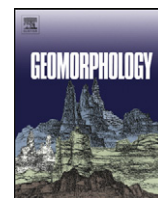


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Sediment fingerprinting in agricultural catchments: A critical re-examination of source discrimination and data corrections

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ABSTRACT

Fine sediment source fingerprinting techniques have been widely applied in agricultural river catchments. Successful source discrimination in agricultural environments depends on the key assumption that land-use source signatures imprinted on catchment soils are decipherable from those due to other landscape factors affecting soil and sediment properties. In this study, we re-examine this critical assumption by investigating (i) the physical and chemical basis for source discrimination and (ii) potential factors that may confound source un-mixing in agricultural catchments, including particle size and organic matter effects on tracer properties. The study is situated in the River Tamar, a predominantly agricultural catchment (920 km²) in south-west England that has also been affected by mining. Source discrimination focused on pasture and cultivated land uses and channel banks. Monthly, time-integrated suspended sediment samples were collected across seven catchments for a 12-month period. Physical and chemical properties measured in source soils and sediment included fallout radionuclides (¹³⁷Cs, excess ²¹⁰Pb), major and minor element geochemical constituents, total organic carbon and particle size. Source discrimination was entirely dependent on differences in tracer property concentrations between surface and sub-surface soils. This is based on fallout radionuclide concentrations that are surface-elevated, while many geochemical properties are surface-depleted due to weathering and pedogenetic effects, although surface soil contamination can reverse this trend. However, source discrimination in the study catchments was limited by (i) rotation of cultivated and pasture fields resulting in reduced differences between these two sources, and (ii) the cultivated source signature resembling a mix of the pasture and channel bank sources for many tracer properties. Furthermore, a combination of metal pollution from abandoned historic mines and organic enrichment of sediment from upland areas of peaty soils resulted in the non-conservative behaviour of some tracer properties in several catchments. Differences in the particle size and organic carbon content of source soils could explain much of the variation in these properties in downstream sediment, rather than selective transport effects. Inconsistent relationships between particle size, organic carbon and tracer property concentrations further undermined the basis for the use of widely applied corrections to tracer datasets. Sensitivity analysis showed that correcting source tracer data for differences in organic matter can produce large changes to source contribution estimates that cannot be justified, and such corrections should not be used. Confounding factors related to poor source discrimination and non-conservative behaviour are highly likely to affect sediment fingerprinting studies in many agricultural catchments. As a result, estimates of source contributions in many fingerprinting studies may contain significant unquantified errors.

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1. Introduction

Fine sediment fingerprinting involves the discrimination of sediment sources based on differences in source material properties and quantification of the relative contributions from these sources to sediment delivered downstream in river catchments. The fingerprinting procedure employs statistical testing of a range of source material tracer properties to select a subset that discriminate sources (Collins and Walling, 2002). These tracers may include geochemical, radionuclide,

mineral magnetic, organic constituent, stable isotope and colour properties (Foster and Lees, 2000). Source un-mixing requires solutions to a set of linear equations that represent the value of an individual tracer property in sediment as a function of the sum of the values of that tracer for each source multiplied by the unknown proportional contribution from each source. Solutions are obtained using optimisation techniques that minimise the sum of errors associated with the equations (Yu and Oldfield, 1989; Collins et al., 1997; Walden et al., 1997).

Multi-parameter sediment source fingerprinting techniques were initially developed in agricultural catchments, and sought to discriminate pasture, cultivated and forest land uses as well as channel bank sources (Peart and Walling, 1986; Walling et al., 1993; Walling and

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Woodward, 1995). Other early approaches to determine fine sediment sources were based exclusively on selected properties such as fallout radionuclides (Wallbrink and Murray, 1993; Wallbrink et al., 1998) or mineral magnetic measurements (Oldfield et al., 1979; Yu and Oldfield, 1989). The key difference between these early approaches was the a priori selection of specific tracer properties based on well-established source differences, in contrast to multi-parameter source fingerprinting which relies on statistical selection of a subset of properties to discriminate sources. There remains a notable divide in the literature between the multi-parameter fingerprinting studies and those that use only pre-selected tracer properties, most commonly the fallout radionuclides ^{137}Cs and excess ^{210}Pb .

Since the initial studies there has been a rapid expansion in research output based on sediment source fingerprinting techniques (see reviews by Walling, 2005; Mukundan et al., 2012). Besides land use or channel bank sources, other fingerprinting studies have focused on discriminating sources according to geological zones based on soil geochemical as well as spectral–colorimetric properties (e.g. Douglas et al., 2009; Evrard et al., 2011; D'Haen et al., 2012; Legout et al., 2013). Fingerprinting studies have also examined sediment sources in urban environments (Carter et al., 2003; Poletto et al., 2009), forest environments including harvest areas and roads (Motha et al., 2003), and in forest areas disturbed by wildfire, where most studies use fallout radionuclide tracers to discriminate hillslope and channel bank sources (e.g. Wilkinson et al., 2009; Smith et al., 2013).

However, source fingerprinting techniques continue to be most widely applied in agricultural catchments (e.g. Owens et al., 2000; Gruszowski et al., 2003; Stutter et al., 2009; Collins et al., 2010a; Martínez-Carreras et al., 2010b; Blake et al., 2012). This reflects demand from land management agencies for information on fine sediment sources and the need to target resources to reduce elevated sediment pollution from agriculture (Gellis and Walling, 2011). In this context, source discrimination continues to focus on land use, while recent studies have sought to extend this to include sources such as damaged road verges, urban street dust and farm track surfaces (Collins et al., 2010a, 2012). With the demand for greater levels of detail and hence inclusion of additional sources related to highly specific landscape features, it is very important to consider the physical and chemical basis for source discrimination that underpins the entire multi-parameter fingerprinting method.

Recent studies tend to present fine sediment source fingerprinting as a robust and highly transferable technique that can deliver accurate estimates of source apportionment with high precision in a range of catchment environments. However, there is a need for further investigation of the extent to which land use-based sources of fine sediment within agricultural catchments can be reliably discriminated and apportioned. A critical assumption underpinning the widespread use of source fingerprinting in agricultural catchments is that land-use source signatures imprinted on catchment soils are decipherable from those due to other landscape factors affecting soil and sediment properties, such as differences in geology, soil type or previous land-use effects (e.g. historic mining). This key underlying assumption for discriminating and apportioning land-use sources has not been adequately acknowledged or challenged in the literature to date.

In this study, we re-examine the application of the fine sediment source fingerprinting procedure to discriminate land use and channel bank sources in agricultural river catchments. The study focuses on the discrimination of pasture, cultivated and channel bank sources of suspended sediment. The objectives are (i) to identify the physical and chemical basis for source discrimination by tracer properties selected using the fingerprinting procedure in agricultural catchments, and (ii) to re-examine the treatment of tracer data for particle size and organic matter effects. It is essential to establish that land use and channel bank source categories can be discriminated and apportioned with confidence, given that these sources form part of all fingerprinting studies

in agricultural catchments. Additionally, because source fingerprinting produces proportional results, a large error in the estimated contribution for one source must affect the results for one or more other sources. Therefore, it is very important that errors in source discrimination and apportionment are constrained, and preferably contextualised using catchment sediment load data to assess source-specific mass contributions.

2. Methods

2.1. Study catchments

The study was situated in the River Tamar, a predominantly agricultural catchment located in south-west England (Fig. 1). The river forms the main boundary between the counties of Devon and Cornwall and drains south into the Tamar Estuary at Plymouth. All source soil and river sediment sampling were conducted above the tidal limit. River monitoring sites were situated at 7 locations comprising 6 sub-catchments nested within the main Tamar catchment (920 km²) upstream of the village of Gunnislake, the study catchment outlet. The monitored sub-catchments include the Rivers Carey (67 km²), Inny (97 km²), Kensey (38 km²), Lyd (219 km²), Ottery (124 km²), and a second measurement site on the main channel of the Tamar in the upper catchment (Tamar Upper; 238 km²).

The topography of the River Tamar is characterised by short, steep hillslopes in the lower and mid-catchment and lower relief, undulating

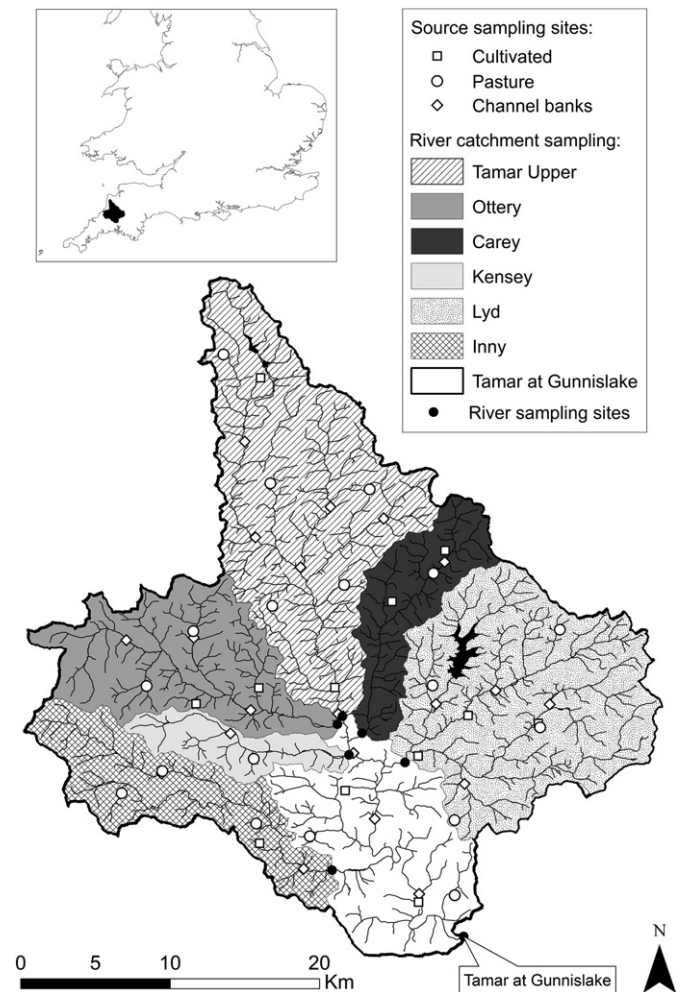


Fig. 1. River Tamar catchment with source soil and river sediment sampling locations displayed.

terrain in the upper catchment, where the maximum elevation is only 226 m. The highest elevation areas are located in the east and west of the catchment where the headwaters of the Rivers Inny (maximum 369 m) and Lyd (maximum 581 m) drain the margins of the granitic uplands of Bodmin Moor and Dartmoor, respectively. Most of the catchment is underlain by fine sedimentary rocks that include mudstones, shales and sandstones. However in the Inny and lower Tamar, there are small areas of extrusive igneous rocks (lavas and tuffs). Soils are predominantly loamy, with some peaty soils in upland areas. The extent of floodplain in the Tamar is limited and confined by narrow steep-sided valleys and shallow bed-rock. The largest floodplain area is located in the mid catchment, where all the main tributary rivers join the main channel with the exception of the Inny (Fig. 1).

The River Tamar at Gunnislake has a mean daily flow of $22.4 \text{ m}^3 \text{ s}^{-1}$, with a range in daily flows from 0.58 to $482 \text{ m}^3 \text{ s}^{-1}$ over the period from 1956 to 2012. Mean annual rainfall for the catchment is $1284 \pm 156 \text{ mm}$ based on 1971–2000 gridded rainfall data ($1 \times 1 \text{ km}$). There is a pronounced spatial variability in rainfall, with highest annual totals over the upland areas in the east and west. There is also pronounced seasonality in annual rainfall and river flows, with the highest discharge generally from November to March. During the 12-month monitoring period from September 2011 to the start of October 2012, mean daily flow was $23.9 \text{ m}^3 \text{ s}^{-1}$ and ranged from 4.5 to $155 \text{ m}^3 \text{ s}^{-1}$. Flows were elevated between November 2011 and early February 2012 after which there was an extended spring dry period (March–April 2012) followed by an unseasonably wet late spring and summer that was characterised by frequent high flows between 40 and $100 \text{ m}^3 \text{ s}^{-1}$.

The 2007 UK Land Cover Map (Morton et al., 2011) indicated that for the Tamar catchment above Gunnislake, all types of grassland accounted for 50% of the land area, with 36% covered by arable land, and 11% by deciduous and coniferous woodlands. The proportion of land classified as arable is changeable in relation to seasons and field rotation, such that many pasture fields may also be periodically cultivated. There are large numbers of mostly 19th Century abandoned metal mines in the southern part of the catchment, mainly in the area around Gunnislake, as well as in the Lyd, Inny and Kensey tributaries. The other sub-catchments are unaffected by mine drainage. Metal pollution from abandoned mines is a problem in the lower catchment. Previous work has estimated mine point source contributions to downstream metal contaminant fluxes and found that >50% was unaccounted for by the surveyed point sources (Mighanetara et al., 2009).

2.2. Source and suspended sediment sampling

Catchment sources were classified as either surface soil divided according to pasture and cultivated land uses or sub-surface soil derived predominantly from channel banks. No gullies were observed in the catchments. Sub-surface drainage of agricultural land could contribute subsoil to streams, although previous work indicated drains are a delivery pathway for mostly topsoil-derived sediment (Foster et al., 2003; Chapman et al., 2005). Surface soil sampling locations were selected from across the Tamar catchment based on the general criteria of (i) proximity and potential connectivity to streams, (ii) access, and (iii) possible evidence of erosion or degradation of pasture sites. Due to analytical constraints on source sample numbers, it was not possible to collect a discrete set of source samples for each sub-catchment. Instead, source samples collected from across the Tamar were pooled and used in un-mixing source contributions for each river sampling location. Sampling of pasture and cultivated sites was distributed across the entire catchment (Fig. 1) to capture potential variability in fingerprint properties associated with differences in rainfall, geology and aspect within these two land use categories. However, it should be noted that the geology of the catchment is

very uniform, with 94% of its area underlain by similar sedimentary rocks.

Surface soils under woodland were not sampled as part of the source characterisation. Initially, woodland soils were to be collected for analysis. However, following inspection of several woodland sites it was found that a plant litter layer 0–5 cm deep and comprised almost entirely of organic material covered the soil. This made sampling of mineral surface soil that could be exposed to surface erosion impossible. Furthermore, there was no evidence of surface erosion in these woodland locations, which is supported by studies in the UK that show minimal erosion and sediment contributions from woodlands (Evans, 1990; Walling et al., 1999). Therefore, it was decided to focus the sampling effort on those land uses that covered most of the catchment and represent a credible source of mineral sediment.

Composite soil samples were collected from all sources. This included 18 composite samples from pasture areas, 12 composites for cultivated areas and 20 composites from channel banks. For surface soils, a minimum of 10 individual samples were collected from 0 to 2 cm depth along transects at approximately 10 m intervals and combined in the field to form a single composite sample. At some sites more individual samples were taken in order to collect material from a wider area. In total, 349 individual surface soil samples were collected from 30 locations around the catchment.

For channel bank sampling, actively eroding channel reaches were selected for sampling following reconnaissance of the channels within each sub-catchment and along the main channel of the River Tamar. In total, 8 composite samples were taken from along the main channel and the remaining 12 were collected from tributary streams. Channel bank sampling involved collection of even scrapes of bank material from the bank top to base. This sampling protocol was based on the recognition that over sufficient time banks will erode across the entire bank height, either by instantaneous collapse or non-synchronous lower and upper bank retreat through a combination of erosion by flow scour and sub-aerial processes (Prosser et al., 2000; Couper and Maddock, 2001; Smith and Dragovich, 2008). A minimum of 10 scrapes were collected for each composite sample. Sampled banks varied in height between 0.5 and 1.5 m.

Suspended sediment was collected at the 7 river monitoring sites using in situ time-integrated samplers based on the design outlined by Phillips et al. (2000). The samplers were made from polyvinylchloride (PVC) tubes 1 m in length and 0.11 m in diameter with sealed caps at both ends that contained 3 mm diameter inlet and outlet tubes. Water and suspended sediment pass through the narrow inlet tube and enter the PVC tube where the change in cross-sectional area promotes a reduction in flow velocity and sedimentation (Phillips et al., 2000). The samplers were installed in pairs at riffles and fixed to lengths of rebar that were hammered into the channel bed. Sampling intervals were approximately monthly, although this varied in relation to water level which sometimes limited site access. Suspended sediment sampling was undertaken over a 12-month period from mid-September 2011 until the start of October 2012 for all sites except the River Carey. At this site, sampling commenced in November 2011 and only 10 samples were collected monthly.

2.3. Laboratory analyses

Source soil samples were initially air-dried, gently disaggregated using a mortar and pestle and sieved to $<63 \mu\text{m}$. It was necessary to oven-dry some wet soil samples at $40 \text{ }^\circ\text{C}$. Water and sediment captured by the time-integrated samplers were removed from the field in 20 l containers and stored in a cold room for 24 h. This allowed settling and extraction of most of the water by siphon. The remaining sediment-water mix was centrifuged at 3000 rpm for 20 min and the supernatant decanted. The sediment samples were freeze-dried for 48 h, then gently disaggregated and sieved to $<63 \mu\text{m}$ for analysis.

Soil and sediment samples were analysed for fallout radionuclides (^{137}Cs , excess ^{210}Pb), geochemical constituents, total organic carbon and particle size. Initially, all soil and most sediment samples were packed into 50 mm Petri dishes in preparation for gamma spectrometer analysis. Some low mass sediment samples were measured in 4 mm vials. The petri dishes and vials were sealed for 21 days to allow equilibration between ^{214}Pb and its progenitor ^{226}Ra . Activity concentrations of the radionuclides were measured using a low background EG&G Ortec planar (GMX50-83-LB-C-SMN-S) and well (GWL-170-15-S) HPGe gamma spectrometers at the Plymouth University Consolidated Radioisotope Facility. Total ^{210}Pb was measured by its gamma emissions at 46.5 keV and its unsupported component calculated by subtraction of ^{226}Ra activity, which was measured using ^{214}Pb gamma emissions at 295 and 352 keV. ^{137}Cs was determined by its gamma emissions at 662 keV (with correction for ^{214}Bi emissions). Count times were typically 24 h, although some low mass sediment samples were counted for 48 h. Analytical performance was assessed by inter-laboratory comparison tests using reference materials supplied by the International Atomic Energy Agency.

Following gamma spectrometer measurements, all samples were unpacked and sub-sampled for analysis by X-Ray Fluorescence (XRF) using a Niton XL3T 950 He GOLDD+ XRF Analyser mounted in a laboratory test stand with He gas purging to permit measurement of light elements. Samples were analysed for major and minor elements (Mo, Nb, Zr, Sr, Rb, Bi, As, Se, Au, Pb, W, Zn, Cu, Re, Ta, Hf, Ni, Co, Fe, Mn, Cr, V, Ti, Ca, K, Ba, Sb, Sn, Cd, Pd, Ag, Al, P, Si, Cl, S and Mg). Only those elements returning measurements above the limit of detection have been employed in the analysis. P was also excluded on the basis of the risk of non-conservative behaviour during downstream transport (Granger et al., 2007).

The unpacked soil and sediment samples were further sub-sampled and measured for total organic carbon (TOC) by the difference between total carbon and inorganic carbon using a Skalar Primacs Carbon Analyser. The particle size distribution of the sieved samples was measured using a Malvern 2000 series laser granulometer. Sub-samples were digested in hydrogen peroxide over 24 h to remove organic matter and disaggregated in an ultrasonic bath prior to particle size analysis. Each sample was run in quintuplicate and the resulting data was checked for any large deviations from the average particle size distributions. Particle size data were used to calculate the specific surface area (SSA, $\text{m}^2 \text{g}^{-1}$) by assuming particle sphericity.

2.4. Sediment fingerprinting procedure

The standard sediment source fingerprinting procedure is based on (i) statistical analysis of difference to identify a subset of tracer properties that discriminate the target sediment sources followed by (ii) the use of multivariate mixing models comprised of a set of linear equations for each selected tracer property to estimate the proportional contributions from each source (Yu and Oldfield, 1989; Collins et al., 1997; Walden et al., 1997). Tracer data often undergoes pre-treatment for particle size and organic matter differences between source soils and sediment. Uncertainty in source estimates is quantified using a Monte Carlo routine that repeatedly solves the mixing model using random samples drawn from probability distributions derived for source groups (Franks and Rowan, 2000).

2.4.1. Particle size and organic matter effects

Prior to the statistical analysis, tracer data is often pre-treated to account for potential particle size or organic matter differences that could affect the comparison of tracer concentrations between source soils and sediment. Pre-treatment of data involves the use of correction factors applied to the $<63 \mu\text{m}$ fraction to account for differences in particle size (e.g. Collins et al., 1997; Gruszowski et al., 2003) and in some studies for organic matter as well (e.g. Collins et al., 1997, 2010a, 2012). These corrections have been justified on the basis of (i) the preferential

adsorption of some tracer properties to finer particles (Horowitz, 1991; He and Walling, 1996) and (ii) the potential for selective transport of fines and organic matter which can become enriched in downstream sediment compared to source soils (Collins et al., 1997; Walling, 2005). As an alternative, a very fine fraction ($<10 \mu\text{m}$) may be extracted to minimise the particle size effect on tracer concentrations and avoid the need for particle size correction (e.g. Wallbrink et al., 2003; Smith et al., 2012). While this might be preferred over the use of correction factors, such a very fine fraction may be less representative of the transported sediment (Koiter et al., 2013). Several fingerprinting studies have not corrected for particle size differences because analysis of particle size indicated no difference between source soils and sediment (Evrard et al., 2011, 2013), while others have not corrected for organic matter due to the risk of over-correction (Walling et al., 1999; Martínez-Carreras et al., 2010a).

The standard particle size and organic matter correction is based on the ratio of specific surface area (SSA) or total organic carbon (TOC) content of each individual sediment sample to the mean SSA or TOC of each source type multiplied by the mean tracer concentration for each source (Collins et al., 1997). Therefore, for each sediment sample, there is a set of corrected mean tracer concentrations for each source type to use in source un-mixing. This straightforward approach to particle size and organic matter corrections relies on the assumption that a positive linear relationship exists between SSA or TOC and tracer concentrations for all tracer properties used. There is evidence of a general positive relationship between SSA and various acid extractable metals (Horowitz and Elrick, 1987) and fallout radionuclides (He and Owens, 1995; He and Walling, 1996), reflecting the increasing adsorption potential of larger SSA (in $\text{m}^2 \text{g}^{-1}$). However, it appears that these relationships are often non-linear and probably logarithmic in form, particularly over $1.0 \text{m}^2 \text{g}^{-1}$ (Horowitz, 1991; Russell et al., 2001). Nonetheless, simple linear corrections may be a reasonable approximation over narrow ranges in SSA. For larger ranges, such as in the study by Russell et al. (2001) where SSA varied from 0.5 to $4.0 \text{m}^2 \text{g}^{-1}$, or where the relationships between particle size and tracer properties are more complex (e.g. Foster et al., 1998), measurement of the specific relationships between particle size and individual tracer property concentrations will be required. In contrast to SSA, no clearly generalizable relationship is apparent for organic matter, with the relationship highly dependent on individual tracer properties and the type of organic matter (Horowitz, 1991). Furthermore, SSA and organic matter content tend to exhibit a positive correlation (Horowitz and Elrick, 1987). As a result, correcting for both SSA and organic matter content could lead to significant over correction and errors in source apportionment.

In the present study, the relations between source soil and sediment SSA, TOC and tracer property concentrations were explored. Bi-plots of SSA versus TOC were used to examine the distribution of sediment from the 7 river monitoring sites relative to data for the three source categories. Bi-plots offer a simple visual means to qualitatively assess conservative behaviour in these two key variables. The strength and direction of linear relationships between individual tracer property concentrations and both SSA and TOC were measured using Pearson correlation coefficients for source soil and sediment datasets.

2.4.2. Statistical analysis for source discrimination

The range in tracer property concentrations in sediment relative to concentrations in source soils has not been specifically reported in source fingerprinting studies until recently (Martínez-Carreras et al., 2010a; Wilkinson et al., 2012). In contrast, source tracing studies using mineral magnetic and fallout radionuclides have frequently provided such information in the form of bi-plots showing source and sediment sample concentrations (e.g. Walden et al., 1997; Wallbrink et al., 2003; Blake et al., 2006; Smith et al., 2011, 2012; Owens et al., 2012). While it is impractical to use bi-plots to examine the multiple tracer properties used in most fingerprinting studies,

examination of the range of source and sediment tracer concentrations is an important assessment of the conservative behaviour of each tracer property. In the present study, the range in source tracer concentrations was compared to the range in sediment concentrations for each river, with those tracer properties falling outside the range in source values removed from subsequent analysis.

Statistical analysis of tracer properties first involves using the non-parametric Kruskal–Wallis *H* test to identify those tracer properties that do not exhibit a significant difference between source categories (Collins and Walling, 2002). It tests the null hypothesis that tracer properties exhibit no significant differences between source categories. Larger differences between categories result in an increase in the *H* statistic. However, the *H* test does not confirm differences between all possible paired combinations of source categories. Therefore, stepwise Discriminant Function Analysis (DFA) is used to further assess the discriminatory power of those tracer properties that pass the Kruskal–Wallis *H* test (Collins and Walling, 2002). The DFA identifies an optimum source fingerprint that comprises the minimum number of tracer properties that provide the greatest discrimination between the analysed source materials based on the minimisation of Wilks' lambda. The lambda value approaches zero as the variability within source categories is reduced relative to the variability between categories based on the entry or removal of tracer properties from the analysis. The results of the DFA are used to examine the proportion of samples accurately classified into the correct source groups.

2.4.3. Source un-mixing and sensitivity analysis

The multivariate mixing model is based on a set of linear equations where each selected tracer property has an equation relating the tracer concentration in a sediment sample to the sum of the mean tracer concentrations for each source multiplied by the respective unknown proportional source contributions. Solutions to the mixing model are obtained by using an optimisation procedure that selects values for P_s which minimises the sum of squares of the relative errors in the objective function (*f*), as in Eq. (1):

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

where C_i is the concentration of tracer property (*i*) in the monthly suspended sediment samples; P_s is the optimized proportional contribution from source (*s*); S_{si} is the mean concentration of tracer property (*i*) in source (*s*); Z_s is the particle size and O_s is the organic matter correction factor for source (*s*); W_i is the tracer specific weighting; *n* is the number of tracers and *m* is the number of sediment sources. In the present study, the particle size and organic matter correction factors were only used in a sensitivity analysis of source apportionment results.

The model is constrained by the requirements that proportional source contributions lie between 0 and 1 and the proportional source contributions sum to 1. The tracer-specific weighting was included so that the tracer properties with least variance exerted greater influence on mixing model solutions. It was calculated as the inverse of the square root of the variance of tracer data for each source that had been standardised by the respective source means (Collins et al., 1997). Furthermore, testing of the local optimisation procedure using multiple random start values resulted in no change compared to single solutions for un-mixing of monthly suspended sediments samples for all catchments, indicating that this local optimisation method was sufficient and use of global optimisation was unnecessary (see also Collins et al., 2010b; Wilkinson et al., 2012).

The model Goodness of Fit (GOF) was tested for every suspended sediment sample and each tracer property that formed part of the optimum fingerprint selected for each catchment. The GOF (%) was based

on the calculated relative difference between actual and modelled values (Motha et al., 2003), as in Eq. (2):

$$\text{GOF} = \left\{ 1 - \left(\left| C_i - \sum_{s=1}^m P_s S_{si} \right| \right) / C_i \right\} * 100. \quad (2)$$

Uncertainty in source apportionment results was determined using a Monte Carlo sampling routine (cf. Franks and Rowan, 2000; Small et al., 2002). This procedure involved solving the mixing model based on random sampling of mean source tracer concentrations for 1000 iterations. The mean values were represented by Student's *t* distributions derived from the mean, standard deviation and sample number for each source sample group. Individual monthly sediment samples were represented by a single tracer concentration. Proportional source estimates generated by the sampling routine were used to provide 95% confidence intervals for mean source contributions based on the 97.5 and 2.5 percentiles for each monthly sediment sample.

Sensitivity analysis of source apportionment results was performed by changing specific input terms to the mixing model related to different data treatments. This analysis quantified the difference in estimates of proportional source contributions between test runs. Model runs used the optimum composite fingerprints (i.e. all tracer properties that were selected by the DFA) and the following inputs: (i) uncorrected mean source values, (ii) uncorrected median source values, (iii) mean source values corrected for SSA only and (iv) mean source values corrected for both SSA and TOC. Solutions to the mixing model were obtained by directly using the mean or median values of the source tracer concentrations for each set of input conditions to isolate the effect of the change in inputs on mean monthly source apportionment results. Comparison of mean monthly proportional source contributions based on the Monte Carlo sampling routine with solutions based directly on mean values of the tracer concentrations indicated a difference of only ± 0.01 for all catchments except the Carey, where the difference was 0.03.

3. Results and discussion

3.1. Testing particle size and organic matter corrections

Bi-plots show that differences in SSA and TOC between source soils may have a large effect on SSA and TOC characteristics in sediment from each of the river monitoring sites (Fig. 2). Kruskal–Wallis *H* tests indicated that source category differences were significant for both SSA ($H = 17.95$; $p < 0.000$) and TOC ($H = 37.11$; $p < 0.000$). For the Tamar Upper, Ottery, Carey, and Tamar Gunnislake sites, SSA and TOC variations in suspended sediment could be entirely explained by source properties alone. For the Kensey, Lyd and Inny, there was clear evidence of TOC enrichment in some sediment samples compared to sources, which could result from erosion of areas of peaty soils in the headwaters of these three tributaries. The Inny exhibited a slight reduction in SSA, reflecting an increase in particle size relative to sources. Temporal changes in contributions from sources could also have an important effect on the SSA and TOC content of suspended sediment samples. However, in many previous fingerprinting studies the difference in particle size and organic matter content between sources and sediment samples has only been attributed to particle sorting and the enrichment of fines and organic matter associated with downstream selective transport (e.g. Collins et al., 1997), rather than to differences between sources. As such, correcting tracer concentrations for each source group using the ratio of sediment-to-source SSA or TOC could alter the key relative differences in tracer concentrations between sources that form the basis for effective source discrimination.

As an illustrative example of the effect of corrections on surface–subsurface signals, mean sources values of $^{210}\text{Pb}_{\text{ex}}$ for the Tamar

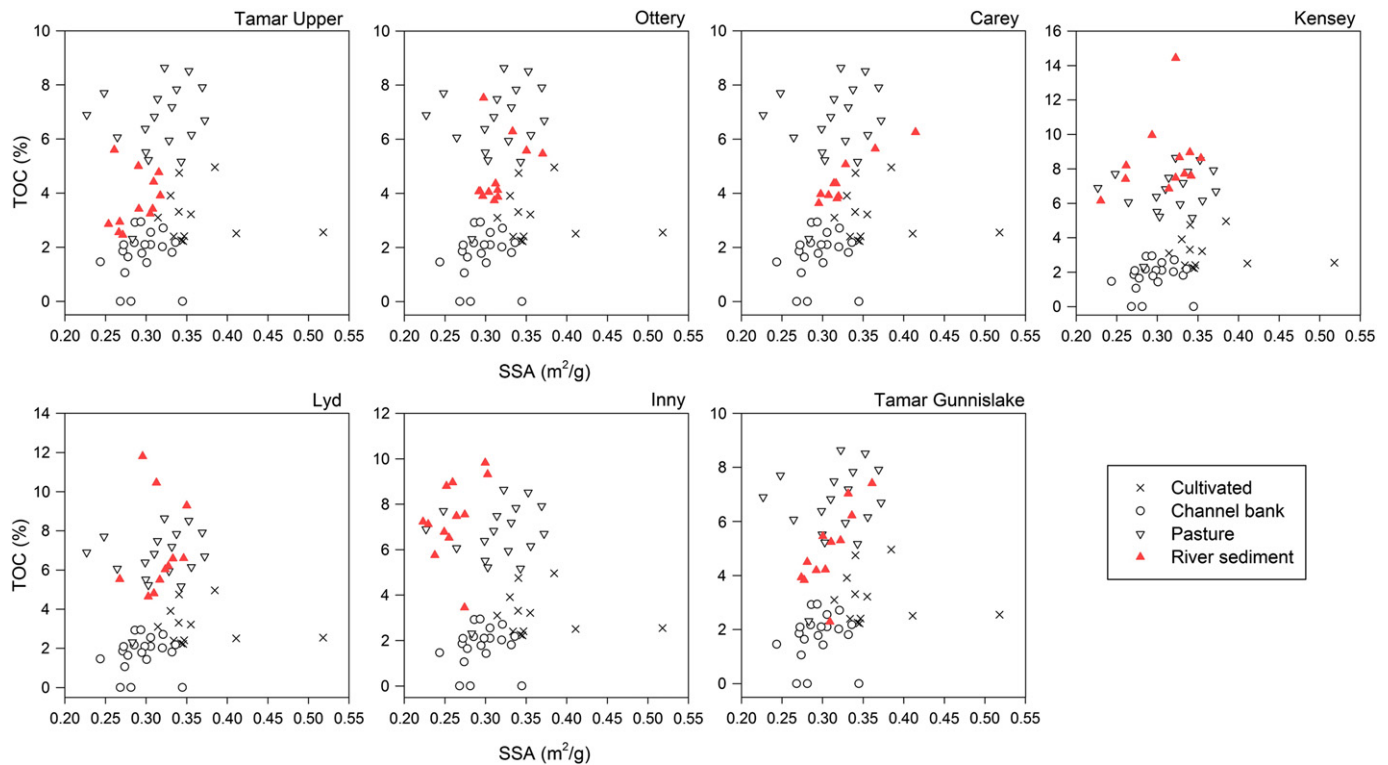


Fig. 2. Plots of specific surface area (SSA) versus total organic carbon (TOC) for monthly suspended sediment samples collected from each river sampling site compared with grouped data for source soil samples collected across the entire Tamar catchment. Note the source data are the same in each plot as well as the differences in y-axis scales.

catchment were 23, 30 and 55 Bq kg^{-1} for channel bank, cultivated and pasture sources, respectively. Applying the combined mean SSA and TOC correction factors (values in brackets) for the Tamar Upper site based on 12 monthly suspended sediment samples gave corrected mean source values of 47 (2.1), 28 (0.9) and 29 (0.5) Bq kg^{-1} for channel bank, cultivated and pasture sources, respectively. This completely altered the basis for source discrimination using $^{210}\text{Pb}_{\text{ex}}$ and produced corrected source values that were not representative by inverting the $^{210}\text{Pb}_{\text{ex}}$ soil depth profile such that the highest mean activity concentration occurred in the channel bank source which contained mostly sub-surface soil with low activity. In another example, mean source values for Si were 293, 320 and 272 g kg^{-1} for channel bank, cultivated and pasture sources. Following correction, mean values (with correction factors) were 887 (3.0), 437 (1.4) and 205 (0.8) g kg^{-1} , respectively. Again, the relative differences between sources were altered by using corrections. Notably, the SSA and TOC correction factors employed here were within the range of factors previously used to correct data from equivalent source types (Collins et al., 1997).

To examine potential linear relationships with tracer property concentrations in source soils and sediment, Pearson correlation coefficients were computed for SSA (Table 1) and TOC (Table 2). These tables show that the occurrence of significant correlations was variable across tracer properties, source categories and sampled rivers for both SSA and TOC. No tracer properties exhibited significant correlations across all sources and sediment from all rivers for either SSA or TOC, although some properties did show pronounced trends. Nor were the significant correlations all positive, as might have been expected, given that SSA and TOC tracer corrections are based on this assumption. This analysis does not isolate the effect of SSA or TOC on tracer concentrations, which reduced the strength of correlations. However, it does allow the identification of trends across source and suspended sediment groups. For example, Zn, Mn, Fe, Rb, Sr, S and Ca showed significant positive correlations with SSA for at least 4 of the 7 river monitoring sites

(Table 1). This was consistent with previous observations of the relationship with SSA for Zn, Mn, and Fe (Horowitz and Elrick, 1987) as well as for Rb (Rawlins et al., 2010) in river sediment. In contrast, Si and Zr displayed significant negative correlations with SSA for most river sediments, while for Zr this also extended to all three source groups. The negative relationship for Si and Zr may reflect a mineral compositional control related to preferential association with the silt fraction (Cuven et al., 2010), and hence a negative relation to SSA. For TOC, consistent significant positive correlations existed with S, Ca, Zn and Fe, whereas there were significant negative correlations for Zr and Ti for 4 or more source and river sediment groups (Table 2). The positive relationships presumably reflected associations with organic matter and the formation of metal–organic complexes (Horowitz, 1991; House and Denison, 2002). In contrast, the mineral origins of Zr and Ti resulted in a negative relationship as increasing TOC reduces the mineral fraction and therefore the concentration of these elements in the samples.

The correlation analysis demonstrates that a positive linear relationship between SSA or TOC and tracer concentrations cannot be assumed to apply uniformly to all the tracer properties examined in the present study. However, many source fingerprinting studies based on geochemical properties apply uniform SSA and TOC corrections without consideration of either the strength or direction of these relationships. As a result of the evidence indicating that (i) much of the variability in SSA and TOC can be explained by differences between sources with noted exceptions and (ii) the inconsistency in the strength and direction of relationships between tracer concentrations and SSA and TOC, the tracer data employed in the subsequent analysis were not corrected. We considered that errors incurred through inappropriate corrections were more likely to exceed those resulting from the use of uncorrected data. Furthermore, comparison of ranges in source and sediment tracer concentrations provided an additional control on conservative behaviour without the need for corrections.

Table 1
Pearson correlation coefficients (r) and associated p values for correlations between specific surface area (SSA) and tracer property concentrations for source soil and suspended sediment samples. Significant correlations are indicated in bold for both the 0.05 significance level (*) and the 0.01 level (**).

Tracer property	Sources						River sediment													
	Cultivated		Channel banks		Pasture		Tamar Upper		Ottery		Carey		Kensley		Lyd		Inny		Tamar Gunnislake	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
¹³⁷ Cs	0.061	0.852	0.127	0.593	-0.416	0.086	0.417	0.177	-0.135	0.675	-0.512	0.130	0.249	0.434	0.508	0.092	0.422	0.171	0.261	0.413
²¹⁰ Pb _{ex}	0.077	0.813	0.161	0.498	-0.550*	0.018	0.442	0.150	0.399	0.198	-0.051	0.889	0.471	0.122	0.289	0.363	0.149	0.645	-0.305	0.334
Ba	0.264	0.406	0.347	0.134	0.405	0.095	0.088	0.785	-0.208	0.518	0.116	0.749	-0.198	0.537	-0.482	0.112	-0.384	0.218	-0.248	0.437
Nb	0.177	0.582	-0.146	0.538	-0.328	0.183	-0.483	0.111	-0.381	0.222	-0.288	0.420	-0.235	0.463	-0.541	0.069	-0.777**	0.003	-0.657*	0.020
Zr	-0.586*	0.045	-0.673**	0.001	-0.733**	0.001	-0.792**	0.002	-0.756**	0.004	-0.954**	0.000	0.011	0.972	-0.826**	0.001	-0.766**	0.004	-0.936**	0.000
Sr	0.432	0.161	-0.231	0.328	-0.072	0.776	0.492	0.105	0.766**	0.004	0.810**	0.005	-0.062	0.848	0.590*	0.044	-0.172	0.592	0.729**	0.007
Rb	0.384	0.218	0.598**	0.005	0.149	0.556	0.653*	0.021	0.449	0.143	0.899**	0.000	-0.011	0.974	0.855**	0.000	0.290	0.361	0.866**	0.000
Pb	-0.146	0.651	0.191	0.419	0.290	0.243	0.754**	0.005	0.469	0.124	0.085	0.816	-0.261	0.413	0.171	0.596	0.121	0.708	0.526	0.079
Zn	0.246	0.440	0.181	0.445	-0.056	0.827	0.617*	0.033	0.794**	0.002	0.910**	0.000	0.450	0.142	0.217	0.499	0.845**	0.001	0.836**	0.001
Fe	0.120	0.711	0.385	0.094	0.336	0.172	0.655*	0.021	0.796**	0.002	0.934**	0.000	0.149	0.643	0.429	0.164	0.491	0.105	0.980**	0.000
Mn	0.609*	0.036	0.273	0.244	-0.016	0.948	0.668*	0.018	0.656*	0.020	0.929**	0.000	0.387	0.214	0.152	0.636	0.748**	0.005	0.900**	0.000
Cr	0.216	0.500	0.142	0.551	0.158	0.532	0.137	0.671	0.734**	0.007	0.473	0.168	-0.096	0.767	0.577*	0.049	0.665*	0.018	0.670*	0.017
V	0.335	0.287	0.450*	0.046	0.718**	0.001	0.259	0.415	0.513	0.088	0.503	0.139	-0.127	0.695	0.371	0.235	-0.231	0.470	0.358	0.253
Ti	-0.163	0.612	-0.218	0.355	0.011	0.964	-0.407	0.189	-0.519	0.084	-0.499	0.142	0.058	0.857	-0.084	0.795	-0.750**	0.005	-0.765**	0.004
Ca	0.162	0.615	-0.263	0.262	-0.646**	0.004	0.641*	0.025	0.915**	0.000	0.736*	0.015	-0.144	0.655	0.267	0.401	0.657*	0.020	0.846**	0.001
K	0.413	0.182	0.653**	0.002	0.524*	0.025	0.573	0.052	0.366	0.242	0.856**	0.002	-0.190	0.553	0.539	0.070	-0.326	0.301	0.508	0.091
Al	0.084	0.795	0.218	0.355	0.700**	0.001	0.274	0.390	-0.030	0.927	0.820**	0.004	0.073	0.823	0.643*	0.024	-0.459	0.133	-0.483	0.112
Si	0.090	0.781	-0.203	0.391	-0.271	0.277	-0.814**	0.001	-0.622*	0.031	-0.917**	0.000	-0.209	0.514	-0.674*	0.016	-0.548	0.065	-0.862**	0.000
S	-0.249	0.435	-0.005	0.983	-0.141	0.576	0.696*	0.012	0.867**	0.000	0.873**	0.001	0.346	0.271	0.320	0.310	0.800**	0.002	0.790**	0.002
Mg	-0.221	0.490	-0.181	0.445	-0.160	0.526	0.529	0.077	0.133	0.679	0.699*	0.025	0.371	0.235	0.073	0.822	-0.345	0.273	-0.192	0.549
Counts (/20)																				
Sign. correl.	2		4		6		9		9		12		0		6		8		12	
Pos. sign. correl.	1		3		2		7		7		10		0		4		5		8	

Table 2
Pearson correlation coefficients (r) and associated p values for correlations between total organic carbon (TOC) and tracer property concentrations for source soil and suspended sediment samples. Significant correlations are indicated in bold for both the 0.05 significance level (*) and the 0.01 level (**).

Tracer property	Sources						River sediment													
	Cultivated		Channel banks		Pasture		Tamar Upper		Ottery		Carey		Kensey		Lyd		Inny		Tamar Gunnislake	
	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p	r	p
¹³⁷ Cs	0.765**	0.004	0.277	0.237	0.351	0.153	0.483	0.112	-0.401	0.196	-0.310	0.383	-0.603*	0.038	0.805**	0.002	0.592*	0.043	0.329	0.297
²¹⁰ Pb _{ex}	0.620*	0.031	0.482*	0.032	0.524*	0.026	-0.086	0.791	0.269	0.398	0.123	0.735	-0.007	0.982	0.015	0.962	0.377	0.226	-0.667*	0.018
Ba	-0.377	0.227	-0.100	0.675	-0.142	0.573	0.181	0.573	-0.130	0.686	0.230	0.523	-0.902**	0.000	-0.863**	0.000	-0.512	0.089	-0.667*	0.018
Nb	0.314	0.320	0.189	0.424	0.010	0.970	-0.701*	0.011	-0.159	0.622	-0.346	0.328	-0.128	0.692	-0.617*	0.033	-0.656*	0.020	-0.539	0.070
Zr	0.087	0.787	-0.167	0.481	-0.598**	0.009	-0.424	0.170	-0.120	0.711	-0.930**	0.000	-0.655*	0.021	-0.837**	0.001	-0.636*	0.026	-0.639*	0.025
Sr	-0.127	0.694	0.019	0.936	-0.182	0.470	0.318	0.314	-0.019	0.954	0.719*	0.019	0.227	0.479	0.284	0.371	-0.216	0.501	0.461	0.131
Rb	-0.319	0.313	0.057	0.812	0.344	0.162	0.257	0.420	-0.177	0.582	0.801**	0.005	-0.121	0.707	0.263	0.408	0.119	0.712	0.483	0.111
Pb	0.054	0.868	0.001	0.995	-0.019	0.939	0.361	0.249	0.468	0.125	-0.065	0.859	0.027	0.935	0.740**	0.006	0.384	0.218	0.331	0.293
Zn	0.088	0.785	0.249	0.290	0.501*	0.034	0.513	0.088	0.650*	0.022	0.870**	0.001	0.256	0.422	0.846**	0.001	0.500	0.098	0.459	0.133
Fe	-0.410	0.185	0.238	0.313	0.574*	0.013	0.437	0.155	0.481	0.113	0.941**	0.000	0.850**	0.000	0.909**	0.000	0.424	0.170	0.700*	0.011
Mn	0.105	0.744	0.082	0.731	0.321	0.194	0.513	0.088	0.429	0.164	0.899**	0.000	0.432	0.161	0.887**	0.000	0.660*	0.019	0.564	0.056
Cr	-0.336	0.285	0.212	0.368	0.362	0.140	0.280	0.378	0.207	0.518	0.539	0.108	-0.177	0.583	0.797**	0.002	0.204	0.524	0.413	0.182
V	-0.333	0.291	0.204	0.388	0.462	0.053	0.035	0.914	0.289	0.363	0.609	0.061	-0.392	0.207	0.613*	0.034	-0.122	0.707	0.179	0.578
Ti	-0.816**	0.001	0.238	0.312	0.091	0.720	-0.639*	0.025	-0.566	0.055	-0.703*	0.023	-0.814**	0.001	-0.360	0.250	-0.560	0.058	-0.559	0.059
Ca	0.522	0.082	0.389	0.090	-0.022	0.931	0.466	0.127	0.288	0.365	0.663*	0.037	0.611*	0.035	0.820**	0.001	0.727**	0.007	0.590*	0.043
K	-0.379	0.224	0.279	0.234	0.436	0.070	0.224	0.484	-0.122	0.706	0.793**	0.006	-0.465	0.127	0.488	0.107	-0.442	0.150	0.253	0.428
Al	-0.704*	0.011	0.328	0.158	0.310	0.210	0.150	0.641	-0.398	0.200	0.827**	0.003	-0.448	0.144	0.529	0.077	-0.350	0.265	-0.549	0.065
Si	0.302	0.340	-0.076	0.751	-0.677**	0.002	-0.412	0.184	-0.335	0.287	-0.902**	0.000	-0.925**	0.000	-0.523	0.081	-0.485	0.110	-0.472	0.122
S	0.875**	0.000	0.684**	0.001	0.789**	0.000	0.450	0.142	0.366	0.242	0.963**	0.000	0.963**	0.000	0.947**	0.000	0.673*	0.017	0.664*	0.019
Mg	-0.126	0.696	0.187	0.431	0.152	0.546	0.261	0.412	0.174	0.589	0.643*	0.045	0.089	0.782	0.480	0.114	-0.494	0.103	-0.376	0.228
Count (/20)																				
Sign. correl.	5		2		6		2		1		13		8		12		6		6	
Pos. sign. correl.	3		2		4		0		1		10		5		9		4		3	

3.2. Tracer conservative behaviour and selection of optimum source fingerprints

The procedure for selection of the optimum source fingerprint for each river monitoring location in the Tamar catchment is summarised in Table 3, which lists the tracer properties included at each step. The comparison of the range in tracer concentrations for source and sediment samples resulted in the exclusion of the largest number of properties from the Rivers Kensey, Lyd and Inny. This probably reflects organic enrichment in some suspended sediment samples, which may be related to the presence of areas of peaty soil in the headwaters of these rivers. Furthermore, these catchments along with the lower Tamar catchment upstream of Gunnislake contain abandoned 19th Century metal mines. This probably accounts for exclusion of Fe, Mn and Zn due to mining contamination of river sediment.

The Kruskal–Wallis *H* test resulted in the exclusion of Sr, Rb, V, Ti and K for all rivers catchments. This includes 3 alkaline earth and alkali metals (Sr, K and Rb), which may have been expected to vary with soil depth as a function of weathering processes (Tyler, 2004). Examination of box-plots for these elements indicated poor discrimination between cultivated and channel bank soils. Both these sources involve mixing of surface and sub-surface soil, which appears to compromise the discrimination potential for these tracers. In addition, Ti occurs in silicate or oxide minerals that are typically highly resistant to weathering (Dawson et al., 1991; Cornu et al., 1999), which probably explains the poor discrimination between surface and sub-surface soils.

The DFA selected the optimum source fingerprints for each river catchment based on the tracer properties passing the first two steps. The optimum fingerprint comprises the minimum number of properties that provide the greatest discrimination between sources. For the Tamar Upper, Ottery, Carey and Tamar Gunnislake monitoring sites, apparently good source discrimination were achieved based on Wilks' lambdas of 0.066–0.068 and the percentage of correctly classified sources varied from 92 to 98% (Table 3). However, for the remaining Kensey, Lyd and Inny sites, source discrimination was less successful. For the Kensey and Inny, the optimum fingerprint comprised 3 tracer properties each and correctly classified sources in 76 and 86% of cases, respectively (Table 3). For the Lyd only one property passed the DFA (^{137}Cs).

The loss of tracer properties during the preceding steps for the Kensey, Lyd and Inny resulted in reduced source discriminatory power. It is apparent that factors specific to these catchments, namely the presence of peaty soils and mining contamination, probably affected the conservative behaviour of some tracers during downstream transport. These factors did not affect the other tributaries (Tamar Upper, Ottery and Carey). Sediment sampled at Tamar Gunnislake represents a mixture from all upstream tributaries. However, a sufficient number of tracer properties passed each step to provide reasonable source discrimination at this site. Evidently mixing and dilution of sediment from all tributaries lessened the impact of the factors affecting tracer conservative behaviour in several of the tributaries. These results emphasise the importance of identifying non-conservative behaviour in tracer properties when selecting optimum source fingerprints. The conservative behaviour of tracer properties has received comparatively

Table 3

Tracer properties included at each step in the sediment fingerprint selection procedure using all source samples. Suspended sediment samples were only used to compare ranges in tracer property data between sources and sediment for each river catchment (step 1).

Step	Tamar Upper	Ottery	Carey	Kensey	Lyd	Inny	Tamar Gunnislake
1. Range	$^{210}\text{Pb}_{\text{ex}}$ Ba Nb Zr Sr Rb Pb Zn Fe Cr V Ti Ca K Al Si S Mg	$^{210}\text{Pb}_{\text{ex}}$ Ba Nb Sr Rb Pb Fe V Ti Ca K Al Si Mg	$^{210}\text{Pb}_{\text{ex}}$ Ba Nb Sr Rb Pb Zn Fe Mn Cr V Ti Ca K Al Si S Mg	Sr Rb Pb Cr V Ti Ca K Al Mg	^{137}Cs Sr Rb Pb Cr V Ti K Al Mg	^{137}Cs Nb Sr Rb Pb Fe Mn Ti Ca K Al Mg	^{137}Cs $^{210}\text{Pb}_{\text{ex}}$ Ba Nb Sr Rb Pb Fe Cr Ti Ca K Al Mg
2. Kruskal–Wallis <i>H</i> test	$^{210}\text{Pb}_{\text{ex}}$ Ba Nb Zr Pb Zn Fe Cr Ca Al Si S Mg	$^{210}\text{Pb}_{\text{ex}}$ Ba Nb Pb Fe Cr Ca Si S Mg	$^{210}\text{Pb}_{\text{ex}}$ Ba Nb Pb Zn Fe Mn Cr Ca Al Si S Mg	Pb Cr Ca Al Mg	^{137}Cs Pb Cr Al Mg	^{137}Cs Nb Pb Fe Mn Cr Ca Al Mg	^{137}Cs $^{210}\text{Pb}_{\text{ex}}$ Ba Nb Pb Fe Cr Ca Al Si Mg
3. DFA	$^{210}\text{Pb}_{\text{ex}}$ Al Pb S Si Zn	Al Cr Pb S Si Fe	$^{210}\text{Pb}_{\text{ex}}$ Al Pb S Si Zn	Al Cr Ca	^{137}Cs	^{137}Cs Al Fe	^{137}Cs $^{210}\text{Pb}_{\text{ex}}$ Al Si Fe
Wilks' lambda	0.066	0.068	0.066	0.441	0.426	0.185	0.067
% correctly classified	92	96	92	76	70	86	98

limited attention in previous studies, despite its importance for source fingerprinting (Foster and Lees, 2000; Koiter et al., 2013).

3.3. Physical and chemical basis for source discrimination by fingerprint properties

Differences in tracer concentrations between the three sources reflect processes differentiating physical and chemical properties of surface and sub-surface soils. Channel banks comprised mostly sub-soil material, with inclusion of some surface soil through sampling of the entire bank profile. In the Tamar catchment, the sampled bank heights ranged from 0.5 to 1.5 m. Cultivated soils included a mixture of surface and sub-surface soil that had been turned over by ploughing to an approximate depth of 25 cm, whereas pasture soils should have included only surface soil, which was sampled to a depth of 2 cm.

Comparison of tracer properties selected by the statistical procedure for all rivers indicated general coherence in the relative differences between sources for mean and median values (Table 4). Key exceptions were Al, where the mean value for cultivated was less than channel banks, but the reverse was true for medians. For Pb, the mean source value for cultivated exceeded pasture, but this was reversed for medians, while cultivated was less than pasture for mean Fe values, but was reversed for medians. In all cases the concentration differences between these source pairs were small, and mean and median values were within uncertainty. However, this indicated that these tracers provided low discriminatory power between these source pairs.

Fallout radionuclides (^{137}Cs , $^{210}\text{Pb}_{\text{ex}}$) are effective sediment source tracers because of their accumulation in the surface soil and tendency to strongly adsorb to fine particles (Wallbrink and Murray, 1993; He and Walling, 1996). Both radionuclides are gradually transferred down the soil profile by a combination of geochemical diffusion, bioturbation and elluviation processes (Walling, 2003; Mabit et al., 2008). This results in distinct undisturbed soil depth profiles for these radionuclides, which peak at or near the soil surface and decline exponentially with depth (Wallbrink et al., 1999). Cultivated soils tend to display a relatively uniform activity concentration to the depth of the mixed plough layer, with generally negligible levels below that depth (Walling, 2003).

These patterns were evident in measured ^{137}Cs and $^{210}\text{Pb}_{\text{ex}}$ activity concentrations (Table 4). Minimum values occurred in channel bank soil, increased for cultivated soils and reached a maximum in pasture surface soils. Radionuclide concentrations were lower in channel bank samples because these comprised mostly sub-soil material containing negligible activity. Depending on the slope of the bank profile, some

direct contributions of $^{210}\text{Pb}_{\text{ex}}$ may have occurred through continuing fallout, whereas for ^{137}Cs bomb-test fallout has ceased and there was negligible fallout from the 1986 Chernobyl nuclear disaster in south-west England (Walling et al., 1989). In the sampled pasture soils, there was a large range in activity concentrations of ^{137}Cs (7.4–21.8 Bq kg⁻¹) and $^{210}\text{Pb}_{\text{ex}}$ (27–106 Bq kg⁻¹). Besides variability in fallout and surface soil redistribution, this probably also reflects previous cultivation of many fields that were under pasture at the time of sampling. The cultivation effect will persist for ^{137}Cs in the absence of continued fallout, whereas it will gradually reset for $^{210}\text{Pb}_{\text{ex}}$ with continuing fallout and down-profile transfer. However, the frequency of field rotation may prevent re-establishment of an undisturbed pasture profile. Therefore, fallout radionuclides are likely to provide reduced precision in the discrimination of pasture versus cultivated surface soils in agricultural areas where pasture fields are periodically cultivated.

Soil geochemical properties may discriminate surface and sub-surface soil on the basis of differences resulting from weathering gradients that vary with soil depth, surface soil contamination or through vegetation decomposition and nutrient cycling in surface soils. Higher concentrations of Al, Cr, Fe, and Zn observed in channel bank sources compared to cultivated or pasture soils could reflect the larger contribution of less weathered sub-surface material, in the absence of a contamination signal in surface soils (Dawson et al., 1991; Tyler, 2004; Křibek et al., 2010; Bini et al., 2011). Si may have been expected to follow a similar pattern. The lowest concentrations of Si occurred in pasture surface soils, whereas the highest occurred in cultivated soils, which is inconsistent with a purely depth-dependent weathering profile. In contrast, pasture soils had the highest concentrations of S and Ca, presumably reflecting the supply to surface soils by atmospheric deposition, vegetation decomposition and nutrient cycling (Evans et al., 1997; Jobbágy and Jackson, 2001, 2004). S exhibited a significant positive relationship with TOC for all source soils (Table 3). Higher values of Pb occurred in pasture and cultivated soils than in channel banks. Differences were small but the higher Pb could reflect atmospheric deposition from anthropogenic sources (Blake and Goulding, 2002).

Principal components analysis (PCA) provides a useful means to analyse variance in multi-tracer datasets and reduce dimensionality (D'Haen et al., 2012). In the present study, we used PCA to examine trends in tracer properties selected by the DFA to form the optimum composite fingerprints (Table 3). Score and loading plots are shown for the first two principal components for each river monitoring site (excluding the River Lyd) in Fig. 3. Combined, the first two components

Table 4
Mean and median values for the uncorrected tracer properties selected as part of the optimum composite fingerprint for each catchment. Means are reported with standard errors (SE) and medians with median absolute deviations (MAD). The units are Bq kg⁻¹ for the fallout radionuclides (^{137}Cs and $^{210}\text{Pb}_{\text{ex}}$) and mg kg⁻¹ for the other tracer properties.

Tracer property		Channel bank (n = 20)	Cultivated (n = 12)	Pasture (n = 18)
^{137}Cs	Mean (SE)	4.9 (0.3)	9.4 (0.6)	11.9 (0.9)
	Median (MAD)	4.9 (1.0)	9.6 (1.5)	10.5 (1.9)
$^{210}\text{Pb}_{\text{ex}}$	Mean (SE)	22.5 (1.5)	29.5 (2.4)	55.1 (4.3)
	Median (MAD)	20.9 (3.4)	29.9 (6.2)	52.1 (8.3)
Al	Mean (SE)	50,350 (1279)	46,752 (3264)	36,599 (1870)
	Median (MAD)	49,118 (2359)	50,065 (6779)	38,193 (4583)
Ca	Mean (SE)	2580 (221)	4784 (777)	5431 (590)
	Median (MAD)	2404 (530)	4277 (1347)	4661 (882)
Cr	Mean (SE)	174 (15)	124 (9.4)	141 (14)
	Median (MAD)	157 (21)	129 (21)	130 (31)
Fe	Mean (SE)	57,412 (2445)	38,565 (2736)	39,329 (2383)
	Median (MAD)	56,918 (5206)	38,738 (3418)	37,310 (6745)
Pb	Mean (SE)	113.0 (0.2)	117.0 (3.3)	114.2 (0.4)
	Median (MAD)	112.9 (0.5)	113.6 (0.3)	114.5 (0.6)
S	Mean (SE)	422 (34)	719 (95)	1473 (97)
	Median (MAD)	383 (67)	700 (209)	1544 (254)
Si	Mean (SE)	293,123 (3809)	319,961 (6672)	272,229 (7321)
	Median (MAD)	291,957 (10867)	316,309 (7406)	270,204 (17624)
Zn	Mean (SE)	123 (9.3)	60 (10)	63 (7.0)
	Median (MAD)	123 (26)	46 (9.5)	56 (18)

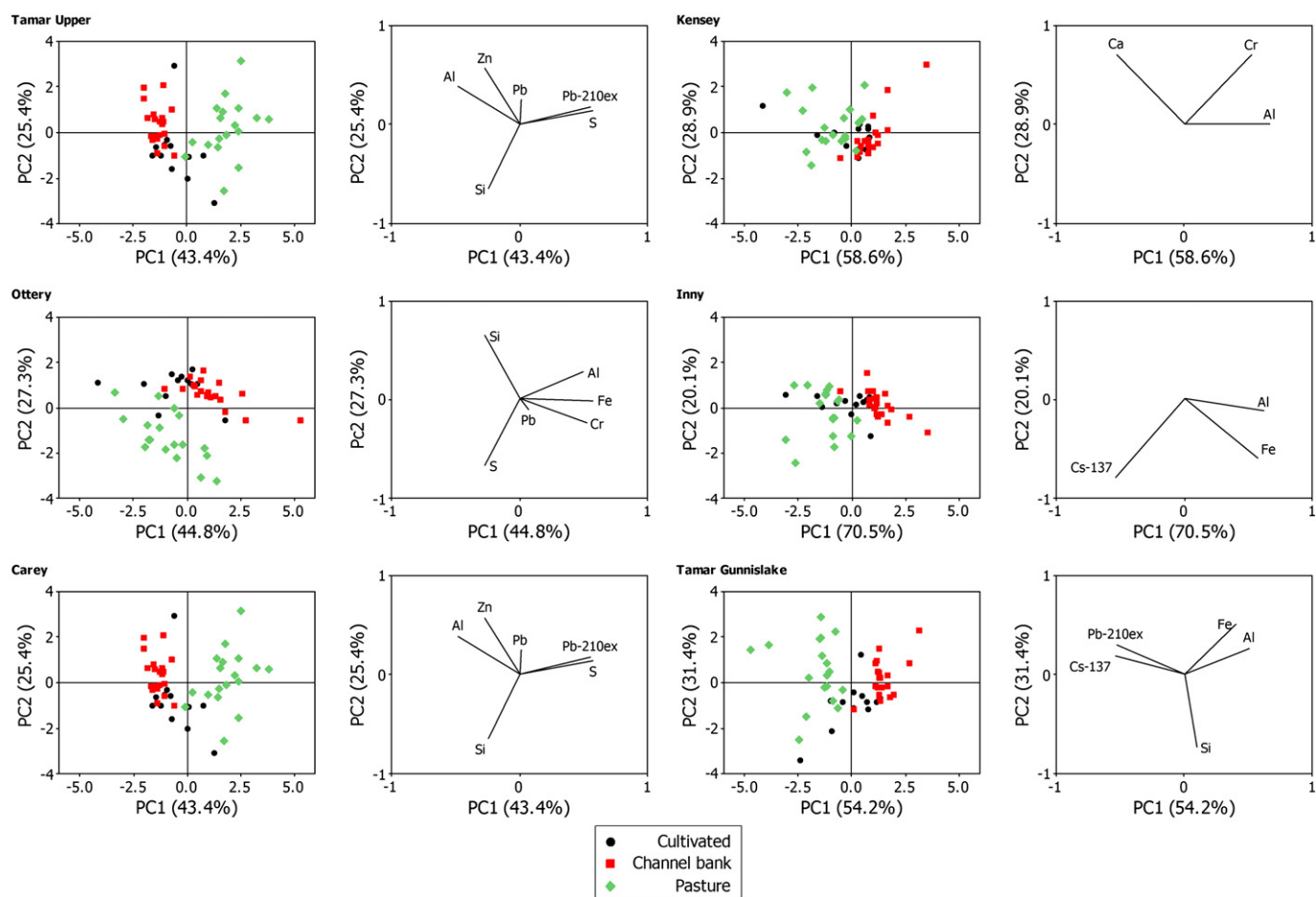


Fig. 3. Principal components analysis (PCA) score (left column) and loading (right column) plots of the first two principal components (PC1 and PC2) for six river sampling sites (excluding Lyd) in the Tamar catchment.

account for between 69 and 91% of the total variance in the source fingerprint data for the catchments. The PCA score plots highlight the better source discrimination achieved for Tamar Upper, Ottery, Carey and Tamar Gunnislake, in contrast to the Kensey and Inny which have fewer tracer properties. The score and loading plots can be used to examine which tracer properties exerted the largest effect on variance in the data. The first principal component largely represents the difference between channel bank and pasture sources. Discrimination between these two sources was dependent on the differences in concentrations of Al, Zn, ²¹⁰Pb_{ex}, ¹³⁷Cs, S and Ca between surface and sub-surface soil. The second component tends to capture the difference between pasture and cultivated sources, and

largely corresponds with discrimination by Si, which formed part of the fingerprint for all catchments in Fig. 3 except the Kensey and Inny. This presumably accounts for the poor discrimination of cultivated sources for these two catchments.

For the successful application of the source fingerprinting procedure, it is essential that the physical and chemical basis for source discrimination is considered. The results from the Tamar catchment show that difficulties may arise when attempting to discriminate surface soils according to pasture versus cultivated land uses. This can result from alternating land-use histories associated with field rotation, such that the pasture and cultivated source signals become less distinct (Blake et al., 2012). Typically, channel bank and pasture

Table 5

Estimated mean proportional source contributions to monthly suspended sediment samples collected at 6 of the 7 river monitoring sites and the associated mean 95% confidence interval (CI) range and mean goodness of fit (GOF) based on the Monte Carlo analysis.

Catchment	Cultivated		Channel banks		Pasture		Mean GOF
	Mean ^a	95% CI range ^b	Mean ^a	95% CI range ^b	Mean ^a	95% CI range ^b	
Tamar Upper	0.01	0.00–0.05	0.52	0.43–0.60	0.47	0.39–0.55	88.4
Ottery	0.00	0.00–0.00	0.40	0.26–0.51	0.60	0.49–0.73	83.7
Carey	0.00	0.00–0.00	0.34	0.23–0.43	0.66	0.57–0.77	81.7
Kensey	0.27	0.00–0.77	0.22	0.07–0.38	0.52	0.02–0.91	79.3
Inny	0.01	0.00–0.16	0.58	0.47–0.67	0.41	0.23–0.51	86.5
Tamar Gunnislake	0.00	0.00–0.00	0.63	0.53–0.72	0.37	0.28–0.47	83.8

^a Suspended sediment load weighting of monthly proportional source contributions would improve accuracy of mean source apportionment results. However, load data was unavailable and flow data (as a surrogate for load) was only available at a few sites. Therefore, un-weighted mean source estimates based on un-mixing of the monthly suspended sediment samples are presented for comparison between the sites.

^b The 95% confidence interval ranges represent the mean of the upper and lower bounds for each monthly measurement interval.

Table 6
Sensitivity analysis of the effect of changes to data treatment on mean monthly proportional source contributions for four of the river catchments that were selected on the basis of reasonable source discrimination (DFA and PCA) and model performance (GOF).

Run	Description of inputs to mixing model	Tamar Upper			Ottery			Carey			Tamar Gunnislake			Max. absolute difference
		Cultivated	Channel bank	Pasture	Cultivated	Channel bank	Pasture	Cultivated	Channel bank	Pasture	Cultivated	Channel bank	Pasture	
<i>Mean monthly proportional source contributions</i>														
1	Uncorrected tracers in optimum fingerprint: mean source values	0.00	0.53	0.47	0.00	0.39	0.61	0.00	0.31	0.69	0.00	0.63	0.37	
2	Uncorrected tracers in optimum fingerprint: median source values	0.00	0.49	0.51	0.00	0.40	0.60	0.00	0.28	0.72	0.00	0.56	0.44	
3	Tracers in optimum fingerprint: mean source values with SSA correction only	0.00	0.52	0.48	0.00	0.37	0.63	0.11	0.26	0.63	0.08	0.57	0.35	
4	Tracers in optimum fingerprint: mean source values with SSA and TOC corrections	0.02	0.37	0.61	0.00	0.17	0.83	0.00	0.17	0.83	0.00	0.18	0.82	
<i>Differences between mean monthly proportional source contributions</i>														
2-1	Mean vs. median source values without corrections	0.00	-0.04	0.04	0.00	0.01	-0.01	0.00	-0.03	0.03	0.00	-0.07	0.07	0.07
3-1	Uncorrected vs. SSA corrected mean source values	0.00	-0.01	0.01	0.00	-0.02	0.02	0.11	-0.05	-0.06	0.08	-0.06	-0.02	0.11
4-1	Uncorrected vs. SSA and TOC corrected mean source values	0.02	-0.16	0.14	0.00	-0.22	0.22	0.00	-0.14	0.14	0.00	-0.45	0.45	0.45

surface soils may be differentiated based on differences in the concentration depth profiles of fallout radionuclides (surface elevated) and geochemical properties sensitive to weathering (surface depleted). During source un-mixing, the cultivated source fingerprint could also resemble a mix of these two sources, unless additional properties can be found to distinguish the cultivated source. In the present study, Si provided this additional discrimination, but it did not pass the statistical selection procedure for all catchments.

3.4. Catchment source contributions and uncertainty

Proportional source contributions to monthly suspended sediment samples were estimated for the river monitoring locations across the River Tamar catchment. This excluded the River Lyd where only one tracer passed the statistical selection procedure (Table 3). Source un-mixing used all tracer properties that were selected by the DFA for each river catchment and the model goodness of fit (GOF) was calculated for each sediment sample and tracer property.

Mean proportional contributions from pasture, cultivated and channel bank sources varied across the six catchments over the 12 month monitoring period (Table 5). Cultivated sources were estimated to contribute an apparently minor amount of sediment to all rivers except the Kensey. However, the Kensey had the lowest mean GOF and the largest predicted uncertainty. Coupled with poor discrimination of cultivated sources by the Kensey fingerprint (Table 3; Fig. 3), the source apportionment results for this catchment should not be considered reliable. Likewise, robust source apportionment for the Inny is unlikely due to poor discrimination of the cultivated source (Fig. 3), despite the higher GOF compared to most other sites. GOF should not be misinterpreted as indicating the accuracy of source apportionment results because it includes no information on the level of source discrimination achieved by selected tracer properties.

The remaining four catchments had mean GOF values of 82–88% and better source discrimination, as reflected in the DFA results and inclusion of Si in each composite fingerprint to distinguish cultivated sources. Nonetheless, the range in predicted upper and lower 95% confidence intervals for these catchments was from 0 to 0.25 with a mean of 0.14. Source apportionment results indicated that channel bank sources (0.63) dominated suspended sediment export for Tamar Gunnislake, whereas pasture sources (0.60–0.66) dominated in the Carey and Ottery catchments (Table 5). The Tamar Upper catchment received suspended

sediment primarily from channel banks and pasture sources in similar proportions, with an apparently negligible input from cultivated sources.

The absence of a cultivated source signal in the source apportionment results for the four catchments was unexpected, given that the Tamar catchment contains a significant cultivated area, which includes maize and wheat. The 2007 land cover map indicated 36% of the catchment area was arable, while in 2000 the area of arable land was approximately 21%. This increase in arable land was almost entirely due to conversion from pasture. On the basis of these land-use data, it seems very plausible that the source un-mixing could have failed to capture a cultivated source input because (i) the rotation of fields between pasture and cultivation contributed to reduced discrimination between current pasture and cultivated fields and (ii) the potential for the cultivated source signature to resemble a mix of pasture and channel bank inputs. Inclusion of Si partly addressed these issues, but it is only 1 tracer out of the 5 or 6 used in source un-mixing for these catchments.

Previous published source fingerprinting work in the Tamar catchment provides a useful context and comparison for the present investigation. These studies focused on determining surface and sub-surface source contributions to fine sediment stored in gravels on the channel bed (Walling et al., 2003). Sediment sampling locations were located in the Inny, Ottery, Lyd and the upper main channel of the Tamar. A repeat study by Collins et al. (2010c) used the same channel bed sampling locations with the aim of identifying the effect of riparian fencing on channel bank sediment contributions. Only mean source contributions were reported in both studies for the whole Tamar, with initial surface and sub-surface inputs of 0.69 and 0.31 (Walling et al., 2003) and subsequent inputs of 0.84 and 0.16 (Collins et al., 2010c). Differences in the method and timing of sampling along with presentation of data hinder direct comparison of previous work with the present study. Nonetheless, channel bank source contributions (0.40–0.52) for the Tamar Upper and Ottery sites are much higher than the overall Tamar mean value of 0.16 reported by Collins et al. (2010c), which is inconsistent with the claim that riparian fencing resulted in a meaningful reduction in channel bank sediment inputs (from 0.31 to 0.16). Attributing changes in proportional source contributions to the effect of catchment management actions or disturbances is tenuous in the absence of sediment load data or an untreated control catchment (Smith et al., 2011). The apparent reduction in proportional channel bank inputs in these previous studies could also be explained by an increase in hillslope

erosion. The fingerprint properties used in source un-mixing may also have had an important effect on the source apportionment results given the potential for non-conservative behaviour of some tracer properties in the Tamar catchment but information on these was not provided to permit comparison. Furthermore, it is relevant to note that Walling et al. (2003) applied both SSA and TOC correction factors in some catchments, while Collins et al. (2010c) used only SSA corrections. These differences in data treatment may have had a large effect on source apportionment results, as is shown in the following sensitivity analysis.

3.5. Sensitivity of source apportionment results to changes in data treatment

Applications of the sediment source fingerprinting procedure involve data treatments that are based on important assumptions which could have large effects on source apportionment results. Perhaps the most critical assumption concerns the relationships between particle size, organic matter content and tracer concentrations in sources and sediment samples. In the present study, we have shown that, contrary to many previous studies, positive linear relationships between tracer concentrations and SSA or TOC cannot be assumed to apply to all tracer properties. To explore the effect of SSA and TOC data corrections, a sensitivity analysis was undertaken to compare source apportionment results using uncorrected, SSA-corrected, and both SSA- and TOC-corrected tracer data. This sensitivity testing also compared the difference in results using mean versus median tracer concentrations to represent source categories.

The sensitivity analysis was performed on the four catchments with apparently reasonable source discrimination and model performance, namely Tamar Upper, Ottery, Carey and Tamar Gunnislake (Table 6). The results of the sensitivity analysis showed that the absolute difference in source estimates between mean and median source tracer values was comparatively small (0–0.07) and within the mean uncertainty range for the four catchments (0.14). SSA corrections to tracer data used in source un-mixing resulted in larger absolute differences in mean monthly source contributions, which ranged from 0 to 0.11. There was a reduction in channel bank contributions for all catchments, but the largest changes were increases to cultivated source contributions. The ranges in mean SSA correction factors used for the catchments were 0.79–0.90, 0.97–1.11 and 0.92–1.04 for cultivated, channel bank and pasture sources, respectively.

The combined SSA and TOC corrections resulted in the largest absolute differences when compared to uncorrected mean monthly data. The combined corrections resulted in changes to source apportionment results between 0 and 0.45. There was a consistent reduction in channel bank and increase in pasture contributions for all catchments (Table 6). The range in mean combined SSA and TOC correction factors for cultivated (0.9–1.4), channel bank (2.1–3.0) and pasture (0.5–0.8) were within the range of values used previously to correct the same source types (Collins et al., 1997). The effect of these combined corrections was to invert the soil depth profiles of tracer concentrations, so that when concentrations in channel banks were less than pasture, use of the combined correction factors resulted in the reverse.

It is clear that use of SSA and TOC correction factors can result in large changes to source apportionment results. The evidence presented in this contribution suggests that use of TOC corrections in particular cannot be supported, given that there is no basis to assume that positive linear relationships exist between TOC and tracer concentrations across all tracer properties. As a result, use of TOC in correcting source tracer data can result in spurious source apportionment results, and those studies that have used TOC corrections are likely to contain unquantified errors. We strongly recommend that source tracer data is not corrected for differences in organic matter. Instead, the exclusion of tracers with sediment concentrations that lie outside the range of sources can be used to limit the effect of any organic enrichment on

tracer properties (Martínez-Carreras et al., 2010a). Likewise, corrections for particle size using SSA may not always be appropriate. Differences in SSA between sources may explain SSA variations in sediment rather than the effects of selective transport, while the specific relationship between different tracer properties and SSA needs to be considered on a case-by-case basis. Careful examination of the SSA characteristics of source soils and sediment is required to determine whether there is a clear transport effect controlling the particle size properties of sediment that warrants correction.

4. Conclusions

This study has re-examined fine sediment source fingerprinting in intensively-farmed agricultural river catchments. It focused on the discrimination and apportionment of contributions of suspended sediment from pasture, cultivated and channel bank sources. These sources have formed the major part of all previous source fingerprinting studies in agricultural catchments. Successful discrimination of land use and channel bank sources in catchments with uniform geological substrate is entirely dependent on differences in tracer property concentrations between surface and sub-surface soil (i.e. vertical controls on properties). This is based on fallout radionuclide concentrations that are surface-elevated, while many geochemical properties are surface-depleted due to weathering and pedogenetic effects, although surface soil contamination can reverse this trend. In the present study, successful source discrimination on this basis was limited by (i) the rotation of cultivated and pasture fields such that the differences in tracer property concentrations between these two sources were less distinct and (ii) the cultivated source signature resembling a mix of the pasture and channel bank sources for many tracer properties, thereby providing poor discrimination during source un-mixing. As a result, negligible sediment contributions were apportioned to cultivated sources, despite the large areas under cultivation across the catchments.

Tracer conservative behaviour during downstream sediment transport is another key assumption underpinning sediment source fingerprinting. In agricultural catchments, it has been assumed that the land-use source signature imprinted on catchment soils is decipherable from that due to other landscape factors affecting soil and sediment properties, such as differences in geology, soil type or previous land use effects. In the present study, a combination of metal pollution from abandoned historic mines and organic enrichment of sediment from upland areas of peaty soils confounded the use of some tracer properties in several catchments. To address this, examination of the ranges in tracer concentrations in soils and sediment is essential for identifying potential non-conservative behaviour and the possible presence of un-sampled sources.

Particle size and organic matter enrichment can exert important effects on tracer concentrations in source soils and sediment. In many previous fingerprinting studies, corrections to source tracer data for differences between sources and sediment have been applied using specific surface area for particle size and total organic carbon content for organic matter. These corrections are based on the assumptions that (i) differences in particle size and organic matter content between sources and sediment are due to selective transport processes and (ii) there are positive linear relationships between concentrations of all tracer properties and SSA or TOC. Findings from this study show that both these assumptions should be routinely challenged. Variations in both SSA and TOC in suspended sediment could be largely attributed to differences in these properties between sources, with noted exceptions. Positive linear relationships between SSA or TOC and tracer concentrations did not apply to all tracer properties. Testing of corrections to tracer concentrations using ratios of sediment-to-source SSA or TOC for each source group altered the key relative differences in tracer concentrations between sources and produced unrepresentative corrected source values leading to spurious results.

Sensitivity testing showed that the use of combined SSA and TOC corrections could result in large changes to source contribution estimates that cannot be justified. Previous studies using organic matter corrections are likely to contain unquantified errors in source apportionment results and we strongly recommend that source tracer datasets are not corrected for differences in organic matter. The choice of correcting for particle size should be carefully considered alongside no correction when assessing uncertainties in source ascription. In cases where particle size corrections seem appropriate, the development of specific relationships between individual tracer properties and particle size fractions should be the preferred basis for corrections. The selection of tracer properties based on knowledge of their likely geochemical behaviour in terrestrial and freshwater environments is an essential part of the sediment source fingerprinting procedure. Statistical analysis techniques should not form a substitute for careful consideration of the physical and chemical basis of tracer property behaviour.

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