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Channel erosion dominates sediment sources in an agricultural catchment in the Upper Yangtze basin of China: Evidence from geochemical fingerprints

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Abstract: A sediment fingerprinting approach was applied to identify dominant sediment sources in an area where soil conservation measures (i.e. terracing) had been carried out on steep, intensively cultivated lands but the outcome was unknown. The wider purpose was to provide scientific evidence to inform decisions on where erosion control and sediment mitigation strategies could be further targeted. Geochemical fingerprints were used to quantify sediment contributions from three potential sources, i.e. surface soil under cropland and woodland land use, and channel banks, in a managed small catchment in the Upper Yangtze River basin in southwestern China. In parallel, artificial mixtures with known source proportions were evaluated to examine the effects of grain size selection (<125 µm and <63 µm) on the accuracy of modeled source contributions. Source apportionment results suggest that materials originating from incised and actively eroding channel banks were the most important source of sediment, which contribute over 80% of sediment to the catchment outlet. Sediment inputs from cropland (10-20%) and woodland (<10%) areas as a result of surface erosion were less important, since effective soil conservation measures have been implemented in this catchment. Although apportionment of sampled sediment provided comparable results for both coarser (<125 μm) and fine (<63 μm) size fractions, the artificial mixture results indicated that unmixing the coarse fraction alone could yield poor agreement between modeled source contributions and actual source proportions. The mean absolute error (MAE) for the coarse fraction mixtures ranged between 8.8% and 19.6%, with a mean of 13.6%, compared to the values of 4.0-7.4%, with a mean of 5.2% for the fine fractions. The results of this study highlight that channel bank materials constitute a significant fraction of suspended sediment exports in a heavily managed agricultural catchment, suggesting that future conservation works should be focused on drivers of erosion from this particular source type. Herein, it is surmised that reworking of legacy valley fill deposits is tempering the downstream benefits (e.g. reduced siltation) of recent upslope soil conservation, an important message for policy makers. The findings of this work also emphasize the methodological need to take account of potential uncertainties associate with source apportionments when using specific particle size fractions in fingerprinting studies.

Keywords: sediment tracing; geochemical fingerprinting; soil conservation; sediment

sources; channel erosion; particle size

1. Introduction

The harmful impacts of soil erosion and sedimentation are widely acknowledged across the globe. These include on-site effects of land degradation and crop productivity reduction, as well as off-site influences such as siltation and eutrophication (e.g. Borrelli et al., 2017; Walling et al., 2003; Warren et al., 2003) with negative consequences for food, water and energy security (Blake et al., 2018). In this regard, the Yangtze River ranks 5th globally in terms of water discharge (900 km^3 $year^{-1}$) and 4th in terms of sediment load (470 Mt $year^{-1}$) (Yang et al., 2011). The Upper Yangtze basin, generally referred to as the area upstream of Yichang in Hubei Province, is one of the most important agricultural areas in southwestern China. It drains an area of 1.04×10^6 km^2, accounting for 55% of the total Yangtze basin area. During the 1950s and early 1990s, the average annual sediment yield was as high as 5.17×10^8 t in the Upper Yangtze basin, which makes it the principal area of sediment supply to the river (Zhang and Wen, 2004). Since the construction of the Three Gorges Dam, the world's largest hydroelectric project located at the mainstream of the Yangtze River in Yichang, the potential impacts of sedimentation has been one of the major environmental issues surrounding the project leading to widespread implementation of measures to combat soil erosion on hillslopes within the river basin.

Characterized by severe soil and water loss (Zhang et al., 2003), steeply sloping cultivated land was identified as a main area of sediment production in the Upper

Yangtze basin. In the late 1980s, this triggered a large-scale soil conservation program known as the 'State Key Soil and Water Conservation Project in the Upper Yangtze River Basin' which was undertaken across catchments of the upper reaches of the Yangtze River. Major soil conservation practices implemented included terracing, conservation tillage, reforestation, and construction of sediment detention ponds and reservoirs. It was reported that during the period 1989-1996, over 3.4×10^4 km^2 of conservation measures have been undertaken in the Jialing and Lower Jinsha river basins, the two largest tributaries of the Upper Yangtze River which have drainage areas of 15.6×10^4 and 48.5×10^4 km^2, respectively (Zhang and Wen, 2004).

With continuous and unprecedented investment by the Chinese government, the sustainability of rural land systems in the Yangtze Basin has been greatly improved (Bryan et al., 2018). For example, soil erosion has decreased by 58.8% on average from 2003-2007 compared to the period 1998-2002 in the Yangtze basin, associated with the Grain-for-Green program (Deng et al., 2012). In parallel, the annual sediment load of the Yangtze River at Yichang has sharply decreased from ~5×10^8 t in the 1980s to ~1×10^8 t in 2010s (Li et al., 2020), which could be attributed, at least partially, to the soil and water conservation projects implemented in this basin.

Despite significant mitigation of soil loss and therefore a reduction of sediment supply on hillslopes, eroding channel banks are often overlooked components in current catchment management policies in China, especially in the upper reaches of the Yangtze River, and little is known about the contribution of this type of erosion to the overall catchment sediment production. In this context, sediment source apportionment data can be used to understand and contextualize soil conservation strategies that limit sediment production and thus to support future land management policy (Tang et al., 2019). However, such information is difficult to obtain, especially in remote areas where the traditional monitoring and modelling techniques (e.g. erosion plots, erosion pins and gauging station) face a number of limitations in terms of the practicalities, representativeness and the costs involved (Collins and Walling, 2004). Since the mid-1970s, the sediment source fingerprinting approach has been widely used as an alternative and effective means of assembling such information (Walling, 2013). This technique has also been increasingly adopted in China to resolve critical soil and sediment management questions that challenge ecosystem service provision in river basins (e.g. Chen et al., 2016; Lin et al., 2015; Zhang et al., 2017; Zhao et al., 2017; Zhou et al., 2016). To date, however, the application of sediment fingerprinting is rather limited in the upper reaches of the Yangtze River; and reliable quantitative information on sediment provenance is believed to be helpful in supporting future catchment management decisions in this area especially with regard to food security and protection of downstream water quality and hydropower production.

The concept of sediment fingerprinting approach is that a single or a suit of the natural physical or biogeochemical sediment properties (i.e. tracers or fingerprints) can be used diagnostically to identify sediment derived from a particular source. One of the most fundamental assumptions underpinning the fingerprinting application is therefore that these tracer properties used behave conservatively during sediment delivery processes (e.g. Foster and Lees, 2000). One key challenge to this assumption is the enrichment and depletion effects caused by particle size selectivity during sediment mobilization and deposition (Walling, 2013). In this context, the choice of an appropriate particle size fraction of sediment is of great concern in fingerprinting studies (Laceby et al., 2017). On one hand, it is widely recognized that particle size can exert important impacts on sediment properties and thus the source ascription results (e.g. Batista et al., 2019; Gaspar et al., 2019; Haddadchi et al., 2015; Koiter et al., 2018; Smith and Blake, 2014). On the other hand, the size fraction selected for analysis should represent the majority of sediment in transport, or closely related to the research or management objectives (Wilkinson et al., 2013). Although the use of a narrow grain size range (e.g. <10 μm) may reduce the potential for particle size related uncertainties, such a very fine fraction may not be representative of the transported sediment (Collins et al., 2017; Walling, 2013).Therefore, there is likely a need to make a compromise between the representativeness of selected particle size fraction and the need to limit it to a relatively narrow range to reduce the potential uncertainties associated (Collins et al., 2017; Laceby et al., 2017).

In this study, the provenance of contemporary suspended sediment was examined in a small agricultural catchment in the Upper Yangtze River basin in southwestern China where soil conservation measures had been recently implemented. While evaluating sediment fingerprinting in a novel context of Chinese catchment-scale soil conservation, a secondary methodological aim was to address the effects of particle size selection on the accuracy of sediment fingerprinting procedures wherein sediment unmixing results were assessed by use of artificial mixtures. A novel aspect of this study is that fingerprinting techniques were applied to identify the predominant source of sediment in an area where soil conservation measures (i.e. terracing) have been implemented on slope cultivated lands, so that erosion control and sediment mitigation strategies could be further targeted.

2. Materials and methods

2.1 Catchment description

The Liangshan catchment (101.9°E, 25.7°N) is located in the Yuanmou County of Yunnan Province, the Lower Jinsha River basin, and drains an area of 4.34 km^2. The Jinsha River is the biggest tributary of the Upper Yangtze and has a drainage area of 48.5×10^4 km^2. Elevation ranges from 2835 m at the summit to 1350 m at the catchment outlet. The local area is characterized by a subtropical monsoonal climate with an average annual temperature of 10.5 °C and a mean annual precipitation of 914.9 mm. The lithology is dominated by Mesozoic sedimentary rocks (mudstone and red sandstone). Soils are yellow-brown and purple soils with bulk densities of 1.2-1.4 g cm^{-3} and are silt loam in texture (Su et al., 2019). Land use consists mainly of woodland (80.2%), with cropland (18.4%) and residential areas (1.4%) comprising the remainder (Figure 1). Woodland is primarily covered by broadleaf trees (e.g. *Quercus semecarpifolia* and *Quercus glauca*) and shrubs (e.g. *Dodonaea viscosa*) (Su et al., 2019), and characterized by high vegetation density. Cropland is concentrated in the middle of the catchment.

Since 1989, soil conservation measures have been implemented in this catchment by both the Chinese government and local farmers, as a part of the 'State Key Soil and

Water Conservation Project in the Upper Yangtze River Basin' project (Zhang and Wen, 2004). Most cropland with gentle gradient in the mid catchment has been converted to terrace and paddy fields. The remaining fields of the cropland were maintained as steep slopes with average gradient of ~20°, which are vulnerable to erosion although these make up just 7.8% of the total catchment area and are patchily distributed across the catchment. Main crops are rain-fed wheat (*Triticum aestivum L.*), corn (*Zeamays L.*), sweet potato (*Ipomoea batatas (L.) Lam*) and groundnut (*Arachis hypogaea L.*) (Su et al., 2019).

Three deeply incised and well-connected 'V' channels approximately 2300 m long and 20 m wide have developed within the study catchment (Figure 1). Although soil erosion control practices has been successfully conducted in the cultivated lands, field investigation indicated that active gravity erosion, e.g. channel bank collapse, was distributed along the main channels especially in sections near the outlet of the catchment where there is evidence of channel incision into valley floor deposits. Within Upper Yangtze tributaries such as the study area, excessive sediment production during floods threatens cropland and residences downstream.

2.2 Sample collection and analysis

Three main potential sediment sources, including cropland, woodland and eroding channel banks, were defined based on land use and field observations. All source materials collected for analysis comprised composite samples formed by combining multiple subsamples (20-30) from different areas in a specific zone to underpin spatial representativeness. Thus, for cropland and woodland sources, each of five composite samples were obtained by scraping surface soils at the depth of 0-2 cm using a plastic trowel. Although terrace and paddy fields cover 10.6% of the catchment area and the puddling process during rice cultivation is known in some cases to generate sediment export, field observations indicate that these lands afford little opportunity for sediment delivery in this system since most of them are protected by well-established field ridges of approximately 60 cm in height (Fig. 1c). Collection of cropland source samples was restricted to the steep slope locations with loose materials that prone to erosion. It was noted, however, that the geochemical properties of these cultivated soils would be representative across the system. To characterize incised and eroding channel banks, samples were taken by scraping exposed channel bank sidewalls from top to base. At locations where channel banks had collapsed, the loose materials deposited at the bottom of the banks were collected as alternatives because these materials are more easily to be transported during floods and hence fully representative of this source material. Valley fill materials potentially comprise legacy material from upland slopes so a key assumption to be tested was that the deposited and stored material carried a geochemical signature discernable from contemporary topsoil. Again, a total of five integrated samples representing the channel bank sources were obtained. Suspended sediment samples were collected at the catchment outlet using three time-integrating samplers (Phillips et al., 2000). The samplers were fixed to the channel bed with steel rods before the wet season on March 8, 2016. Suspended sediment sampling was conducted during the rainy months, when two major runoff events on July 16 and September 20 were recorded. It should be noted here that, although only two storm events were manually recorded since there was no gauge station at our study site, the suspended samples collected were time-integrated materials transported by multiple runoff events which covered the whole wet period of the year. Unfortunately, one sampler was washed away during the second flood. Consequently, five time-integrated sediment samples (~1200 g dry mass per sample) were recovered where the high mass of recovery is indicative of a significant sediment load.

Source and sediment samples were air-dried at room temperature, gently disaggregated using a pestle and mortar, and initially sieved to <2 mm. To determine the dominant grain size in sediment samples, the grain size composition was determined using a Malvern Mastersizer 2000 laser diffraction device (Malven Instruments Ltd.). Prior to analysis, the samples were treated with 10% H_2O_2 to remove organic matter and 10% HCl to remove $CaCO_3$ before being dispersed by use of 0.5 mol L^{-1} sodium hexametaphosphate solution and 2-min ultrasonic agitation. Particle size data in Figure 2 revealed that the majority (>80%) of the target suspended sediments was <125 μm in size; therefore, all source and sediment samples were sieved to <125 μm for measurement. Many studies, however, utilize a finer grained fraction for tracing. Hence, to explore the potential effects of particle size selection on sediment source apportionment, subsamples of the <125 μm fraction of all source and sediment samples were sieved to isolate the <63 μm fraction, which is commonly used in sediment source fingerprinting studies.

Subsamples of 0.2 g (*n* = 20 for each size fraction) were analyzed for their elemental geochemistry using ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry, Optima 8300, Perkin Elmer) and ICP-MS (Inductively Coupled Plasma-Mass Spectrometry, NexION 300, Perkin Elmer) after HNO_3/HF (8.0 mL of concentrated HNO_3 and 4.0 mL concentrated HF) microwave digestion (Mars 6, CEM). The digestion procedure consisted of a temperature–time ramp for 20 min with a final temperature of 180 °C held for 20 min. A total of 41 properties were determined: Ni, Pb, Cu, Cd, Sr, Co, Be, Li, Tl, V, Cr, Zn, Se, In, Cs, U, Ga, Rb, Tm, Yb, Nd, Y, Eu, Dy, Er, Gd, Ho, Lu, Pr, Sm, Tb, Al, Ca, K, Mg, Na, Ti, Fe, Mn, P and S. Elements (Se, In, Tm, Eu, Ho, Lu and Tb) with measurements below the detection limit were excluded from further use. Particle size distributions of the target and source material samples (both <125 μm and <63 μ m) were analyzed to examine the potential differences in grain size between the sources and sediments, using the method described above.

2.3 Tracer selection

A tracer screening procedure that comprised four steps commonly used in sediment source fingerprinting studies was applied to identify a subset of fingerprint properties that discriminate the potential suspended sediment sources: (1) normality test; (2) range test; (3) Kruskal-Wallis *H* test (KW-*H*); and (4) stepwise Discrimination Function Analysis (DFA).

In the first step, the properties returned measurements above the detection limits were tested for normality by using the Shapiro-Wilk test. Whilst this test does not necessarily lead to removal of any property, it was considered an important step in characterizing the statistical distributions of the fingerprint properties in subsequent testing and unmixing processes (Collins et al., 2012a). In step 2, a range or bracket test was employed to ensure that the minimum - maximum concentrations of each tracer in target sediment samples fall within the corresponding range of source groups (Martínez-Carreras et al., 2010). Tracers failing the range test were presumed to be non-conservative in terms of environmental behavior within the soil-sediment continuum, i.e. it was likely that the properties had been altered in some way between source and sink, and were excluded from further use. Subsequently, the nonparametric KW-*H* test was applied to select tracers that exhibited significant difference among source categories. Elements with *p*-values lower than 0.05 were identified as tracers with a significant difference between at least two source groups. Finally, forward stepwise DFA was used to establish an optimum subset of fingerprint that comprises the minimum number of tracer properties but provides the greatest discrimination between sources based on the minimization of the Wilk's Lambda (Collins and Walling, 2002). Default values of the minimum *F to Enter* (3.84) and the maximum *F to Remove* (2.71) were used in this step (SPSS v22).

2.4 Unmixing procedures

An established multivariate mixing model that takes the form of a system of linear equations was used to quantify the relative contribution of each source type to the target sediments (i.e. real catchment sediments and artificial mixtures):

$$\sum_{s=1}^{m} C_{si} \cdot P_s = C_i \quad \text{with} \quad \sum_{s=1}^{m} P_s = 1 \quad \text{and} \quad 0 \le P_s \le 1 \qquad (1)$$

where C_i is the concentration of a tracer property in the target sediment (*i*=1 to *n*, *n* represents the number of tracer properties comprising the optimum composite fingerprint); C_{si} is the concentration of the corresponding tracer property in source type (s=1 to m, m represents the number of potential sediment sources); and P_s is the proportional contribution from individual source type.

Since the number of selected tracers typically exceeds the number of source types (i.e. n>m), the system of Equation (1) is over-determined and a 'solution' can be achieved *via* optimization of an objective function. Traditionally, the objective function has been solved by minimizing of the sum of squares of relative errors (Collins et al., 1997) where:

$$f = \sum_{i=1}^{n} \left(\frac{C_i - \sum_{s=1}^{m} C_{si} \cdot P_s}{C_i} \right)^2 \qquad (2)$$

Early studies recognized the inherent variability of the properties within the source and sediments, and thus the uncertainty associated with the use of single values of tracer concentration (e.g. mean or median) to represent a given source or sediment (Walling, 2013). To address this uncertainty, a Monte Carlo sampling framework has been widely applied. The property values associated with a given source or sediment are characterized by a statistical distribution generated on the basis of their measured values. Using the Monte Carlo method, the property values incorporated into the modelling process can be varied and different possible values of tracer properties can therefore be used. In this study, Student's *t* distributions were simulated for each fingerprint property of both source and sediment samples, since this distribution is considered to be an appropriate distribution when the number of samples is small (Laceby and Olley, 2015). During the distribution modelling, the median value of a specific property within a given source or sediment group was used as the midpoint, the median absolute deviation as the scale and the number of samples minus one as the degree of freedom. Non-negative constraints were set for all property values.

The objective function was repeatedly solved 1000 times with 1000 stratified samples (Latin Hypercube – 500 bins) drawn from the Student's *t* distributions of each tracer property, using the Optquest algorithm in Oracle's Crystal Ball software (Laceby and Olley, 2015). Using the stratified Latin Hypercube approach, the entire domain of the tracer property distributions were sampled systematically (Collins et al., 2012b). Median values of the sum of squares of relative errors were minimized during modelling. The proportional source contributions optimized from the 1000 iterations were used to construct their probability density functions (pdfs). Moreover, the median and the interquartile range of the mixing model solutions were used to interpret the source ascription result, given that the mixing model solutions are typically highly skewed (Batista et al., 2019).

2.5 Artificial mixtures

To validate the accuracy of the fingerprinting method in predicting sediment source contributions within this system, three groups of artificial mixtures with known source proportions were created for each size fraction (i.e. <125 μm and <63 μm). Subsamples of equal weight (10 g) were taken from each of the source samples. The subsamples from the same source types were then manually mixed in a polythene vessel to form a composite sample to represent individual sources. Artificial mixtures were prepared in the laboratory by combining different known proportions of sources based on their weight (Table 1). Taking Mixture 1 as an example, an equivalent 5 g aliquot was retrieved from each source type and mixed to produce one artificial mixture (15 g); thus, the three source types each made a contribution of 33.3% to the mixture. The mixing procedures were undertaken in triplicate and consequently nine artificial mixtures were obtained for each size fraction.

When artificial mixtures are modelled, the accuracy of the model outputs was evaluated using the mean absolute error (MAE) between the predicted and known source contributions (Gholami et al., 2019; Haddadchi et al., 2014):

$$MAE = \frac{1}{m}\left(\sum_{s=1}^{m}\left|P_{predicted} - P_{actual}\right|\right) \qquad (3)$$

where $P_{predicted}$ is the median of the percentage source contribution estimated from the mixing model, P_{actual} is the real percentage source contribution used to create the artificial mixture, and m is the number of sources.

3. Results

3.1 Particle size characteristics of the fractionated material

Comparisons of the median (d_{50}) grain size between source and sediment samples are summarized in Figure 3. Results of the KW-*H* test suggest that there was no significant discrimination between the particle size distributions (in d_{50}) of the three source groups for both fractions. However, significant differences between source and sediment d_{50} were observed using the Mann-Whitney *U* test. Larger d_{50}

values for sediment samples compared to the source materials indicate an enrichment of coarse-grained particles in sediments. This observation further demonstrates that notable contrast can still exist between source and sediment particle size composition, even when sieving all samples to a relatively fine fraction (e.g. <63 μm).

To address the potential effects of contrasting grain size composition between source and sediment samples on tracer properties and therefore the uncertainties in source apportionment results, several studies have incorporated a particle size correction factor into the unmixing model based on the assumption that significant relationships are exist between property values and grain size composition (e.g. Collins et al., 1997; Gellis and Noe, 2013; Motha et al., 2003; Russell et al., 2001). Such assumptions, however, are challenged by increasing evidence that the relations of grain size and tracer property are quite complex, which could be site- or event- or property-specific (e.g. Koiter et al., 2018; Smith and Blake, 2014; Smith et al., 2018). Thus, such correction applications may result in an over-correction and introduce unexpected errors to the results.

Figure 4 plots the concentration of each property against the median grain size of source and sediment samples. Most properties analyzed did not exhibit a significant correlation with the grain size, indicating that an application of particle size correction may not be appropriate. For this reason, no correction factors were employed in the present study to avoid the possibility of over-correction.

3.2 Optimum composite fingerprints

Full geochemical data are provided in Electronic Supplementary material for sources and mixtures (Table S1). Results of the Shapiro-Wilk normality assessment (Tables S2-S5) show that a number of tracer properties failed this test (p<0.05), indicating that they were non-uniform in distribution. Consequently, property distributions for both source and target sediments were characterized using the measured median as location and the median absolute deviation (MAD) as scale. Existing source fingerprinting studies have suggested that, when using frequentist mixing models, median and MAD are more robust statistics than the conventional mean and standard deviation, especially when small number of samples were collected (Collins et al., 2012a; Collins et al., 2012b).

Results of the range test for conservative behavior of the tracers are listed in Tables 2 and 3. Of the 34 properties associated with the real sediment, 23 failed the test for the < 63 µm fraction and 20 for the < 125 µm fraction. For the 34 properties associated with the artificial mixtures, however, relatively few tracers (seven and nine for < 63 µm and <125 µm fractions, respectively) were identified as outliers with their minimum-maximum ranges of mixture samples fall outside the corresponding ranges of source materials. Given that the mixtures were artificial in this case, the high degree of tracer failure can be seen as an artifact of the analytical uncertainty for many tracers measured. The significantly higher failure rates of tracers associated with the real sediments compared to the laboratory mixtures highlight the potential non-conservatism of the elements during their transport along with sediment particles. These findings thereby strengthen the importance of employing an appropriate range test as a filter to eliminate properties that are prone to change during mobilization and transportation through the catchment system.

Tracer properties passing the range test were then assessed for their ability to discriminate between sources using the KW-*H* test (Tables 4 and 5). For the <63 μm fraction in real sediment sources, eight properties (Pb, Co, Cr, Cs, Rb, Al, Mg and S) of the 11 tracers passed the KW-*H* test at $p<0.05$; but for the <125 μm fraction, only three tracers (Rb, Mg and S) provide discrimination, significant at the 95% confidence level, between sources. In the case of the properties associated with sources of artificial mixtures, most elements (74% for <63 μm fraction and 80% for <125 μm fraction) were significantly different at $p<0.05$ and were used in the next step.

Table 6 presents the results from the stepwise DFA to deliver the 'optimum' composite fingerprints for modelling. Generally, high levels of source discrimination were provided, in terms of the percentage of sources correctly classified, through use of these final signatures. All sets of tracers were capable of allocating 100% of source samples to the correct source type, with the exception of the tracers for the <125 μm fraction of real sediment, for which the combination of S and Rb correctly classified 86.7% of source samples.

3.3 Source apportionment for artificial mixtures

Figure 5 presents the probability density functions (pdfs) for the predicted source contributions to the artificial mixtures with different grain size composition. For all mixtures, the relative contributions from each source type exhibit a unimodal and very narrow frequency distribution. This result reflects the high convergence of the model solutions and limited uncertainties associated with the source ascription results.

Defined proportional source contributions can therefore be confidently obtained from the most frequent model solution.

The comparison between estimated source contributions and known mixture proportions reveals that generally good agreement was achieved for the fine-grained (<63 µm) mixtures, with a mean MAE of 5.2% (range 4.0-7.4%) (Table 7). In the case of the <125 µm fractions, the source contribution predictions showed poor consistency with their corresponding real proportions presumably because it was harder to get consistent mixtures. Compositional differences due to correlation between mineral and particle size might also be exaggerated by analytical uncertainty where tracer concentration differences between source groups is small. The much higher MAE errors (mean 13.6%; range 8.8-19.6%) demonstrate weak model performance on coarser particles.

3.4 Source apportionment for catchment sediments

Source ascription results for suspended sediment at the catchment outlet provide clear and unambiguous mixing model solutions (Figure 6). Overall, comparable source apportionment estimates were obtained for the two different grain size fractions (Table 8). Eroding channel banks represented the most important sediment source in the study catchment, with sediment contribution typically exceeded 80% (medians 82.6% and 93.0% for <63 µm and <125 µm fractions, respectively). In contrast, sediment input from cropland appeared to be less important, with median proportions ranging from 17.4% for the <63 µm fraction to 7.0 for the <125 µm fraction. The contribution from woodland areas was negligible during the study period in this catchment. The very narrow interquartile ranges (0-1.3%) of source apportionment data generated using the Monte Carlo routines indicated little variability, and thus low uncertainty of the relative contributions.

4. Discussion

4.1 Geochemical properties and methodological sensitivity to particle size effects

In the context of a relatively uniform geological substrate in the catchment, the geochemical basis of differences between the tracers selected (Table 6) must be grounded in differential weathering impacts between the sources relating to land use (cultivated versus uncultivated) and depth in the soil profile (e.g. surface soil versus incised subsurface channel banks). A large proportion of measured tracers were excluded based on the strict quantitative range test employed in this case noting other authors have promoted more inclusive qualitative approaches based on overlap of the interquartile range (e.g. Blake et al., 2018). It is useful to reflect on the geochemical process rationale for tracer discrimination by the selected properties Pb, Co, Cs, Rb, Mg and S (cf Smith and Blake, 2014). Cropland was relatively depleted in Pb, Cs, Rb, and Mg compared to channel bank samples comprising older valley fill material. This supports a leaching/weathering control on contemporary intensively cultivated soils and clarifies that the valley fill material was geochemically different to upslope materials. For example, the cultivated soil has been preferentially weathered and leached due to disturbance by high intensity agricultural processes. The exception was Co where a wider range was observed in cultivated materials which can be surmised to be linked to application of sewage sludge as a fertilizer. Sulphur was notably greater in topsoil sources due to its well reported correlation with organic matter (see Smith and Blake (2014) and references therein).

Source apportionment modelling results of the artificial mixtures indicated higher absolute error of model predictions to materials with coarser particle size composition (Table 7). Results reported by Batista et al. (2019) also show that sediment source estimates based on the unmixing models were highly uncertain for coarser fractions with grain size >62 µm. These findings suggest that sediment source contribution based on the fingerprinting approaches may be highly sensitive to the grain sizes used. Given that in this case the particle size effect was most pronounced in the artificial mixtures, the differences could be related to the greater challenge in deriving sub samples of the same particle size composition as grain size increases. This is also therefore true in the context of fine sediment sampling and highlights the importance of consistent sampling approaches to capture bulk sediment in transit or storage.

Although a wide range of particle size fractions, ranging between 0 and 2000 µm, have been used in different fingerprinting investigations, an increasing number of studies have emphasized the need of choosing the particle size most relevant to the research and management objectives (Collins et al., 2017; Laceby et al., 2017). Consequently, it is important for fingerprinting studies to support their choice of particle size fraction by, as an initial step, examining the grain size distribution of the target sediment samples. For example, some studies in Australia have focused on the <10 µm fraction on the basis that this fraction is either the dominant particle size in transport (Laceby and Olley, 2015; Olley and Caitcheon, 2000) or the fraction responsible for the environmental problems (Hughes et al., 2009; Wilkinson et al., 2013). Nosrati et al. (2018) used <63 µm fraction based on the particle size information on sediment samples. Unfortunately, such good practice has seldom, if ever, been adhered to. Most researchers have sieved their sediment and source samples simply to a specific particle size fraction, e.g. <63 µm which nominally represents suspended sediment in many temperate systems, without taking the initial grain size composition of the target 'problem' sediments into account. It is also noteworthy that 'fine' sediment particle size is perceived differently in different ecological and socio-economic contexts.

Whilst the suspended sediments collected in this study were predominantly <125 µm in grain size (Figure 2), the methodological validation using artificial mixtures indicate that applying such wide range particle size fraction could introduce significant errors to the source apportionment results (Table 7) if particle size distribution varies within the environment or as an artifact of sampling or sediment processing. Therefore, it is likely that there should be a trade-off between selecting an appropriate size fraction that represents the sediment being transported or targeted and addressing the uncertainties associated with the utilization of coarse particles. In the present research, the similarity between estimated source contributions and actual proportions of the artificial mixtures with <63 µm size increased our confidence in the model predictions for this fraction, although it is less representative (~60% by volume) of the sediment reaching the catchment outlet compared to the broader <125 µm fraction. Herein the size fraction chosen must also reflect the ecological or socio-economic river basin management questions in hand.

Most previous sediment fingerprinting studies have utilized <63 µm as the choice of particle size fraction based on the justifications that, firstly, it represents the dominant proportion of fluvial suspended sediment (Nosrati et al., 2018), it is the most chemically reactive fraction in terms of pollutant transfer, and thirdly, a generally comparable particle size characteristics between source and sediment samples may be achieved by restricting analysis to this fraction (Collins and Walling, 2007; Palazon et al., 2016). The latter is aimed at limiting the potential impacts of particle size differences on tracer concentrations. Whilst coarse size fractions have occasionally been adopted (e.g. Evrard et al., 2011; Rodrigues et al., 2018; Sherriff et al., 2015), the results of this study highlight that the fingerprinting approaches should be applied with caution to coarse particles, especially when geochemical elements are used as tracers. Our findings also imply that, even when restricting the analysis to the <63 µm fraction, there could still be significant differences between particle size composition of source and sediment samples. In such cases, the relation between tracer properties and the grain size should be tested to decide if corrections are feasible.

4.2 Catchment source contributions

Whilst modelled source contributions are highly uncertain for the <125 µm fraction, as indicated by the unmixing results of the artificial mixtures, source apportionment for the catchment outlet sediments appear generally comparable between the two grain sizes (Table 8). Channel banks contributed over 80% of suspended sediment to the outlet of this catchment. In the absence of load data this result can only be used to imply the relative impacts of sources but given the widely observed high turbidity in the system this still has some bearing on management decisions. Field survey suggested that channels have become incised by concentrated high flow during storm events in the Liangshan catchment with well-developed banks comprising thick units (over 2 m depth) former valley fill material that are subjected to active erosion that is effectively reworking legacy deposits from the period prior to soil conservation. As a result, a large amount of loose materials were collapsed from the channel banks due to gravity erosion, which can be transported directly to the channels during rainstorm events. Meanwhile, the adjacency of the sampling locations of channel bank sources to those of the target sediments means that there was greater opportunity for the channel bank materials to be delivered to the catchment outlet than material mobilized from more distal sources. This is further supported by the findings of Haddadchi et al. (2015) and Rodrigues et al. (2018), who have suggested that the closer a source is to the target sediment sampling site, the higher this source contribution. Indeed, the importance of incision processes as a sediment generation factor due to changes in upslope hydrological response has long been recognized in many areas of the world. In Australia, for example, channel and gully incision has been documented to contribute as high as 90% of the sediment yield (Caitcheon et al., 2012; Krause et al., 2003; Olley et al., 2013) often triggered by conversion of native forest vegetation to agriculture. Similarly, considerable contributions from channel banks/subsurface sources have also been determined in some European catchments although relative importance of land management changes is quite catchment-specific

(Collins et al., 2013; Kitch et al., 2019; Palazon et al., 2016; Walling et al., 2008).

Cropland areas represented a less important source of suspended sediment in this catchment at the time of sampling compared to the channel banks. This coheres with most sloping cultivated land within this catchment having been converted into terraces and paddy fields during the implementation of the 'State Key Soil and Water Conservation Project in the Upper Yangtze River Basin' project since 1989. Consequently, the remaining small area of steep cultivated slopes (>15°), which have potential to supply sediment to the catchment channel system, contributed less than 20% of the suspended sediment load.

The contribution from woodland fields was found to be insignificant although this land use type dominates the catchment in terms of area. Evidence from catchment walkovers revealed that most woodland soils are covered by thick litter layer and undergrowth, where both sediment detachment and transport were retarded.

4.3 Management implications

Source apportionment results suggest that a large proportion of the suspended sediment reaching the catchment outlet originated from well-developed and active eroding channel banks that are effectively reworking stored valley fill material deposited in the past. This finding implies that future sediment management strategies should direct particular attention to channel bank stability in areas with similar environmental settings and furthermore identify the root cause of channel incision (Gellis and Sanisaca, 2018). While soil conservation strategies reduce dramatically the influence of agricultural activities on sediment flux and reduce on-site food security challenges of soil erosion, reworking of valley fill materials by runoff can act to maintain the downstream delivery of sediment during catchment recovery (Trimble, 1999). This would appear to be the case in this system where a gradual relaxation to equilibrium of the sediment continuum after the implementation of conservation measures may temper downstream benefits in terms of catchment sediment yield. Herein it is inferred that valley sediment storage was augmented by historic upslope soil erosion in the past and the contemporary sediment output of the system still carries this legacy with downstream consequences for water and energy security. This is an important message for policy makers.

Although steep cultivated slopes in this region have high rates of soil erosion (Zhang et al., 2003), the area of steep sloping cultivated land is relatively small especially in the Lower Jinsha River Basin (Valentin et al., 2015). Natural factors including topography, climate and lithology are key potential contributing factors to soil erosion in this particular area (Valentin et al., 2015). With the continuous investments in ecological conservation and restoration by the Chinese government, diverse soil conservation practices (e.g. reforestation, terracing) have been implemented in the Upper Yangtze River Basin, which further reduced soil loss and sediment production. Perhaps more importantly, rapid urbanization characterized by the migration of the rural population to cities in recent years has led to a significant increase in abandoned farmland in many agricultural catchments in China (Tang et al., 2019). In this context, decreasing sediment contribution from cultivated land and therefore an increased proportion of the river sediment load originating from channel erosion due to incision processes can be expected in such catchments. The progressive refinement of the sediment source fingerprinting techniques offers considerable potential for decision makers in developing targeted sediment control strategies and testing their effectiveness once implemented (e.g. Chen et al., 2016).

4.4 Limitations

It is important to recognize that the lack of instantaneous value of discharge and suspended sediment concentration, and thus sediment load data, represents one potential limitation of this work. Since the mixing model results provide relative, rather than absolute, source contributions, the absence of monitoring on discharge and turbidity at the sediment sampling sites would hamper the definite assessment of the realistic significance of individual source to the total suspended sediment load (Walling et al., 1999). However, the relatively large mass of sediment stored in the traps along with the muddy scenes across the channel indicated high turbidity and discharge of stream flows during wet periods. Thus it could be inferred that the modeled percentages in this study are likely to provide realistic estimates of the contributions from individual source types and that channel incision and mobilization/reworking of valley floor materials is a significant factor.

5. Conclusions

This study has reported the application of a geochemical fingerprinting to determine the sediment provenance in a small agricultural catchment in the Upper Yangtze River basin, southwestern China. Eroding channel banks were demonstrated to be the dominant sediment source, suggesting that future management works should be focused on this particular source type in such catchments. While measures such as improving the integrity of the valley bottom vegetation and reducing contributions of excess runoff to the channel will be important, this challenge needs to be considered within the wider context of reworking of legacy valley fill deposits from the pre-soil conservation eras. This presents a formidable management challenge to mitigate the downstream impacts of enhanced sediment flux. The positive is that intensive agricultural land in this system, where there has been widespread implementation of soil conservation techniques, does not make a substantial contribution to downstream sediment flux confirming the long-term benefit of the regional policies for soil resource retention and food security.

This study has demonstrated the utility of sediment fingerprinting in quantifying sediment sources in a small catchment where effective conservation practices have been implemented. Future studies are undeniably needed to verify the efficiency of the fingerprinting approach in different areas with different sizes and physiographic settings. To evaluate the effectiveness of specific conservation measures and thus to guide more precision land management, targeted and contrastive studies are clearly needed in areas where different management strategies have been taken.

The findings of this work also emphasized that the grain size of particles can exert important effects on sediment source apportionment results. Since the application of broader size ranges has great potential to bias the source ascription results, the use of a properly narrow particle size range is recommended in future fingerprinting investigations.

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References

Batista, P.V.G., Laceby, J.P., Silva, M.L.N., Tassinari, D., Bispo, D.F.A., Curi, N., Davies, J., Quinton, J.N., 2019. Using pedological knowledge to improve sediment source apportionment in tropical environments. J Soil Sediment 19, 3274-3289.

Blake, W.H., Boeckx, P., Stock, B.C., Smith, H.G., Bode, S., Upadhayay, H.R., Gaspar, L., Goddard, R., Lennard, A.T., Lizaga, I., Lobb, D.A., Owens, P.N., Petticrew, E.L., Kuzyk, Z.Z.A., Gari, B.D., Munishi, L., Mtei, K., Nebiyu, A., Mabit, L., Navas, A., Semmens, B.X., 2018. A deconvolutional Bayesian mixing model approach for river basin sediment source apportionment. Sci Rep-Uk 8.

Borrelli, P., Robinson, D.A., Fleischer, L.R., Lugato, E., Ballabio, C., Alewell, C., Meusburger, K., Modugno, S., Schutt, B., Ferro, V., Bagarello, V., Van Oost, K., Montanarella, L., Panagos, P., 2017. An assessment of the global impact of 21st century land use change on soil erosion. Nat Commun 8.

Bryan, B.A., Gao, L., Ye, Y.Q., Sun, X.F., Connor, J.D., Crossman, N.D., Stafford-Smith, M., Wu, J.G., He, C.Y., Yu, D.Y., Liu, Z.F., Li, A., Huang, Q.X., Ren, H., Deng, X.Z., Zheng, H., Niu, J.M., Han, G.D., Hou, X.Y., 2018. China's response to a national land-system sustainability emergency. Nature 559, 193-204.

Caitcheon, G.G., Olley, J.M., Pantus, F., Hancock, G., Leslie, C., 2012. The dominant erosion processes supplying fine sediment to three major rivers in tropical Australia, the Daly (NT), Mitchell (Qld) and Flinders (Qld) Rivers. Geomorphology 151, 188-195.

Chen, F.X., Zhang, F.B., Fang, N.F., Shi, Z.H., 2016. Sediment source analysis using the fingerprinting method in a small catchment of the Loess Plateau, China. J Soil Sediment 16, 1655-1669.

Collins, A.L., Pulley, S., Foster, I.D.L., Gellis, A., Porto, P., Horowitz, A.J., 2017. Sediment source fingerprinting as an aid to catchment management: A review of the current state of knowledge and a methodological decision-tree for end-users. J Environ Manage 194, 86-108.

Collins, A.L., Walling, D.E., 2002. Selecting fingerprint properties for discriminating potential suspended sediment sources in river basins. J Hydrol 261, 218-244.

Collins, A.L., Walling, D.E., 2004. Documenting catchment suspended sediment sources: problems, approaches and prospects. Prog Phys Geog 28, 159-196.

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

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

Collins, A.L., Zhang, Y., McChesney, D., Walling, D.E., Haley, S.M., Smith, P., 2012a. Sediment source tracing in a lowland agricultural catchment in southern England using a modified procedure combining statistical analysis and numerical modelling. Sci Total Environ 414, 301-317.

Collins, A.L., Zhang, Y., Walling, D.E., Grenfell, S.E., Smith, P., Grischeff, J., Locke, A., Sweetapple, A., Brogden, D., 2012b. Quantifying fine-grained sediment sources in the River Axe catchment, southwest England: application of a Monte Carlo numerical modelling framework incorporating local and genetic algorithm optimisation. Hydrol Process 26, 1962-1983.

Collins, A.L., Zhang, Y.S., Hickinbotham, R., Bailey, G., Darlington, S., Grenfell, S.E., Evans, R., Blackwell, M., 2013. Contemporary fine-grained bed sediment sources across the River Wensum Demonstration Test Catchment, UK. Hydrol Process 27, 857-884.

Deng, L., Shangguan, Z.P., Li, R., 2012. Effects of the grain-for-green program on soil erosion in China. Int J Sediment Res 27, 120-127.

Evrard, O., Navratil, O., Ayrault, S., Ahmadi, M., Nemery, J., Legout, C., Lefevre, I., Poirel, A., Bonte, P., Esteves, M., 2011. Combining suspended sediment monitoring and fingerprinting to determine the spatial origin of fine sediment in a mountainous river catchment. Earth Surf Proc Land 36, 1072-1089.

Foster, I.D.L., Lees, J.A., 2000. Tracers in geomorphology: theory and applications in tracing fine particulate sediments. In: Foster, I.D.L. (Ed.), Tracers in Geomorphology. John Wiley

& Sons, Chichester, UK, pp. 3-20.

Gaspar, L., Blake, W.H., Smith, H.G., Lizaga, I., Navas, A., 2019. Testing the sensitivity of a multivariate mixing model using geochemical fingerprints with artificial mixtures. Geoderma 337, 498-510.

Gellis, A.C., Noe, G.B., 2013. Sediment source analysis in the Linganore Creek watershed, Maryland, USA, using the sediment fingerprinting approach: 2008-2010. J Soil Sediment 13, 1735-1753.

Gellis, A.C., Sanisaca, L.G., 2018. Sediment Fingerprinting to Delineate Sources of Sediment in the Agricultural and Forested Smith Creek Watershed, Virginia, USA. J Am Water Resour As 54, 1197-1221.

Gholami, H., Jafari TakhtiNajad, E., Collins, A.L., Fathabadi, A., 2019. Monte Carlo fingerprinting of the terrestrial sources of different particle size fractions of coastal sediment deposits using geochemical tracers: some lessons for the user community. Environ Sci Pollut Res Int.

Haddadchi, A., Olley, J., Laceby, P., 2014. Accuracy of mixing models in predicting sediment source contributions. Sci Total Environ 497, 139-152.

Haddadchi, A., Olley, J., Pietsch, T., 2015. Quantifying sources of suspended sediment in three size fractions. J Soil Sediment 15, 2086-2100.

Hughes, A.O., Olley, J.M., Croke, J.C., McKergow, L.A., 2009. Sediment source changes over the last 250 years in a dry-tropical catchment, central Queensland, Australia. Geomorphology

104, 262-275.

Kitch, J.L., Phillips, J., Peukert, S., Taylor, A., Blake, W.H., 2019. Understanding the geomorphic consequences of enhanced overland flow in mixed agricultural systems: sediment fingerprinting demonstrates the need for integrated upstream and downstream thinking. J Soil Sediment 19, 3319-3331.

Koiter, A.J., Owens, P.N., Petticrew, E.L., Lobb, D.A., 2018. Assessment of particle size and organic matter correction factors in sediment source fingerprinting investigations: An example of two contrasting watersheds in Canada. Geoderma 325, 195-207.

Krause, A.K., Franks, S.W., Kalma, J.D., Loughran, R.J., Rowan, J.S., 2003. Multi-parameter fingerprinting of sediment deposition in a small gullied catchment in SE Australia. Catena 53, 327-348.

Laceby, J.P., Evrard, O., Smith, H.G., Blake, W.H., Olley, J.M., Minella, J.P.G., Owens, P.N., 2017. The challenges and opportunities of addressing particle size effects in sediment source fingerprinting: A review. Earth-Sci Rev 169, 85-103.

Laceby, J.P., Olley, J., 2015. An examination of geochemical modelling approaches to tracing sediment sources incorporating distribution mixing and elemental correlations. Hydrol Process 29, 1669-1685.

Li, L., Ni, J.R., Chang, F., Yue, Y., Frolova, N., Magritsky, D., Borthwick, A.G.L., Ciais, P., Wang, Y.C., Zheng, C.M., Walling, D.E., 2020. Global trends in water and sediment fluxes of the world's large rivers. Sci Bull 65, 62-69.

Lin, J.S., Huang, Y.H., Wang, M.K., Jiang, F.S., Zhang, X.B., Ge, H.L., 2015. Assessing the sources of sediment transported in gully systems using a fingerprinting approach: An example from South-east China. Catena 129, 9-17.

Martínez-Carreras, N., Udelhoven, T., Krein, A., Gallart, F., Iffly, J.F., Ziebel, J., Hoffmann, L., Pfister, L., Walling, D.E., 2010. The use of sediment colour measured by diffuse reflectance spectrometry to determine sediment sources: Application to the Attert River catchment (Luxembourg). J Hydrol 382, 49-63.

Motha, J.A., Wallbrink, P.J., Hairsine, P.B., Grayson, R.B., 2003. Determining the sources of suspended sediment in a forested catchment in southeastern Australia. Water Resour Res 39, 1056.

Nosrati, K., Collins, A.L., Madankan, M., 2018. Fingerprinting sub-basin spatial sediment sources using different multivariate statistical techniques and the Modified MixSIR model. Catena 164, 32-43.

Olley, J., Burton, J., Smolders, K., Pantus, F., Pietsch, T., 2013. The application of fallout radionuclides to determine the dominant erosion process in water supply catchments of subtropical South-east Queensland, Australia. Hydrol Process 27, 885-895.

Olley, J., Caitcheon, G., 2000. Major element chemistry of sediments from the Darling-Barwon River and its tributaries: implications for sediment and phosphorus sources. Hydrol Process 14, 1159-1175.

Palazon, L., Latorre, B., Gaspar, L., Blake, W.H., Smith, H.G., Navas, A., 2016. Combining catchment modelling and sediment fingerprinting to assess sediment dynamics in a

Spanish Pyrenean river system. Sci Total Environ 569, 1136-1148.

Phillips, J.M., Russell, M.A., Walling, D.E., 2000. Time-integrated sampling of fluvial suspended sediment: a simple methodology for small catchments. Hydrol Process 14, 2589-2602.

Rodrigues, M.F., Reichert, J.M., Burrow, R.A., Flores, E.M.M., Minella, J.P.G., Rodrigues, L.A., Oliveira, J.S.S., Cavalcante, R.B.L., 2018. Coarse and fine sediment sources in nested watersheds with eucalyptus forest. Land Degrad Dev 29, 2237-2253.

Russell, M.A., Walling, D.E., Hodgkinson, R.A., 2001. Suspended sediment sources in two small lowland agricultural catchments in the UK. J Hydrol 252, 1-24.

Sherriff, S.C., Franks, S.W., Rowan, J.S., Fenton, O., O'hUallachain, D., 2015. Uncertainty-based assessment of tracer selection, tracer non-conservativeness and multiple solutions in sediment fingerprinting using synthetic and field data. J Soil Sediment 15, 2101-2116.

Smith, H.G., Blake, W.H., 2014. Sediment fingerprinting in agricultural catchments: A critical re-examination of source discrimination and data corrections. Geomorphology 204, 177-191.

Smith, H.G., Karam, D.S., Lennard, A.T., 2018. Evaluating tracer selection for catchment sediment fingerprinting. J Soil Sediment 18, 3005-3019.

Su, Z.A., Xiong, D.H., Zhang, J.H., Zhou, T., Yang, H.K., Dong, Y.F., Fang, H.D., Shi, L.T., 2019. Variation in the vertical zonality of erodibility and critical shear stress of rill erosion in China's Hengduan Mountains. Earth Surf Proc Land 44, 88-97.

Tang, Q., Fu, B.J., Wen, A.B., Zhang, X.B., He, X.B., Collins, A.L., 2019. Fingerprinting the sources of water-mobilized sediment threatening agricultural and water resource sustainability: Progress, challenges and prospects in China. Sci China Earth Sci 62, 2017-2030.

Trimble, S.W., 1999. Decreased rates of alluvial sediment storage in the Coon Creek Basin, Wisconsin, 1975-93. Science 285, 1244-1246.

Valentin, G., Zhang, X.B., He, X.B., Tang, Q., Zhou, P., 2015. Principal Denudation Processes and Their Contribution to Fluvial Suspended Sediment Yields in the Upper Yangtze River Basin and Volga River Basin. J Mt Sci-Engl 12, 101-122.

Walling, D.E., 2013. The evolution of sediment source fingerprinting investigations in fluvial systems. J Soil Sediment 13, 1658-1675.

Walling, D.E., Collins, A.L., Stroud, R.W., 2008. Tracing suspended sediment and particulate phosphorus sources in catchments. J Hydrol 350, 274-289.

Walling, D.E., Owens, P.N., Carter, J., Leeks, G.J.L., Lewis, S., Meharg, A.A., Wright, J., 2003. Storage of sediment-associated nutrients and contaminants in river channel and floodplain systems. Appl Geochem 18, 195-220.

Walling, D.E., Owens, P.N., Leeks, G.J.L., 1999. Fingerprinting suspended sediment sources in the catchment of the River Ouse, Yorkshire, UK. Hydrol Process 13, 955-975.

Warren, N., Allan, I.J., Carter, J.E., House, W.A., Parker, A., 2003. Pesticides and other micro-organic contaminants in freshwater sedimentary environments - a review. Appl Geochem 18, 159-194.

Wilkinson, S.N., Hancock, G.J., Bartley, R., Hawdon, A.A., Keen, R.J., 2013. Using sediment tracing to assess processes and spatial patterns of erosion in grazed rangelands, Burdekin River basin, Australia. Agr Ecosyst Environ 180, 90-102.

Yang, S.L., Milliman, J.D., Li, P., Xu, K., 2011. 50,000 dams later: Erosion of the Yangtze River and its delta. Global Planet Change 75, 14-20.

Zhang, J.Q., Yang, M.Y., Zhang, F.B., Zhang, W., Zhao, T.Y., Li, Y.Y., 2017. Fingerprinting Sediment Sources After an Extreme Rainstorm Event in a Small Catchment on the Loess Plateau, PR China. Land Degrad Dev 28, 2527-2539.

Zhang, X.B., Wen, A.B., 2004. Current changes of sediment yields in the upper Yangtze River and its two biggest tributaries, China. Global Planet Change 41, 221-227.

Zhang, X.B., Zhang, Y.Y., Wen, A.B., Feng, M.Y., 2003. Assessment of soil losses on cultivated land by using the Cs-137 technique in the Upper Yangtze River Basin of China. Soil Till Res 69, 99-106.

Zhao, G.J., Mu, X.M., Han, M.W., An, Z.F., Gao, P., Sun, W.Y., Xu, W.L., 2017. Sediment yield and sources in dam-controlled watersheds on the northern Loess Plateau. Catena 149, 110-119.

Zhou, H.P., Chang, W.N., Zhang, L.J., 2016. Sediment sources in a small agricultural catchment: A composite fingerprinting approach based on the selection of potential sources. Geomorphology 266, 11-19.

Figure captions

Figure 1 (a) Locations of the study catchment and sampling sites. Note that the source sample collected at each location represents a mixture of 20-30 small samples scraped from adjacent areas in the field, (b) overview of the catchment, (c) soil conservation measures, and (d) eroding channel banks.

Figure 2 Particle size distribution (mean ± 1σ) of the suspended sediment samples collected at the catchment outlet.

Figure 3 Boxplots of the median (d_{50}) particle size for source and sediment samples of different size fraction.

Figure 4 Plots of particle size (d_{50}) versus tracer concentration for all properties analyzed.

Figure 5 Probability density functions (pdfs) for the estimated source contribution (between 0 and 1) to the artificial mixtures based on the 1000 Monte Carlo iterations.

Figure 6 Probability density functions (pdfs) for the estimated source contribution (between 0 and 1) to the real sediments collected at the outlet of the catchment based on the 1000 Monte Carlo iterations.

Table 1 Artificial mixtures with known source proportions used for model validation for each size fraction

Artificial mixture	Real source contribution (%)		
	Cropland	Woodland	Channel banks
Mixture 1 (*n*=3)	33.3	33.3	33.3
Mixture 2 (*n*=3)	66.6	0	33.3
Mixture 3 (*n*=3)	33.3	0	66.6

Table 2 Results of applying the minimum-maximum range test to the potential fingerprint properties for different size fraction associated with real sediments

Grain size <63 µm				Grain size <125 µm			
Property	Source	Sediment	Range test	Property	Source	Sediment	Range test
Ni	26.90-44.24	24.19-37.17	Fail	Ni	25.62-42.09	19.51-34.23	Fail
Pb	14.96-26.65	17.97-22.07	Pass	Pb	16.07-29.72	15.99-21.01	Fail
Cu	18.00-41.19	21.36-31.30	Pass	Cu	18.62-41.23	19.85-29.09	Pass
Cd	0.13-0.34	0.10-0.14	Fail	Cd	0.12-0.38	0.06-0.12	Fail
Sr	10.16-89.87	22.74-231.40	Fail	Sr	7.99-86.33	23.53-201.34	Fail
Co	9.41-15.88	11.69-14.20	Pass	Co	10.13-14.80	9.60-13.36	Fail
Be	1.41-2.42	1.28-1.95	Fail	Be	1.28-2.40	1.09-1.95	Fail
Li	36.84-65.76	32.29-46.98	Fail	Li	34.49-69.17	28.36-51.61	Fail
Tl	0.48-0.67	0.38-0.53	Fail	Tl	0.46-0.67	0.34-0.51	Fail
V	80.21-118.98	74.92-106.59	Fail	V	74.39-108.69	65.86-89.56	Fail
Cr	68.19-99.25	72.21-97.03	Pass	Cr	58.08-88.54	54.51-79.96	Fail
Zn	61.60-96.68	55.97-81.92	Fail	Zn	59.95-85.33	45.44-73.38	Fail
Cs	1.18-9.68	4.80-7.42	Pass	Cs	1.15-8.87	3.87-6.76	Pass
U	1.70-3.90	1.94-3.12	Pass	U	1.45-3.16	1.81-2.97	Pass
Ga	8.59-16.40	8.71-22.70	Fail	Ga	7.82-15.27	7.61-19.51	Fail
Rb	46.41-152.78	79.07-127.00	Pass	Rb	49.45-136.36	66.84-104.39	Pass
Yb	0.04-2.65	0.24-2.72	Fail	Yb	0.03-2.74	0.18-2.34	Pass
Nd	0.31-28.48	0.97-32.33	Fail	Nd	0.28-30.98	1.07-31.79	Fail
Y	0.23-18.03	0.75-21.51	Fail	Y	0.18-22.90	0.84-21.38	Pass
Dy	0.07-4.53	0.25-4.57	Fail	Dy	0.05-4.95	0.24-4.48	Pass
Er	0.04-2.69	0.19-2.71	Fail	Er	0.03-2.71	0.14-2.38	Pass
Gd	0.06-5.02	0.20-5.39	Fail	Gd	0.05-5.25	0.21-5.16	Pass
Pr	0.08-7.56	0.24-8.97	Fail	Pr	0.07-8.27	0.30-8.63	Fail
Sm	0.08-5.71	0.25-6.29	Fail	Sm	0.07-5.85	0.26-5.98	Fail
Al	17.78-75.39	27.18-68.47	Pass	Al	18.23-70.22	31.16-58.28	Pass
Ca	0.94-50.27	7.75-84.58	Fail	Ca	0.76-42.90	9.59-65.29	Fail
K	13.99-30.89	12.28-20.70	Fail	K	13.97-31.42	11.42-19.38	Fail
Mg	3.76-17.94	4.74-13.02	Pass	Mg	2.92-15.45	3.77-10.83	Pass
Na	4.58-12.72	8.39-12.78	Fail	Na	2.42-28.23	6.88-10.47	Pass
Ti	4.08-6.38	3.77-4.90	Fail	Ti	3.77-5.67	3.65-4.11	Fail
Fe	23.89-36.14	23.62-32.88	Fail	Fe	21.41-36.54	19.60-31.11	Fail
Mn	0.34-0.79	0.48-0.64	Pass	Mn	0.41-0.80	0.39-0.60	Pass
P	0.33-0.75	0.31-0.56	Fail	P	0.33-0.70	0.27-0.54	Fail
S	0.03-0.28	0.05-0.27	Pass	S	0.02-0.29	0.04-0.22	Pass

Table 3 Results of applying the minimum-maximum range test to the potential fingerprint properties for different size fraction associated with the artificial mixtures

Grain size <63 µm				Grain size <125 µm			
Tracer	Source	Mixture	Range test	Tracer	Source	Mixture	Range test
Ni	31.26-40.16	34.82-38.03	Pass	Ni	29.55-37.68	32.61-35.25	Pass
Pb	19.80-23.97	20.39-21.84	Pass	Pb	19.16-24.09	19.25-21.15	Pass
Cu	28.11-34.17	28.89-31.03	Pass	Cu	27.14-30.66	28.28-29.47	Pass
Cd	0.16-0.29	0.17-0.22	Pass	Cd	0.14-0.31	0.15-0.21	Pass
Sr	10.96-30.62	14.18-23.24	Pass	Sr	11.38-31.76	14.27-21.03	Pass
Co	11.60-14.47	13.07-14.31	Pass	Co	11.48-13.56	12.27-13.09	Pass
Be	1.57-2.10	1.62-1.95	Pass	Be	1.52-1.99	1.53-1.70	Pass
Li	43.71-50.67	43.25-50.26	Fail	Li	40.05-47.91	40.83-44.76	Pass
Tl	0.49-0.57	0.51-0.54	Pass	Tl	0.48-0.54	0.47-0.49	Fail
V	88.43-112.91	97.50-110.28	Pass	V	84.28-99.94	90.38-96.41	Pass
Cr	72.35-89.52	81.79-92.80	Fail	Cr	67.90-79.74	77.62-86.39	Fail
Zn	78.52-90.37	82.68-88.72	Pass	Zn	69.69-83.26	75.84-80.55	Pass
Cs	1.74-8.72	5.66-7.94	Pass	Cs	2.37-8.13	4.79-6.32	Pass
U	1.86-2.84	2.23-2.69	Pass	U	1.69-2.10	1.88-2.20	Fail
Ga	9.57-12.88	10.57-12.07	Pass	Ga	9.19-12.42	9.83-10.91	Pass
Rb	60.06-125.62	57.01-119.58	Fail	Rb	55.11-130.05	40.69-68.83	Fail
Yb	0.05-0.65	0.11-0.39	Pass	Yb	0.07-0.76	0.12-0.53	Pass
Nd	0.33-2.28	0.38-1.10	Pass	Nd	0.50-3.09	0.43-1.71	Fail
Y	0.30-2.69	0.37-1.23	Pass	Y	0.37-3.33	0.42-1.99	Pass
Dy	0.08-0.80	0.11-0.36	Pass	Dy	0.10-0.99	0.12-0.57	Pass
Er	0.05-0.53	0.08-0.27	Pass	Er	0.06-0.64	0.08-0.41	Pass
Gd	0.07-0.61	0.08-0.27	Pass	Gd	0.09-0.80	0.09-0.44	Pass
Pr	0.09-0.55	0.10-0.27	Pass	Pr	0.12-0.71	0.11-0.39	Fail
Sm	0.09-0.65	0.12-0.31	Pass	Sm	0.12-0.85	0.11-0.46	Fail
Al	23.60-53.52	21.59-45.86	Fail	Al	23.60-57.63	26.92-56.21	Pass
Ca	6.19-19.93	11.21-20.66	Fail	Ca	2.86-36.80	13.74-146.62	Fail
K	16.53-20.66	16.76-20.28	Pass	K	15.42-20.65	15.95-20.07	Pass
Mg	6.92-11.45	6.90-10.66	Fail	Mg	5.76-11.10	6.71-10.18	Pass
Na	8.11-11.59	10.92-17.25	Fail	Na	6.80-16.98	9.74-12.74	Pass
Ti	4.49-5.35	4.81-5.09	Pass	Ti	3.96-5.04	4.39-4.79	Pass
Fe	27.74-34.73	28.26-33.33	Pass	Fe	26.11-31.43	28.28-31.47	Fail
Mn	0.52-0.66	0.58-0.63	Pass	Mn	0.52-0.75	0.55-0.59	Pass
P	0.50-0.59	0.53-0.58	Pass	P	0.45-0.57	0.46-0.53	Pass
S	0.06-0.25	0.10-0.15	Pass	S	0.03-0.25	0.08-0.17	Pass

Table 4 The results of the Kruskal-Wallis H test for elements associated with different size fraction for real sediments

Grain size <63 µm			Grain size <125 µm		
Tracer	*H* value	*P* value	Tracer	*H* value	*P* value
Pb	6.54	0.038*	Cu	1.04	0.595
Cu	1.68	0.432	Cs	5.04	0.08
Co	6.26	0.044*	U	4.56	0.102
Cr	7.46	0.024*	Rb	8.64	0.013*
Cs	8.66	0.013*	Yb	5.274	0.072
U	5.274	0.072	Y	5.18	0.075
Rb	9.74	0.008*	Dy	5.049	0.08
Al	7.98	0.018*	Er	4.697	0.096
Mg	8.54	0.014*	Gd	4.994	0.082
Mn	0.423	0.809	Al	5.82	0.054
S	10.022	0.007*	Mg	7.34	0.025*
			Na	0.86	0.651
			Mn	3.311	0.191
			S	10.257	0.006*

* Statistically significant values at $p<0.05$

Table 5 The results of the Kruskal-Wallis H test for elements associated with different size fraction for artificial mixtures

Grain size <63 µm			Grain size <125 µm		
Tracer	*H* value	*P* value	Tracer	*H* value	*P* value
Ni	7.261	0.027*	Ni	7.2	0.027*
Pb	7.261	0.027*	Pb	7.2	0.027*
Cu	7.2	0.027*	Cu	7.2	0.027*
Cd	6.771	0.034*	Cd	6.713	0.035*
Sr	7.2	0.027*	Sr	7.2	0.027*
Co	7.2	0.027*	Co	7.2	0.027*
Be	5.956	0.051	Be	5.804	0.055
Tl	7.513	0.023*	Li	5.689	0.058
V	7.2	0.027*	V	7.2	0.027*
Zn	5.6	0.061	Zn	5.422	0.066
Cs	7.2	0.027*	Cs	7.2	0.027*
U	7.261	0.027*	Ga	7.2	0.027*
Ga	6.88	0.032*	Yb	7.261	0.027*
Yb	6.938	0.031*	Y	7.2	0.027*
Nd	5.6	0.061	Dy	7.322	0.026*
Y	5.804	0.055	Er	7.261	0.027*
Dy	6.252	0.044*	Gd	7.322	0.026*
Er	6.252	0.044*	Al	7.2	0.027*
Gd	5.695	0.058	K	5.468	0.065
Pr	5.804	0.055	Mg	7.2	0.027*
Sm	6.056	0.048*	Na	5.6	0.061
K	6.489	0.039*	Ti	7.2	0.027*
Ti	7.261	0.027*	Mn	7.513	0.023*
Fe	5.6	0.061	P	6.771	0.034*
Mn	7.015	0.030*	S	7.2	0.027*
P	7.019	0.030*			
S	7.261	0.027*			

* Statistically significant values at $p<0.05$

Table 6 The results of applying the stepwise Discrimination Function Analysis to select tracers for modelling

Target	Size fraction	Step	Tracer added	Wilk's lambda	Cumulative % of source samples correctly classified
Real sediment	<63 µm	1	S	0.258	66.7
		2	Co	0.067	86.7
		3	Pb	0.019	100.0
		4	Cs	0.010	100.0
	<125 µm	1	S	0.251	86.7
		2	Rb	0.099	86.7
Artificial mixture	<63 µm	1	Ni	0.002	100.0
		2	Mn	0.000	100.0
		3	Cu	0.000	100.0
		4	Ti	0.000	100.0
		5	Pb	0.000	100.0
	<125 µm	1	Dy	0.003	88.9
		2	Pb	0.000	100.0
		3	Co	0.000	100.0
		4	Er	0.000	100.0
		5	Cd	0.000	100.0
		6	Mg	0.000	100.0

Table 7 Comparison between predicted median source contributions and known proportions (in parentheses) for artificial mixtures associated with different grain size composition

Grain size	Mixture	Source contribution (%)			MAE (%)
		Cropland	Woodland	Channel bank	
< 63 µm	Mixture 1	27.3 (33.3)	33.7 (33.3)	39.0 (33.3)	4.0
	Mixture 2	55.5 (66.6)	4.0 (0)	40.5 (33.3)	7.4
	Mixture 3	27.0 (33.3)	0.7 (0)	72.3 (66.6)	4.2
< 125 µm	Mixture 1	52.1 (33.3)	33.1 (33.3)	14.8 (33.3)	12.5
	Mixture 2	91.2 (66.6)	4.9 (0)	3.9 (33.3)	19.6
	Mixture 3	40.1 (33.3)	6.5 (0)	53.4 (66.6)	8.8

Table 8 Unmixing model results of estimated proportional source contributions (%) to the suspended sediment collected at the catchment outlet

Source	Statistic	Size fraction	
		<63 µm	<125 µm
Cropland	25th percentile	16.1	7.0
	Median	17.4	7.0
	75th percentile	17.4	7.0
	Interquartile Range	1.3	0
Woodland	25th percentile	0	0
	Median	0	0
	75th percentile	0.5	0
	Interquartile Range	0.5	0
Channel bank	25th percentile	82.6	93.0
	Median	82.6	93.0
	75th percentile	82.6	93.0
	Interquartile Range	0	0