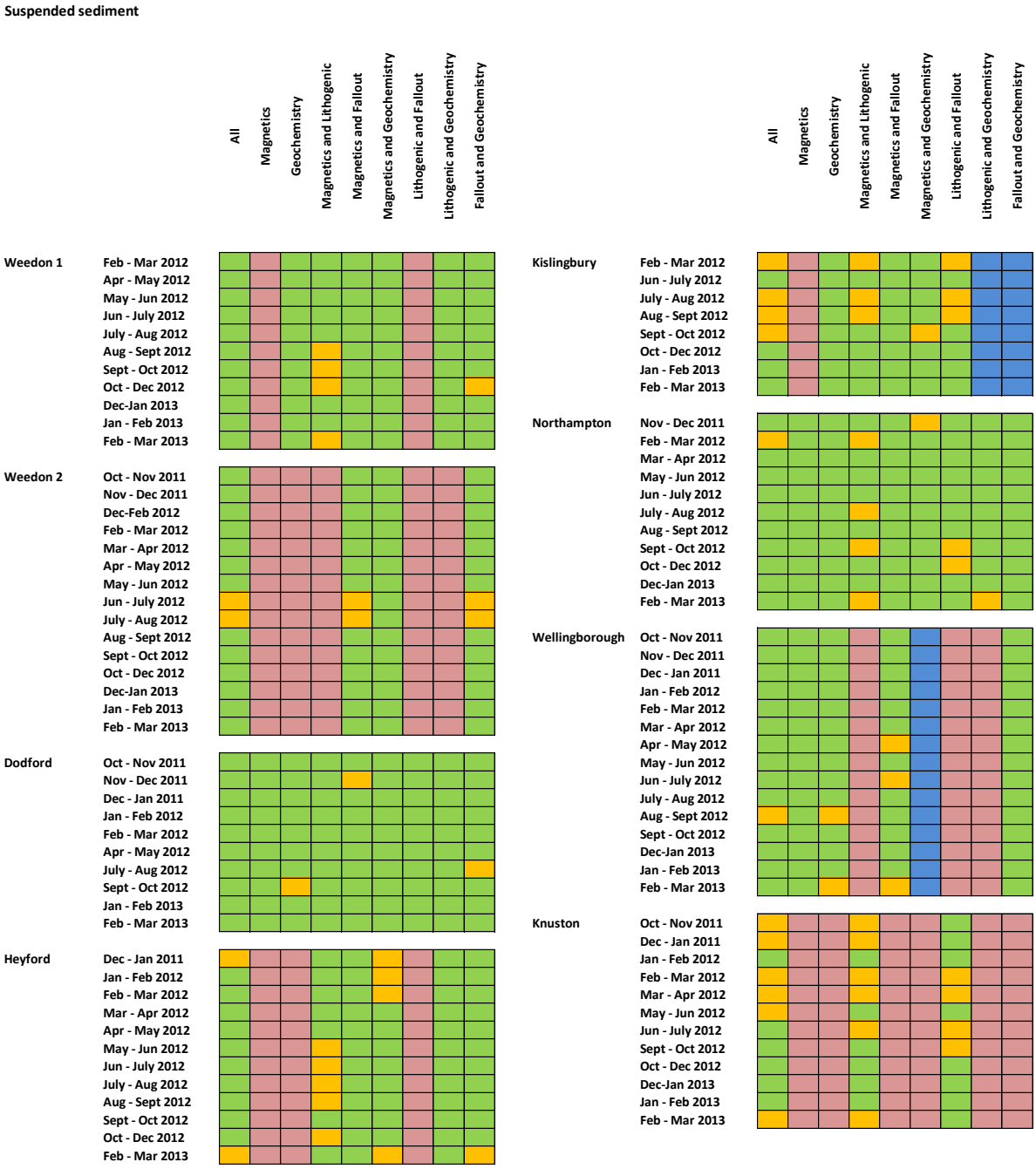
Fig. 2: The mean discriminatory efficiency of tracers used in this study when discriminating between channel banks, surface agricultural sources, and urban street dusts (note y axis starts at 33%).

A genetic algorithm-based linear discriminant analysis (GA-LDA) was used to identify the optimum composite fingerprint for each tracer group at each sampling site. 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 that 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 unmixing modelling. The figure of 80% was selected on the basis that a smaller value was rarely used in published fingerprinting studies. The mean discriminatory efficiency of the composite fingerprints used was 86.0% (standard deviation 4.0%).

Goodness of fit (GOF) is commonly used in published fingerprinting studies to judge how well unmixing model predictions match the input data and is therefore a means of judging the reliability of model results (Haddadchi et al., 2013). On this basis, any model with an average GOF falling below 80% was judged to be potentially unreliable and was not used for further analysis. The mean GOF of the models passing the 80% threshold was 92.6% (standard deviation 5.0%). Fig. 3 shows the results of the discriminant analysis and goodness of fit test.


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
April
July
October
November
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
Jun-11
Sep-11
Jan-12
Jun-12
Sep-12
Northampton
Wellingborough
Knuston
Able to correctly classify >80% of source samples
Model not improved by the additional tracer group
GOF below 80%
Model not able to discriminate



334

335 **Fig. 3.** The ability of tracer groups to form a composite fingerprint able to correctly classify
336 >80% of source samples and produce a goodness of fit in excess of 80% in an unmixing model
337 (when the Mag geochem group is highlighted blue its fingerprint is identical to the 'All' group).

338

339 *4.1.2. Unmixing modelling*

340

The unmixing model used to apportion contributions from the three sediment source groups was based upon that used by Collins et al. (2010b). The model operates by minimising the sum of squares of the relative errors in the objective function (f) by changing the relative source proportions (P_s). The model was constrained so that proportional source contributions lie between 0 and 1 and the proportional source contributions sum to 1, the maximum contribution from any sediment source was left unconstrained.

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

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); 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; and m = number of sediment source categories.

Model uncertainty was determined using Monte Carlo uncertainty analysis that ran the model using 3000 random values for each tracer from between the median +/- one median absolute deviation of each source group. Weightings were applied to prioritise tracers that were best able to differentiate between the sediment sources and had the lowest within-source variability in concentration. These were calculated based upon the methods used by Collins et al. (2010b).

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

where MAD = median absolute deviation.

Tracer discriminatory weighting = E_t/E_a

where E_t= discriminatory efficiency of tracer, and E_a= minimum discriminatory efficiency of any used tracer.

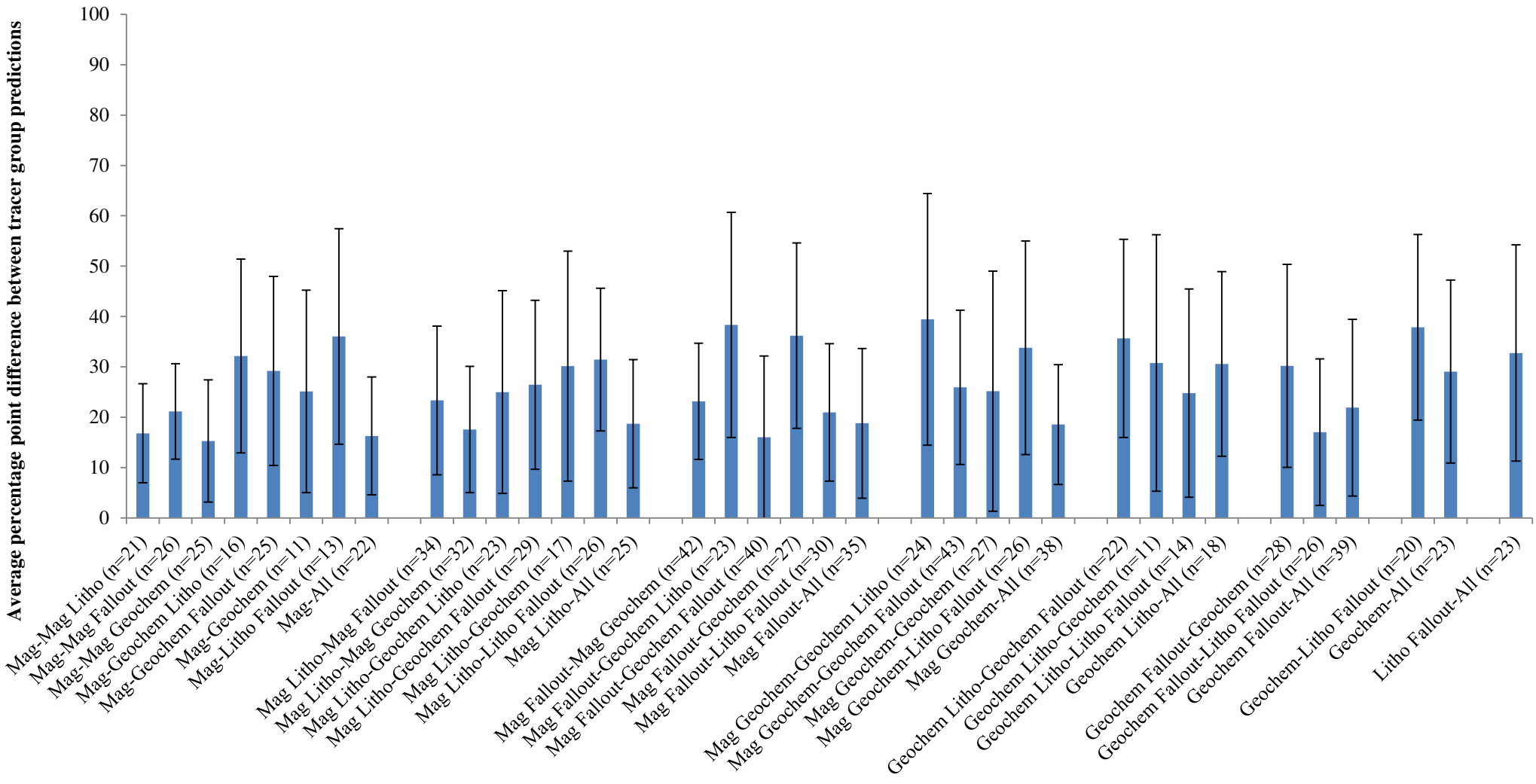
4.1.3. Percentage differences between tracer group provenance predictions

This section quantifies the differences between the tracer group sediment provenance predictions. 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 basin predicted by most tracer groups and was considered representative of the overall unmixing 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 5th and 95th percentile ranked 3000 Monte Carlo iterations for each sample to account for close to the full range of uncertainty predicted by the unmixing 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 (Fig. 4); the lowest average difference of 15.3% was found between the predictions made by the Mag group compared to the predictions 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.



391

392 **Fig. 4.** The mean absolute difference between tracer group predictions of contributions from channel banks to overbank sediment.

393 Fig. 5 shows the mean differences between the predictions of each tracer group and every
394 other tracer group when fingerprinting overbank, suspended, and channel bed sediment. The
395 mean difference between the predictions of all tracer groups in all sediment samples was
396 24.1% with a standard deviation of 0.12%. Little difference was observed in Fig. 5 between
397 the results for each individual tracer group compared to other tracer groups.

398 When the average difference between one tracer group and all others is compared in
399 overbank, suspended, and channel bed sediment, a mean difference of 1.41% is found
400 between the three sampling locations, indicating that sediment sampling location has little
401 effect on the consistency of provenance predictions. This similar average difference indicates
402 that tracer conservatism is not primarily affected by processes occurring during the deposition
403 of suspended sediment onto channel beds or riparian zones, as selective deposition of specific
404 particle size fractions would be expected to alter tracer concentrations (Koiter et al., 2013). It
405 also suggests that during the period of sediment storage on channel beds, few post-
406 depositional alterations to the sediment are occurring. Short residence times of the sediment
407 and the well-oxygenated appearance of the sediment observed during the bed disturbance
408 experiments are a potential explanation for this.

409 The size of the differences between the tracer group predictions in the Nene are higher than
410 most of the comparisons made by Nosrati et al. (2011) and Evrard et al. (2013). However,
411 some of the large differences between fingerprint predictions found by Nosrati et al. (2011)
412 and Evrard et al. (2013) as well as Fu et al. (2006) exceeded those found in the Nene,
413 suggesting that the results found in the Nene could be experienced in other catchments where
414 the discriminatory efficiency of source signatures is relatively poor.

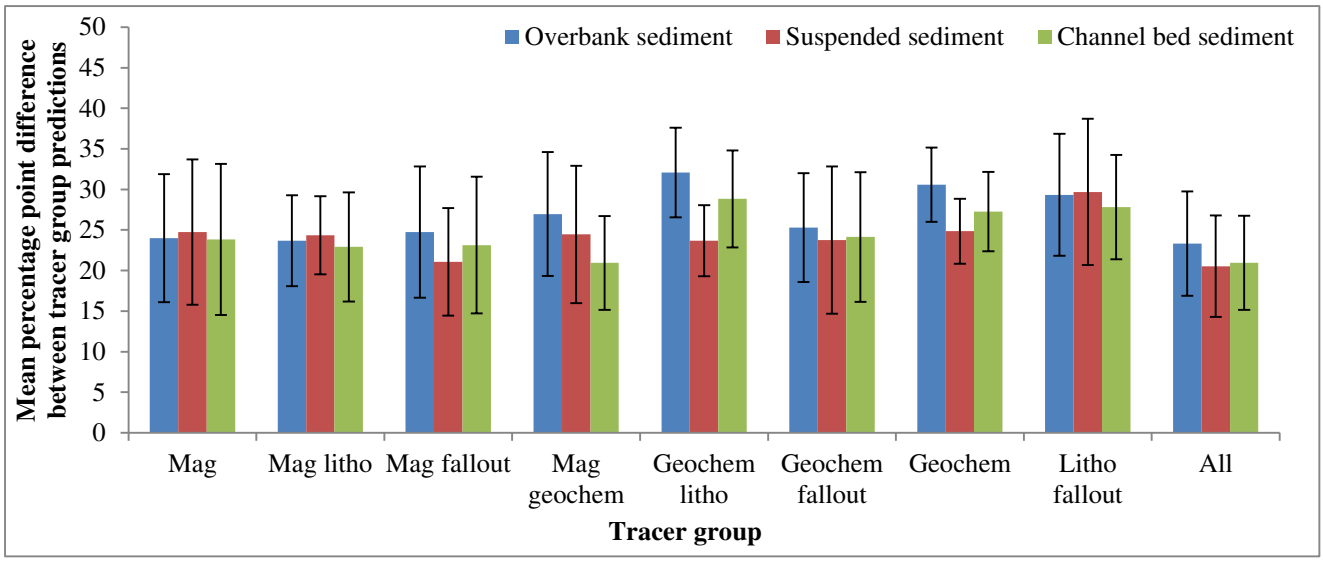


Fig. 5. Mean differences between the predicted contribution of sediment from channel banks made by each tracer group in comparison to all other tracer groups in overbank, suspended, and channel bed sediment samples.

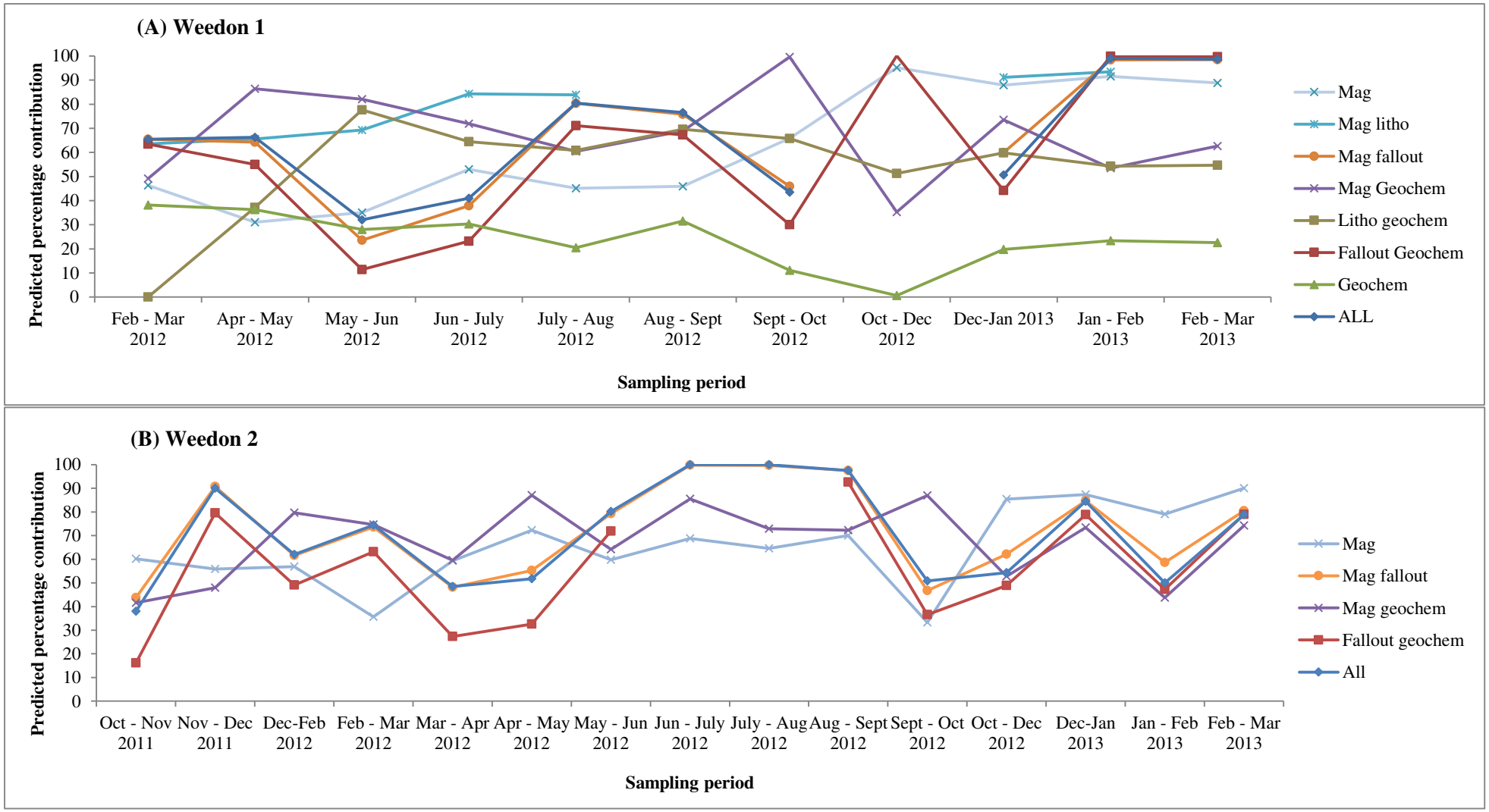
4.1.4. Trends in monthly sediment provenance

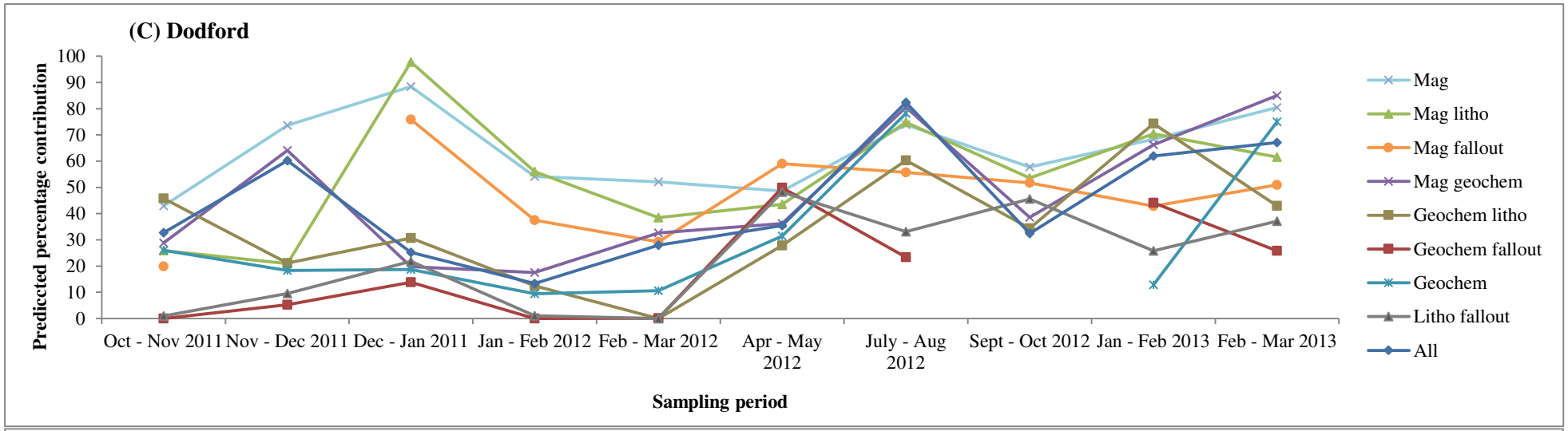
We also investigated whether the trends in changing monthly suspended sediment provenance were consistent between the different fingerprints used as part of objective 1. Trends in provenance predictions are of particular importance when assessing changes occurring after mitigation measures are applied to a catchment (Collins et al., 2010b), or catchment responses to different climatic conditions, or changes to land utilisation (Foster et al., 2012).

Fig 6 shows median predicted contributions from channel banks to suspended sediment and reflect the differences between tracer group predictions presented in Fig. **5**. A reasonable amount of agreement in trends can be seen in the Northampton (Fig 6F) and Dodford (Fig 6C) 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 (Fig

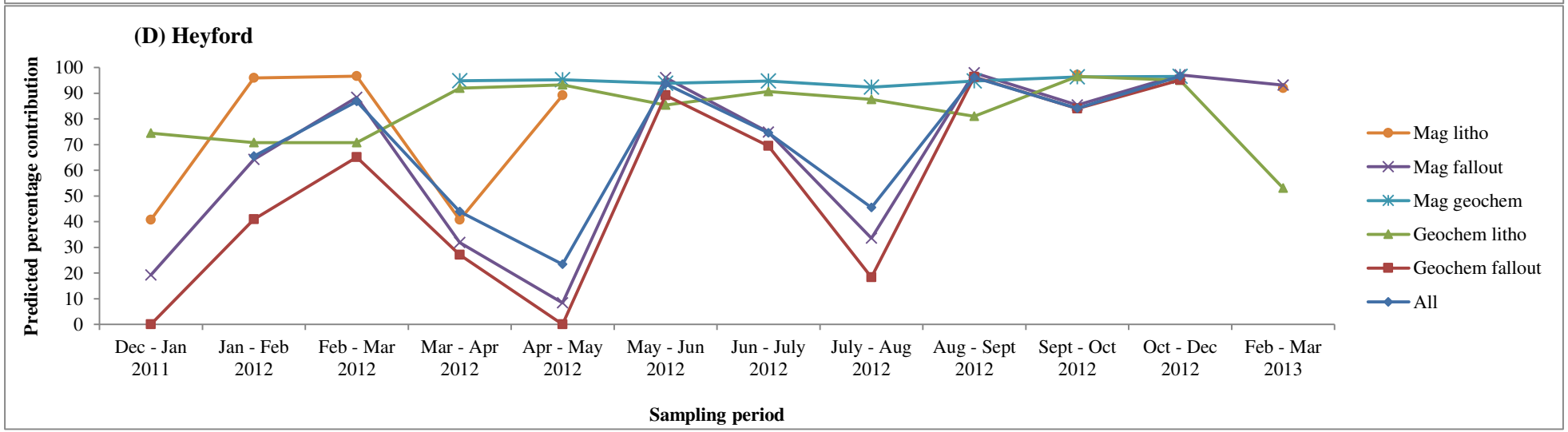
6A), the tracer groups often show very different trends, such as geochemical tracers predicting a decreasing contribution from channel banks and mineral magnetic signatures predicting an increasing contribution.

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. For this reason, methodologies that use multiple composite fingerprints in a single framework, such as that used by Collins et al. (2013a), are strongly supported by these results.

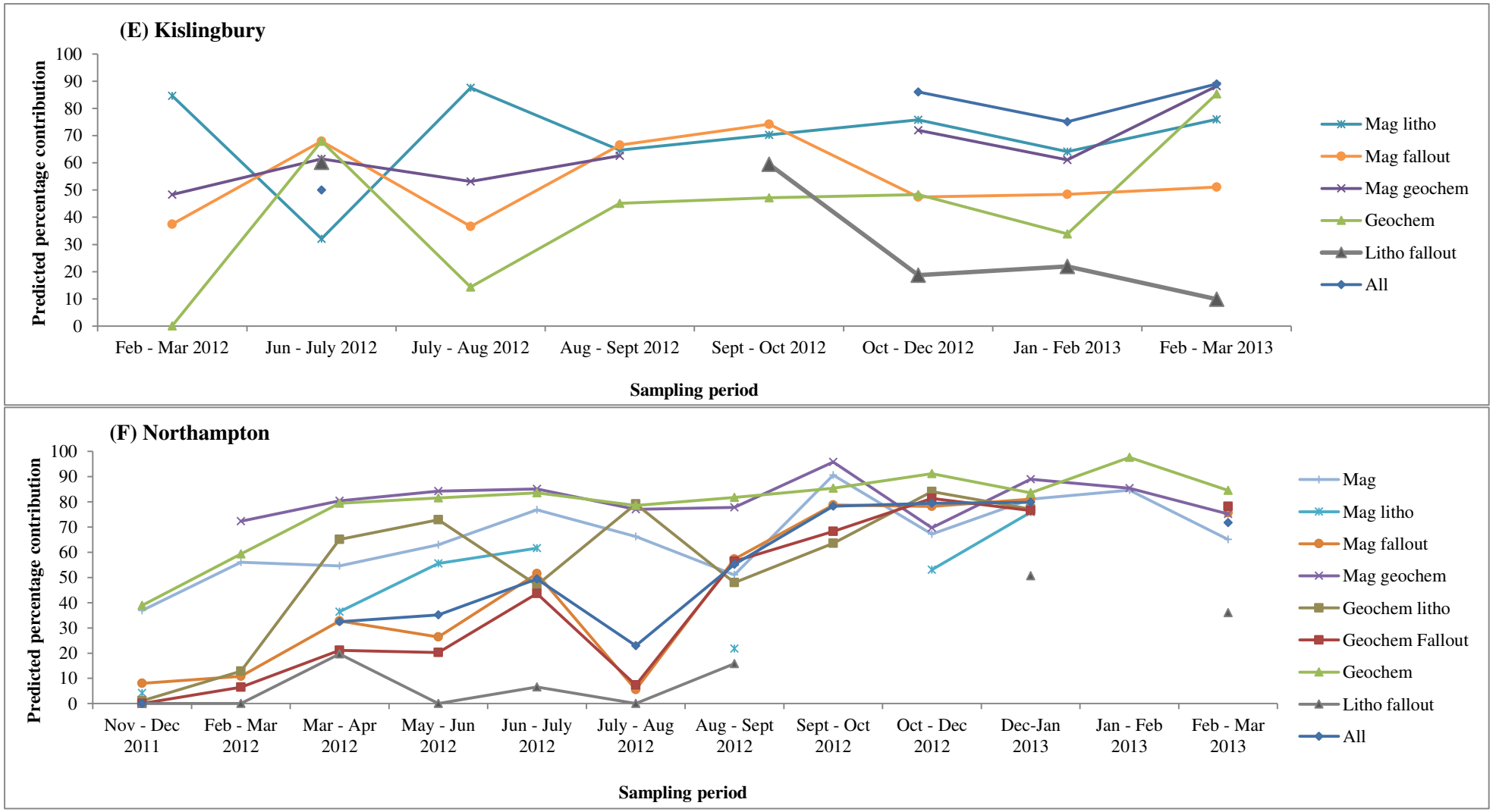

(A) Weedon 1
Predicted percentage contribution
100
90
80
70
60
50
40
30
20
10
0
Feb - Mar 2012
Apr - May 2012
May - Jun 2012
Jun - July 2012
July - Aug 2012
Aug - Sept 2012
Sept - Oct 2012
Oct - Dec 2012
Dec-Jan 2013
Jan - Feb 2013
Feb - Mar 2013
Sampling period
Mag
Mag litho
Mag fallout
Mag Geochem
Litho geochem
Fallout Geochem
Geochem
ALL
(B) Weedon 2
Predicted percentage contribution
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

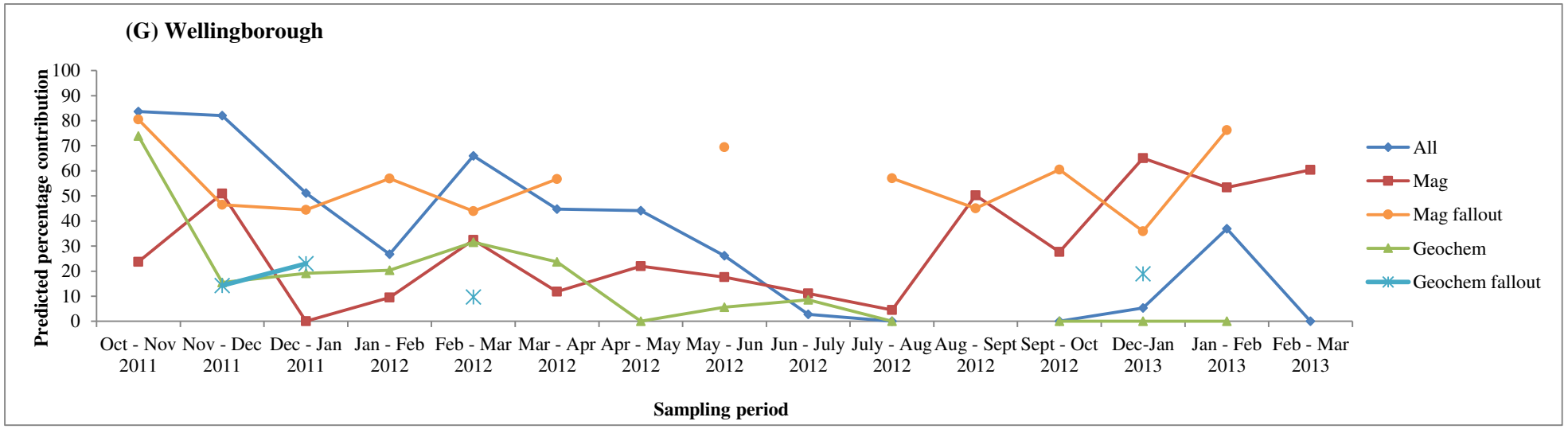

(C) Dodford
Predicted percentage contribution
100
90
80
70
60
50
40
30
20
10
0
Oct - Nov 2011
Nov - Dec 2011
Dec - Jan 2011
Jan - Feb 2012
Feb - Mar 2012
Apr - May 2012
July - Aug 2012
Sept - Oct 2012
Jan - Feb 2013
Feb - Mar 2013
Sampling period
Mag
Mag litho
Mag fallout
Mag geochem
Geochem litho
Geochem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

443


(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

444
445


(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



448

449 **Fig 6.** The monthly median predicted contributions from channel banks to suspended sediment, derived using different tracer groups.

4.2. Objective 2: the effects of changes to the sediment organic matter content and particle size distribution 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 effects of sediment particle size and organic matter content on these differences.

An examination of the SSA and LOI of the sediment samples, compared to the source samples, was initially conducted (Fig 7) to determine if any differences existed. We found that, while the SSA of the sediment (median 1.19 $m^2 g^{-1}$) was comparable to the source samples (median 1.17 $m^2 g^{-1}$) , the LOI of the sediment (median 15.71%) was higher than the majority of channel bank (median 7.47%) and surface agricultural sources (median 10.44%) .

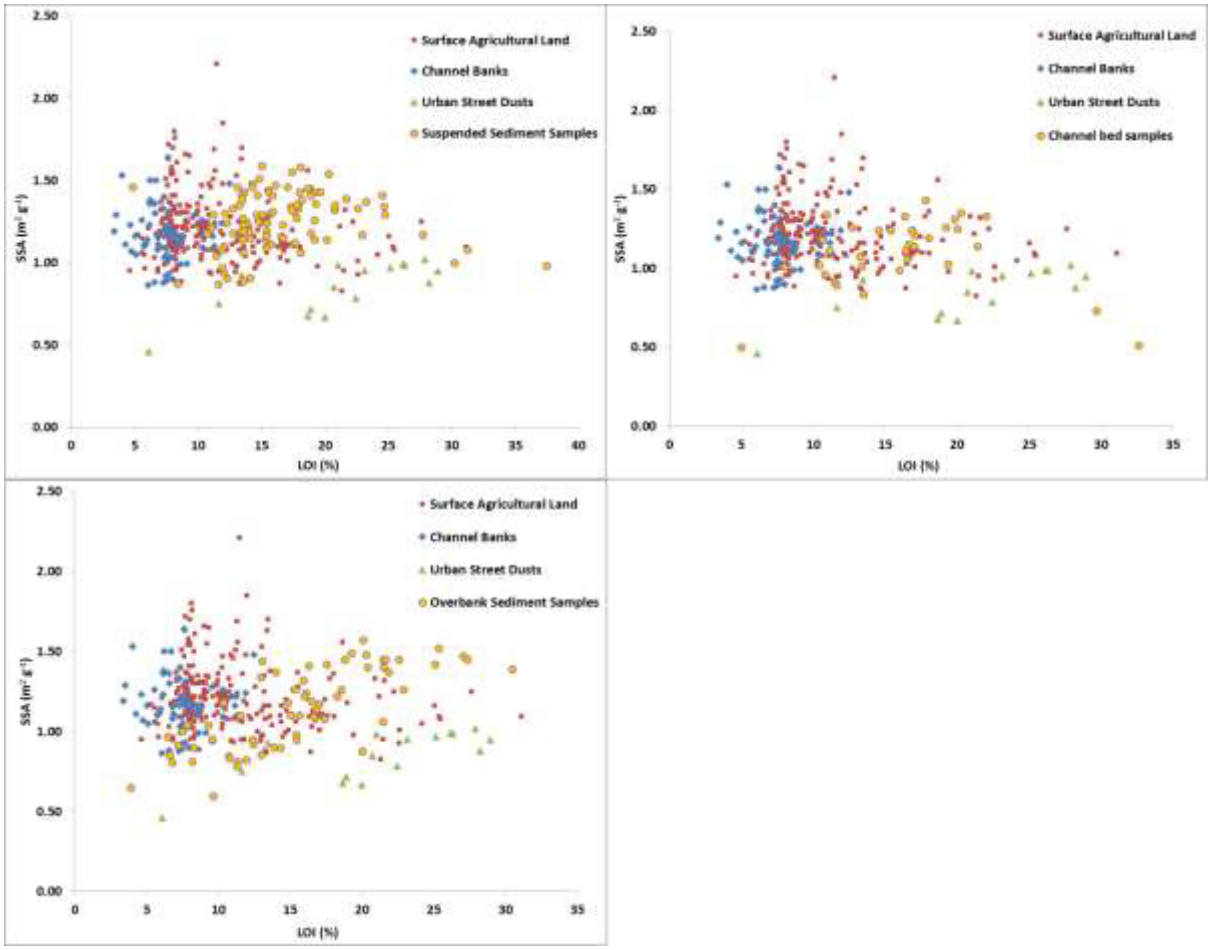


Fig 7. The SSA and LOI of suspended, channel bed and overbank sediment and sediment source samples.

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.

Table 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, we found that in only the Heyford (Table 3E) and Northampton (Table 3G) sites were more than two significant correlations found. These significant correlations were with LOI at both sites and have moderately high correlation coefficients. No significant difference was found between the median LOI of the sediment in these two sampling sites (median 15.62) compared to the other suspended sediment sampling locations (median 15.47), or a large difference in the specific tracers used in the composite fingerprints compared to the other sampling sites. Why an effect of organic matter was only observed at these locations is therefore unclear. 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. Previously published research has highlighted the uncertainty that can potentially be introduced to fingerprinting by changes to the organic matter content and particle size of the sediment. The restriction of the analysis to the < 63µm of sediment in this study, and therefore the generally comparable SSA of the sediment and source samples (Fig. 6), provides a possible explanation as to why these effects were not observed in the Nene. The LOI of the sediment increased in the sediment samples in comparison to the sediment sources. As an effect of this was not apparent when examining the differences between the predictions of most tracer groups in most sampling sites, this suggests that the ~5 to ~8.5% increase in the median LOI of the sediment in comparison to the channel bank and surface agriculture sources was insufficient to have had a major effect on fingerprinting outcomes. Many published fingerprinting studies devote a high priority to accounting for the effects of particle size and organic matter on tracer signatures. The results presented in this section

suggest that in the Nene, the impacts of particle size and organic matter are not the largest causes of uncertainty on fingerprinting outputs. Therefore, the assumption of specific effects of organic matter or particle size should be carefully examined in each individual catchment investigated.

519 **Table 3.** Pearson correlation analysis of percentage point difference between tracer groups and
520 sample SSA and LOI in the monthly sampling period for all suspended sediment samples; only
521 statistically significant (p<0.05) results are displayed

522 **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

523

524 **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	-	-	-

525

526 **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	-	-	-

527

528 **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

529

530 **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	-	-	-

531

532 **F. Kislingbury**

533 No significant correlations found

534

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

4.3. Objective 3: the potential uncertainties associated with catchment and tracer concentration heterogeneity

This section investigates the potential impacts of the heterogeneity of tracer concentrations within sediment source groups. It begins by examining the differences between tracer group provenance predictions when fingerprinting urban street dusts. The fingerprinting of street dusts was examined 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 performed as part of objective 1 was then examined. 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 whether

554 within-source variability in tracer concentrations was sufficient to cause the differences
555 between tracer group predictions observed as part of objective 1.

556

557 *4.3.1. The impacts of a low within-source variability in tracer concentrations and a high contrast*
558 *in tracer concentration between source groups on the differences between tracer group*
559 *predictions*

560

561 If a large amount of spatial variability in erosion and sediment delivery to the river occurred
562 in a catchment, it could potentially result in only a small proportion of the collected sediment
563 source samples actually being from areas that contribute sediment to the river. If this
564 occurred when a large amount of variability in tracer concentrations was present in a source
565 group, a different distribution of tracer concentrations would be found in the collected source
566 samples to that of the sediment's actual sources and a change to model sediment provenance
567 predictions. This subsection explores the potential for this to occur and affect the
568 fingerprinting predictions of different tracer groups observed for objective 1.

569 The potential for error associated with the heterogeneity of sediment source tracer
570 concentrations in the Nene can be seen by examining Fig. 2, which indicates that the
571 discriminatory efficiency of each tracer varied significantly between the different
572 fingerprinting locations used in this study. This finding suggests that either a high spatial
573 variability in tracer discriminatory efficiency exists or that the source sampling was
574 insufficient to fully represent the sediment sources in the regions. Either of these explanations
575 highlights the potential for regional variability in tracer concentration and sediment delivery
576 to introduce uncertainty into the sediment fingerprinting. We can also determine by
577 examining Table 2, 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 4) shows an average COV of 32.8% in the channel bank and surface agriculture source groups and 19.1% for urban street dusts, indicating a significant amount of variability in tracer concentration even within the middle 50% of source samples. The potential for the loss of the basis for source discrimination is therefore clear, as the COV of many tracer concentrations is often larger than the differences in tracer concentrations exploited to form the composite fingerprints.

599 **Table 4.** Coefficients of variation of tracer concentrations in source groups, calculated as
600 (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
^{226}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

601

602 Field-based observations of the localised erosion of small areas of channel bank can be seen
603 in a study reported by Henshaw et al. (2013), who were unable to reliably identify spatial
604 controls on channel bank erosion using factors such as livestock stocking density or channel
605 bank composition. Instead, erosion was thought to occur in 'process-intensity domains'

606 controlled by the hydrology of the river. For surface sediment sources, an examination of
607 modelled rates of erosion in catchments such as that presented by Mutowo and Chikodzi,
608 (2013), indicated that intense soil erosion is predicted to occur in only a small proportion of
609 the overall catchment. Sediment delivery can also be considered as a potential major factor
610 causing localised sediment inputs. Fryirs (2013) highlighted the importance of
611 '(Dis)connectivity' in river catchments; Fryirs argued that (dis)connectivity could result in
612 effective catchment areas greatly reduced in size, in terms of the sediment delivery to the
613 river channel. There therefore exists significant potential for a disparity between sediment
614 sources and the collected source samples.

615 Table 2 shows that larger differences are present between the median concentrations of most
616 tracers in urban street dusts compared to the other sediment sources, than between channel
617 banks and surface agricultural sources. The within-source variability in most tracer
618 concentrations was also lowest in urban street dusts (Table 4). Both of these factors indicate
619 that there is less potential for uncertainty to be introduced into the fingerprinting by regional
620 variations in tracer concentration when fingerprinting urban street dusts. To test this
621 assumption, a comparison was made between the average differences between the tracer
622 group predictions of channel banks and urban street dusts, using the samples of overbank
623 sediment.

624 The results shown in Fig. 8 indicate that average differences between most tracer group
625 predictions range from 8.1 to 11.4% when predicting contributions from urban street dusts,
626 indicating a reduced uncertainty from the average 24.1% difference when predicting
627 contributions from channel banks. This result indicates that there is clearly a positive impact
628 on the reliability of sediment fingerprinting when a robust difference between sediment
629 source tracer concentrations is present. The exception to this improvement is the litho fallout
630 group that continued to have large differences to the predictions of other tracer groups when

fingerprinting contributions from urban street dusts. An analysis of the differences between this tracer and other tracer groups and the organic matter content and particle size of the sediment indicated no effect of either factor. This raises the possibility that other sources of non conservative behaviour exist in the Nene (such as the enrichment (sorption) of $^{210}Pb_{un}$ during sediment transport or chemical alterations to the tracers) are potentially occurring while the sediment is in transit.

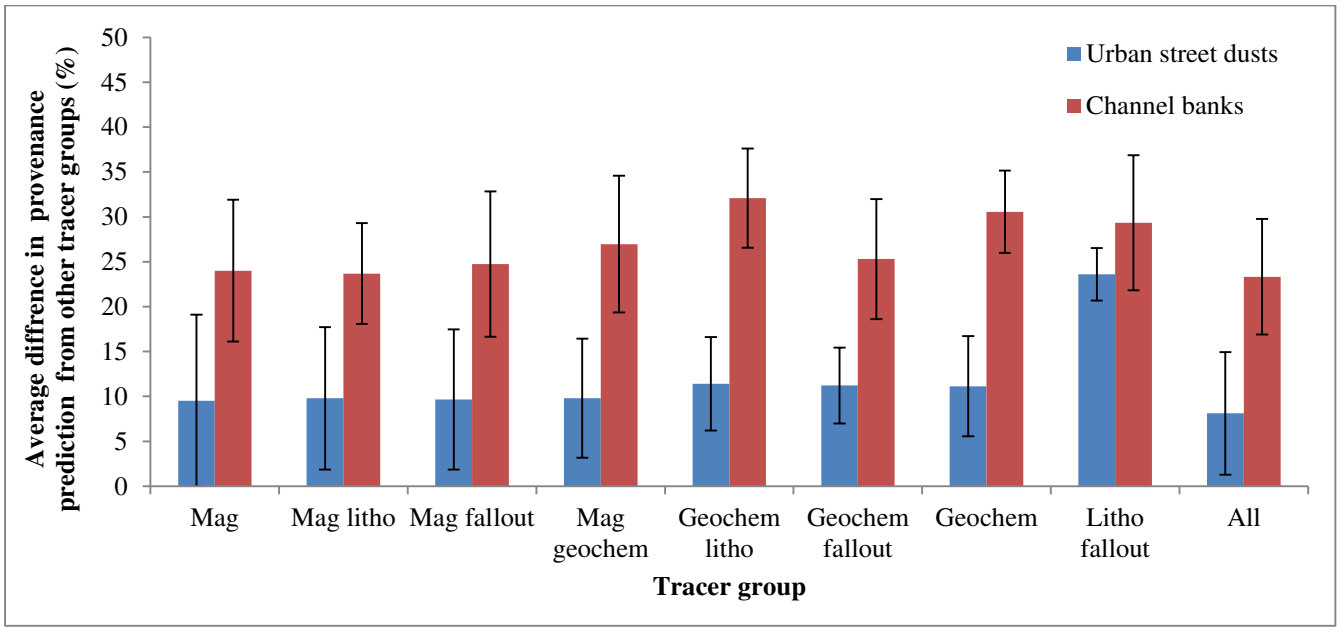


Fig. 8. Mean differences between the predictions of tracer groups, when predicting contributions from channel banks and urban street dusts to sediment deposited overbank after flood events.

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

As part of the fulfillment of objective 3, 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 unmixing model predictions. This was based on the methods used by Small et al. (2002) and 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, unmixing models were run using the range of differences between the median tracer concentrations of two source groups and the range of within-source tracer concentration coefficients of variation shown in Table 5. 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.

668 **Table 5.** The unmixing models run to determine the impact of source tracer concentrations on
669 the variability inherent in unmixing model predictions

Model number	Percentage difference between median tracer concentrations in source groups	Mean within source coefficient of variation (%)	Tracer variability ratio
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

670

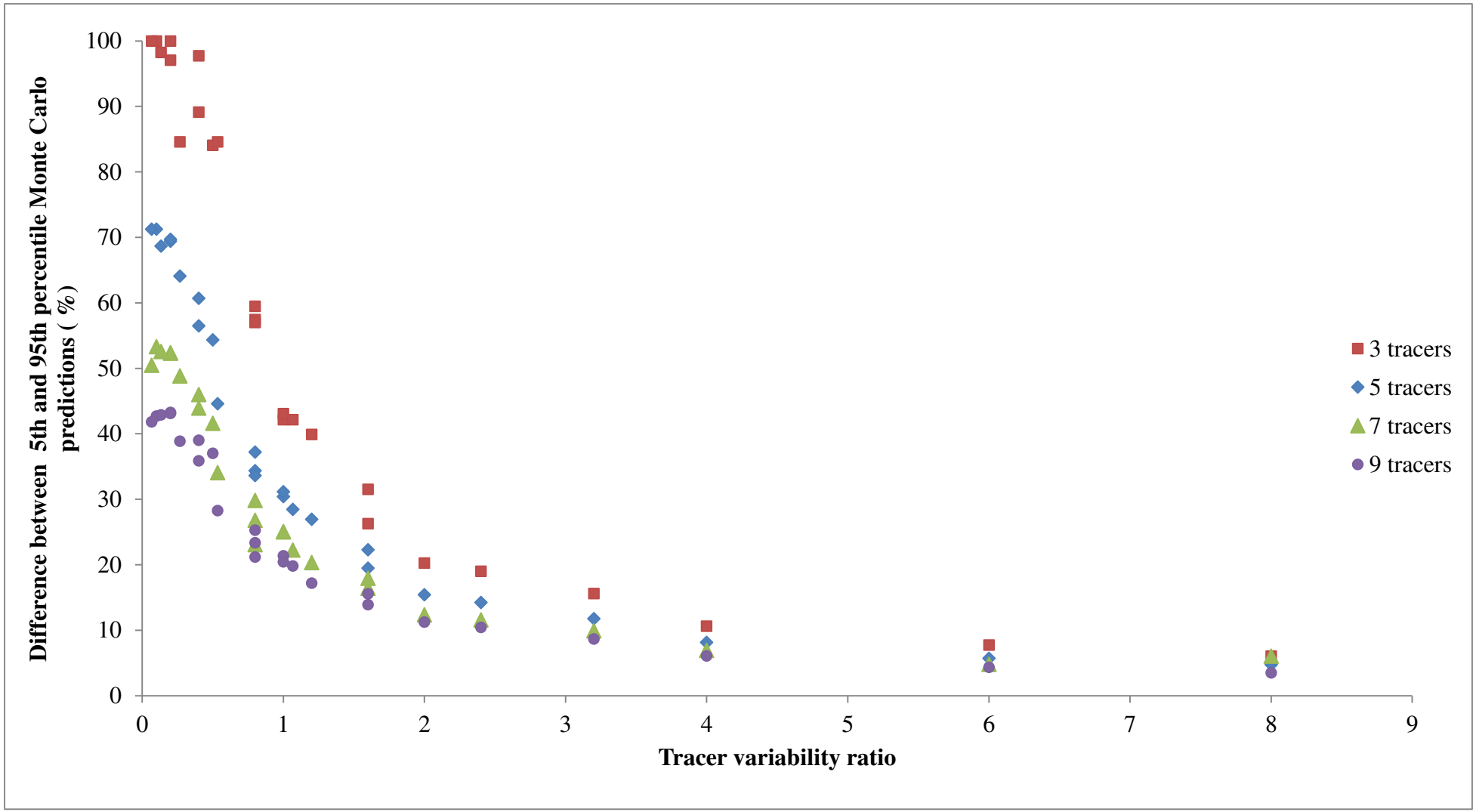
671 The unmixing models were run for 3000 Monte Carlo iterations, and the percentage point
672 difference between the 5th and 95th percentile ranked results were extracted to provide a value
673 close to the maximum potential range of variability for the predictions of each of the
674 unmixing models.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

677 The tracer variability ratio was calculated and plotted against the differences between the 5th
678 and 95th percentile Monte Carlo predictions (Fig 9). This was done for composite fingerprints
679 containing 3, 5, 7, and 9 tracers to determine the additional effects of the number of tracers
680 used in the composite fingerprints. The fingerprints used to fulfil Objective 1 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.

When using 5 tracers, the results in Fig 9 indicate that when the source tracer variability ratio is < 1, the potential uncertainty associated with the fingerprinting steeply increases. 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.

The recommendation can therefore be made 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 > 1. Model uncertainty was also shown to be reduced by using larger composite fingerprints; therefore the recommendation can be made 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, 1993) and to use GOF as a quantification of model reliability (Haddadchi et al., 2013). As section 4.1 showed 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 to the detriment of GOF. The results shown in Fig 9 particularly highlight that fingerprints of only three tracers inherently have a large amount of uncertainty associated with their results.



705

706 **Fig 9.** The ratio of the percentage difference between the median tracer concentrations of source groups / average tracer coefficient of variation in
707 source groups compared to the difference between 5th and 95th percentile Monte Carlo predictions (%).

708 The tracer variability ratios of the tracers used to fulfil Objective 1 were calculated to
709 determine if the tracer variability ratio could account for the differences between tracer group
710 predictions observed as part of objective 1.

711 Fig. 10 shows the tracer variability ratio for each tracer used in this study when comparing
712 tracers in channel banks to those in surface agricultural sources and urban street dusts. The
713 ratio is < 1 for most tracers, and the maximum ratio is 1.3 for ^{137}Cs. The average ratio of 0.6
714 suggests from Fig 9 that a potential uncertainty of ~35% would be expected when 5 to 7
715 tracers were used. The mean difference between tracer group provenance predictions of
716 ~24%, when fingerprinting contributions from channel banks as part of objective 1, was less
717 than the potential uncertainty of ~35% suggested by Fig 9. The uncertainty found is lower
718 than expected, according to the tracer variability ratio, suggesting that the errors caused by
719 regional variability were reduced by a range of sediment inputs more characteristic of source
720 samples used. When comparing tracer variability in channel banks and urban street dusts, the
721 ratio exceeds 1 for the majority of tracers (Fig. 10). The average ratio of 2.3 suggests close to
722 a 14% uncertainty would be expected to be associated with tracer variability; falling close to
723 the average differences of 8.1 to 11.4% between the predicted contributions of sediment from
724 urban street dusts made by the different tracer groups (Fig. 8).

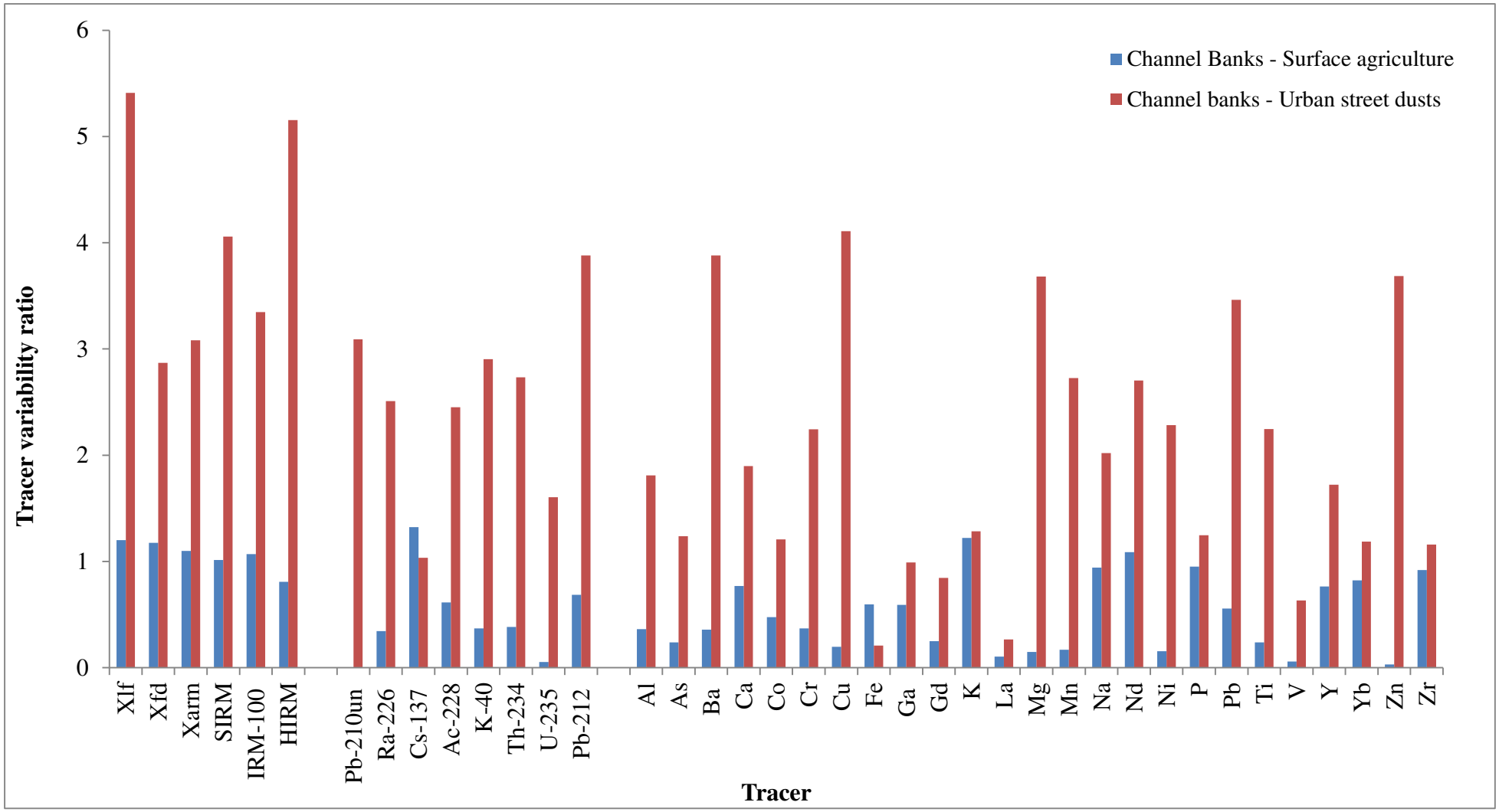


Fig. 10. The ratio of the percentage difference between the median tracer concentrations of source groups / average tracer coefficient of variation in source groups for the tracers in all source samples in the Nene basin.

5. Conclusions

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 and 95%. Therefore a ~24% uncertainty caused by tracer selection is unlikely to change the dominant sediment source identified in most fingerprinting studies. 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 reduced average uncertainty associated with the fingerprinting of urban street dusts (8 to 11%) suggests that sediment sources with significant contrasts between tracer groups are more accurately fingerprinted by almost all tracer groups. Therefore, published results such as those by Collins et al. (2010b) and Carter et al. (2003), who fingerprinted contributions from distinctive road verge and urban street dust sources, are likely to be a more reliable representation of sediment inputs from these sources. This result also suggests 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.

In reviews of the sediment fingerprinting literature by Koiter et al. (2013) and D'Haen et al. (2012), a need to understand the effects of changes to the organic matter content and particle size of sediment on tracers and sediment fingerprinting results was highlighted. The findings of this paper have indicated that variations in sediment organic matter content and particle

size distribution are not the probable causal factors of uncertainty when fingerprinting sediment in the Nene. As a result the findings of this paper support a careful examination of the assumption of particle size and organic effects on a catchment specific basis.

At present, few published sediment fingerprinting investigations have investigated the potential uncertainties associated with within-source variability in tracer concentrations outside of early work by Small et al. (2002). However, the potential for this uncertainty to be present has been recognised. For example, Haddadchi et al. (2013) showed that different unmixing 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 unmixing model approaches used and therefore a potential reason for the differences between model predictions. Smith and Blake (2014) showed that using either mean and standard deviation or median and median absolute deviation to represent the range of sediment source tracer concentrations in unmixing models could produce different provenance 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. It is recommended that the tracer variability ratio be taken into consideration as part of future fingerprinting investigations and is considered as a basis for tracer selection.

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