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

7

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13 **Abstract:** A sediment fingerprinting approach was applied to identify dominant
14 sediment sources in an area where soil conservation measures (i.e. terracing) had
15 been carried out on steep, intensively cultivated lands but the outcome was unknown.
16 The wider purpose was to provide scientific evidence to inform decisions on where
17 erosion control and sediment mitigation strategies could be further targeted.
18 Geochemical fingerprints were used to quantify sediment contributions from three
19 potential sources, i.e. surface soil under cropland and woodland land use, and channel
20 banks, in a managed small catchment in the Upper Yangtze River basin in southwestern
21 China. In parallel, artificial mixtures with known source proportions were evaluated to
22 examine the effects of grain size selection (<125 μm and <63 μm) on the accuracy of

23 modeled source contributions. Source apportionment results suggest that materials
24 originating from incised and actively eroding channel banks were the most important
25 source of sediment, which contribute over 80% of sediment to the catchment outlet.
26 Sediment inputs from cropland (10-20%) and woodland (<10%) areas as a result of
27 surface erosion were less important, since effective soil conservation measures have
28 been implemented in this catchment. Although apportionment of sampled sediment
29 provided comparable results for both coarser (<125 μm) and fine (<63 μm) size
30 fractions, the artificial mixture results indicated that unmixing the coarse fraction
31 alone could yield poor agreement between modeled source contributions and actual
32 source proportions. The mean absolute error (MAE) for the coarse fraction mixtures
33 ranged between 8.8% and 19.6%, with a mean of 13.6%, compared to the values of
34 4.0-7.4%, with a mean of 5.2% for the fine fractions. The results of this study highlight
35 that channel bank materials constitute a significant fraction of suspended sediment
36 exports in a heavily managed agricultural catchment, suggesting that future
37 conservation works should be focused on drivers of erosion from this particular source
38 type. Herein, it is surmised that reworking of legacy valley fill deposits is tempering the
39 downstream benefits (e.g. reduced siltation) of recent upslope soil conservation, an
40 important message for policy makers. The findings of this work also emphasize the
41 methodological need to take account of potential uncertainties associate with source
42 apportionments when using specific particle size fractions in fingerprinting studies.

43

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

45 sources; channel erosion; particle size

46

47 **1. Introduction**

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

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

67 Yangtze basin. In the late 1980s, this triggered a large-scale soil conservation program
68 known as the 'State Key Soil and Water Conservation Project in the Upper Yangtze
69 River Basin' which was undertaken across catchments of the upper reaches of the
70 Yangtze River. Major soil conservation practices implemented included terracing,
71 conservation tillage, reforestation, and construction of sediment detention ponds and
72 reservoirs. It was reported that during the period 1989-1996, over 3.4×10^4 km² of
73 conservation measures have been undertaken in the Jialing and Lower Jinsha river
74 basins, the two largest tributaries of the Upper Yangtze River which have drainage
75 areas of 15.6×10^4 and 48.5×10^4 km², respectively (Zhang and Wen, 2004).

76 With continuous and unprecedented investment by the Chinese government, the
77 sustainability of rural land systems in the Yangtze Basin has been greatly improved
78 (Bryan et al., 2018). For example, soil erosion has decreased by 58.8% on average from
79 2003-2007 compared to the period 1998-2002 in the Yangtze basin, associated with
80 the Grain-for-Green program (Deng et al., 2012). In parallel, the annual sediment load
81 of the Yangtze River at Yichang has sharply decreased from $\sim 5 \times 10^8$ t in the 1980s to
82 $\sim 1 \times 10^8$ t in 2010s (Li et al., 2020), which could be attributed, at least partially, to the
83 soil and water conservation projects implemented in this basin.

84 Despite significant mitigation of soil loss and therefore a reduction of sediment
85 supply on hillslopes, eroding channel banks are often overlooked components in
86 current catchment management policies in China, especially in the upper reaches of
87 the Yangtze River, and little is known about the contribution of this type of erosion to
88 the overall catchment sediment production. In this context, sediment source

89 apportionment data can be used to understand and contextualize soil conservation
90 strategies that limit sediment production and thus to support future land management
91 policy (Tang et al., 2019). However, such information is difficult to obtain, especially in
92 remote areas where the traditional monitoring and modelling techniques (e.g. erosion
93 plots, erosion pins and gauging station) face a number of limitations in terms of the
94 practicalities, representativeness and the costs involved (Collins and Walling, 2004).
95 Since the mid-1970s, the sediment source fingerprinting approach has been widely
96 used as an alternative and effective means of assembling such information (Walling,
97 2013). This technique has also been increasingly adopted in China to resolve critical
98 soil and sediment management questions that challenge ecosystem service provision
99 in river basins (e.g. Chen et al., 2016; Lin et al., 2015; Zhang et al., 2017; Zhao et al.,
100 2017; Zhou et al., 2016). To date, however, the application of sediment fingerprinting
101 is rather limited in the upper reaches of the Yangtze River; and reliable quantitative
102 information on sediment provenance is believed to be helpful in supporting future
103 catchment management decisions in this area especially with regard to food security
104 and protection of downstream water quality and hydropower production.

105 The concept of sediment fingerprinting approach is that a single or a suit of the
106 natural physical or biogeochemical sediment properties (i.e. tracers or fingerprints)
107 can be used diagnostically to identify sediment derived from a particular source. One
108 of the most fundamental assumptions underpinning the fingerprinting application is
109 therefore that these tracer properties used behave conservatively during sediment
110 delivery processes (e.g. Foster and Lees, 2000). One key challenge to this assumption

111 is the enrichment and depletion effects caused by particle size selectivity during
112 sediment mobilization and deposition (Walling, 2013). In this context, the choice of an
113 appropriate particle size fraction of sediment is of great concern in fingerprinting
114 studies (Lacey et al., 2017). On one hand, it is widely recognized that particle size can
115 exert important impacts on sediment properties and thus the source ascription results
116 (e.g. Batista et al., 2019; Gaspar et al., 2019; Haddadchi et al., 2015; Koiter et al., 2018;
117 Smith and Blake, 2014). On the other hand, the size fraction selected for analysis
118 should represent the majority of sediment in transport, or closely related to the
119 research or management objectives (Wilkinson et al., 2013). Although the use of a
120 narrow grain size range (e.g. <10 μm) may reduce the potential for particle size related
121 uncertainties, such a very fine fraction may not be representative of the transported
122 sediment (Collins et al., 2017; Walling, 2013). Therefore, there is likely a need to make
123 a compromise between the representativeness of selected particle size fraction and
124 the need to limit it to a relatively narrow range to reduce the potential uncertainties
125 associated (Collins et al., 2017; Lacey et al., 2017).

126 In this study, the provenance of contemporary suspended sediment was
127 examined in a small agricultural catchment in the Upper Yangtze River basin in
128 southwestern China where soil conservation measures had been recently
129 implemented. While evaluating sediment fingerprinting in a novel context of Chinese
130 catchment-scale soil conservation, a secondary methodological aim was to address the
131 effects of particle size selection on the accuracy of sediment fingerprinting procedures
132 wherein sediment unmixing results were assessed by use of artificial mixtures. A novel

133 aspect of this study is that fingerprinting techniques were applied to identify the
134 predominant source of sediment in an area where soil conservation measures (i.e.
135 terracing) have been implemented on slope cultivated lands, so that erosion control
136 and sediment mitigation strategies could be further targeted.

137 **2. Materials and methods**

138 **2.1 Catchment description**

139 The Liangshan catchment (101.9°E, 25.7°N) is located in the Yuanmou County of
140 Yunnan Province, the Lower Jinsha River basin, and drains an area of 4.34 km². The
141 Jinsha River is the biggest tributary of the Upper Yangtze and has a drainage area of
142 48.5×10⁴ km². Elevation ranges from 2835 m at the summit to 1350 m at the catchment
143 outlet. The local area is characterized by a subtropical monsoonal climate with an
144 average annual temperature of 10.5 °C and a mean annual precipitation of 914.9 mm.
145 The lithology is dominated by Mesozoic sedimentary rocks (mudstone and red
146 sandstone). Soils are yellow-brown and purple soils with bulk densities of 1.2-1.4 g cm⁻³
147 and are silt loam in texture (Su et al., 2019). Land use consists mainly of woodland
148 (80.2%), with cropland (18.4%) and residential areas (1.4%) comprising the remainder
149 (Figure 1). Woodland is primarily covered by broadleaf trees (e.g. *Quercus*
150 *semecarpifolia* and *Quercus glauca*) and shrubs (e.g. *Dodonaea viscosa*) (Su et al.,
151 2019), and characterized by high vegetation density. Cropland is concentrated in the
152 middle of the catchment.

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

155 Water Conservation Project in the Upper Yangtze River Basin' project (Zhang and Wen,
156 2004). Most cropland with gentle gradient in the mid catchment has been converted
157 to terrace and paddy fields. The remaining fields of the cropland were maintained as
158 steep slopes with average gradient of $\sim 20^\circ$, which are vulnerable to erosion although
159 these make up just 7.8% of the total catchment area and are patchily distributed across
160 the catchment. Main crops are rain-fed wheat (*Triticum aestivum L.*), corn (*Zeamays*
161 *L.*), sweet potato (*Ipomoea batatas (L.) Lam*) and groundnut (*Arachis hypogaea L.*) (Su
162 et al., 2019).

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

171 **2.2 Sample collection and analysis**

172 Three main potential sediment sources, including cropland, woodland and
173 eroding channel banks, were defined based on land use and field observations. All
174 source materials collected for analysis comprised composite samples formed by
175 combining multiple subsamples (20-30) from different areas in a specific zone to
176 underpin spatial representativeness. Thus, for cropland and woodland sources, each

177 of five composite samples were obtained by scraping surface soils at the depth of 0-2
178 cm using a plastic trowel. Although terrace and paddy fields cover 10.6% of the
179 catchment area and the puddling process during rice cultivation is known in some
180 cases to generate sediment export, field observations indicate that these lands afford
181 little opportunity for sediment delivery in this system since most of them are protected
182 by well-established field ridges of approximately 60 cm in height (Fig. 1c). Collection
183 of cropland source samples was restricted to the steep slope locations with loose
184 materials that prone to erosion. It was noted, however, that the geochemical
185 properties of these cultivated soils would be representative across the system. To
186 characterize incised and eroding channel banks, samples were taken by scraping
187 exposed channel bank sidewalls from top to base. At locations where channel banks
188 had collapsed, the loose materials deposited at the bottom of the banks were collected
189 as alternatives because these materials are more easily to be transported during floods
190 and hence fully representative of this source material. Valley fill materials potentially
191 comprise legacy material from upland slopes so a key assumption to be tested was
192 that the deposited and stored material carried a geochemical signature discernable
193 from contemporary topsoil. Again, a total of five integrated samples representing the
194 channel bank sources were obtained. Suspended sediment samples were collected at
195 the catchment outlet using three time-integrating samplers (Phillips et al., 2000). The
196 samplers were fixed to the channel bed with steel rods before the wet season on
197 March 8, 2016. Suspended sediment sampling was conducted during the rainy months,
198 when two major runoff events on July 16 and September 20 were recorded. It should

199 be noted here that, although only two storm events were manually recorded since
200 there was no gauge station at our study site, the suspended samples collected were
201 time-integrated materials transported by multiple runoff events which covered the
202 whole wet period of the year. Unfortunately, one sampler was washed away during
203 the second flood. Consequently, five time-integrated sediment samples (~1200 g dry
204 mass per sample) were recovered where the high mass of recovery is indicative of a
205 significant sediment load.

206 Source and sediment samples were air-dried at room temperature, gently
207 disaggregated using a pestle and mortar, and initially sieved to <2 mm. To determine
208 the dominant grain size in sediment samples, the grain size composition was
209 determined using a Malvern Mastersizer 2000 laser diffraction device (Malvern
210 Instruments Ltd.). Prior to analysis, the samples were treated with 10% H₂O₂ to remove
211 organic matter and 10% HCl to remove CaCO₃ before being dispersed by use of 0.5 mol
212 L⁻¹ sodium hexametaphosphate solution and 2-min ultrasonic agitation. Particle size
213 data in Figure 2 revealed that the majority (>80%) of the target suspended sediments
214 was <125 µm in size; therefore, all source and sediment samples were sieved to <125
215 µm for measurement. Many studies, however, utilize a finer grained fraction for tracing.
216 Hence, to explore the potential effects of particle size selection on sediment source
217 apportionment, subsamples of the <125 µm fraction of all source and sediment
218 samples were sieved to isolate the <63 µm fraction, which is commonly used in
219 sediment source fingerprinting studies.

220 Subsamples of 0.2 g (*n* = 20 for each size fraction) were analyzed for their elemental

221 geochemistry using ICP-OES (Inductively Coupled Plasma-Optical Emission
222 Spectrometry, Optima 8300, Perkin Elmer) and ICP-MS (Inductively Coupled Plasma-
223 Mass Spectrometry, NexION 300, Perkin Elmer) after HNO₃/HF (8.0 mL of concentrated
224 HNO₃ and 4.0 mL concentrated HF) microwave digestion (Mars 6, CEM). The digestion
225 procedure consisted of a temperature–time ramp for 20 min with a final temperature
226 of 180 °C held for 20 min. A total of 41 properties were determined: Ni, Pb, Cu, Cd, Sr,
227 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,
228 Tb, Al, Ca, K, Mg, Na, Ti, Fe, Mn, P and S. Elements (Se, In, Tm, Eu, Ho, Lu and Tb) with
229 measurements below the detection limit were excluded from further use. Particle size
230 distributions of the target and source material samples (both <125 μm and <63 μm)
231 were analyzed to examine the potential differences in grain size between the sources
232 and sediments, using the method described above.

233 **2.3 Tracer selection**

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

239 In the first step, the properties returned measurements above the detection
240 limits were tested for normality by using the Shapiro-Wilk test. Whilst this test does
241 not necessarily lead to removal of any property, it was considered an important step
242 in characterizing the statistical distributions of the fingerprint properties in

243 subsequent testing and unmixing processes (Collins et al., 2012a). In step 2, a range or
244 bracket test was employed to ensure that the minimum - maximum concentrations of
245 each tracer in target sediment samples fall within the corresponding range of source
246 groups (Martínez-Carreras et al., 2010). Tracers failing the range test were presumed
247 to be non-conservative in terms of environmental behavior within the soil-sediment
248 continuum, i.e. it was likely that the properties had been altered in some way between
249 source and sink, and were excluded from further use. Subsequently, the
250 nonparametric KW-H test was applied to select tracers that exhibited significant
251 difference among source categories. Elements with p -values lower than 0.05 were
252 identified as tracers with a significant difference between at least two source groups.
253 Finally, forward stepwise DFA was used to establish an optimum subset of fingerprint
254 that comprises the minimum number of tracer properties but provides the greatest
255 discrimination between sources based on the minimization of the Wilk's Lambda
256 (Collins and Walling, 2002). Default values of the minimum F to Enter (3.84) and the
257 maximum F to Remove (2.71) were used in this step (SPSS v22).

258 **2.4 Unmixing procedures**

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

$$262 \quad \sum_{s=1}^m C_{si} \cdot P_s = C_i \quad \text{with} \quad \sum_{s=1}^m P_s = 1 \quad \text{and} \quad 0 \leq P_s \leq 1 \quad (1)$$

263 where C_i is the concentration of a tracer property in the target sediment ($i=1$ to n , n

264 represents the number of tracer properties comprising the optimum composite
265 fingerprint); C_{si} is the concentration of the corresponding tracer property in source
266 type ($s=1$ to m , m represents the number of potential sediment sources); and P_s is the
267 proportional contribution from individual source type.

268 Since the number of selected tracers typically exceeds the number of source
269 types (i.e. $n>m$), the system of Equation (1) is over-determined and a 'solution' can be
270 achieved *via* optimization of an objective function. Traditionally, the objective function
271 has been solved by minimizing of the sum of squares of relative errors (Collins et al.,
272 1997) where:

$$273 \quad f = \sum_{i=1}^n \left(\frac{C_i - \sum_{s=1}^m C_{si} \cdot P_s}{C_i} \right)^2 \quad (2)$$

274 Early studies recognized the inherent variability of the properties within the
275 source and sediments, and thus the uncertainty associated with the use of single
276 values of tracer concentration (e.g. mean or median) to represent a given source or
277 sediment (Walling, 2013). To address this uncertainty, a Monte Carlo sampling
278 framework has been widely applied. The property values associated with a given
279 source or sediment are characterized by a statistical distribution generated on the
280 basis of their measured values. Using the Monte Carlo method, the property values
281 incorporated into the modelling process can be varied and different possible values of
282 tracer properties can therefore be used. In this study, Student's t distributions were
283 simulated for each fingerprint property of both source and sediment samples, since
284 this distribution is considered to be an appropriate distribution when the number of

285 samples is small (Lacey and Olley, 2015). During the distribution modelling, the
286 median value of a specific property within a given source or sediment group was used
287 as the midpoint, the median absolute deviation as the scale and the number of
288 samples minus one as the degree of freedom. Non-negative constraints were set for
289 all property values.

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

301 **2.5 Artificial mixtures**

302 To validate the accuracy of the fingerprinting method in predicting sediment
303 source contributions within this system, three groups of artificial mixtures with known
304 source proportions were created for each size fraction (i.e. <125 μm and <63 μm).
305 Subsamples of equal weight (10 g) were taken from each of the source samples. The
306 subsamples from the same source types were then manually mixed in a polythene

307 vessel to form a composite sample to represent individual sources. Artificial mixtures
308 were prepared in the laboratory by combining different known proportions of sources
309 based on their weight (Table 1). Taking Mixture 1 as an example, an equivalent 5 g
310 aliquot was retrieved from each source type and mixed to produce one artificial
311 mixture (15 g); thus, the three source types each made a contribution of 33.3% to the
312 mixture. The mixing procedures were undertaken in triplicate and consequently nine
313 artificial mixtures were obtained for each size fraction.

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

$$317 \quad MAE = \frac{1}{m} \left(\sum_{s=1}^m |P_{predicted} - P_{actual}| \right) \quad (3)$$

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

321 **3. Results**

322 **3.1 Particle size characteristics of the fractionated material**

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

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

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

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

348 **3.2 Optimum composite fingerprints**

349 Full geochemical data are provided in Electronic Supplementary material for

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

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

372 transportation through the catchment system.

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

381 Table 6 presents the results from the stepwise DFA to deliver the 'optimum'
382 composite fingerprints for modelling. Generally, high levels of source discrimination
383 were provided, in terms of the percentage of sources correctly classified, through use
384 of these final signatures. All sets of tracers were capable of allocating 100% of source
385 samples to the correct source type, with the exception of the tracers for the <125 μm
386 fraction of real sediment, for which the combination of S and Rb correctly classified
387 86.7% of source samples.

388 **3.3 Source apportionment for artificial mixtures**

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

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

396 The comparison between estimated source contributions and known mixture
397 proportions reveals that generally good agreement was achieved for the fine-grained
398 (<63 μm) mixtures, with a mean MAE of 5.2% (range 4.0-7.4%) (Table 7). In the case of
399 the <125 μm fractions, the source contribution predictions showed poor consistency
400 with their corresponding real proportions presumably because it was harder to get
401 consistent mixtures. Compositional differences due to correlation between mineral
402 and particle size might also be exaggerated by analytical uncertainty where tracer
403 concentration differences between source groups is small. The much higher MAE
404 errors (mean 13.6%; range 8.8-19.6%) demonstrate weak model performance on
405 coarser particles.

406 **3.4 Source apportionment for catchment sediments**

407 Source ascription results for suspended sediment at the catchment outlet provide
408 clear and unambiguous mixing model solutions (Figure 6). Overall, comparable source
409 apportionment estimates were obtained for the two different grain size fractions
410 (Table 8). Eroding channel banks represented the most important sediment source in
411 the study catchment, with sediment contribution typically exceeded 80% (medians
412 82.6% and 93.0% for <63 μm and <125 μm fractions, respectively). In contrast,
413 sediment input from cropland appeared to be less important, with median proportions
414 ranging from 17.4% for the <63 μm fraction to 7.0 for the <125 μm fraction. The
415 contribution from woodland areas was negligible during the study period in this

416 catchment. The very narrow interquartile ranges (0-1.3%) of source apportionment
417 data generated using the Monte Carlo routines indicated little variability, and thus low
418 uncertainty of the relative contributions.

419 **4. Discussion**

420 **4.1 Geochemical properties and methodological sensitivity to particle size effects**

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

438 in topsoil sources due to its well reported correlation with organic matter (see Smith
439 and Blake (2014) and references therein).

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

451 Although a wide range of particle size fractions, ranging between 0 and $2000 \mu\text{m}$,
452 have been used in different fingerprinting investigations, an increasing number of
453 studies have emphasized the need of choosing the particle size most relevant to the
454 research and management objectives (Collins et al., 2017; Laceby et al., 2017).
455 Consequently, it is important for fingerprinting studies to support their choice of
456 particle size fraction by, as an initial step, examining the grain size distribution of the
457 target sediment samples. For example, some studies in Australia have focused on the
458 $<10 \mu\text{m}$ fraction on the basis that this fraction is either the dominant particle size in
459 transport (Laceby and Olley, 2015; Olley and Caitcheon, 2000) or the fraction

460 responsible for the environmental problems (Hughes et al., 2009; Wilkinson et al.,
461 2013). Nosrati et al. (2018) used <63 μm fraction based on the particle size information
462 on sediment samples. Unfortunately, such good practice has seldom, if ever, been
463 adhered to. Most researchers have sieved their sediment and source samples simply
464 to a specific particle size fraction, e.g. <63 μm which nominally represents suspended
465 sediment in many temperate systems, without taking the initial grain size composition
466 of the target 'problem' sediments into account. It is also noteworthy that 'fine'
467 sediment particle size is perceived differently in different ecological and socio-
468 economic contexts.

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

482 economic river basin management questions in hand.

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

498 **4.2 Catchment source contributions**

499 Whilst modelled source contributions are highly uncertain for the <125 μm
500 fraction, as indicated by the unmixing results of the artificial mixtures, source
501 apportionment for the catchment outlet sediments appear generally comparable
502 between the two grain sizes (Table 8). Channel banks contributed over 80% of
503 suspended sediment to the outlet of this catchment. In the absence of load data this

504 result can only be used to imply the relative impacts of sources but given the widely
505 observed high turbidity in the system this still has some bearing on management
506 decisions. Field survey suggested that channels have become incised by concentrated
507 high flow during storm events in the Liangshan catchment with well-developed banks
508 comprising thick units (over 2 m depth) former valley fill material that are subjected
509 to active erosion that is effectively reworking legacy deposits from the period prior to
510 soil conservation. As a result, a large amount of loose materials were collapsed from
511 the channel banks due to gravity erosion, which can be transported directly to the
512 channels during rainstorm events. Meanwhile, the adjacency of the sampling locations
513 of channel bank sources to those of the target sediments means that there was greater
514 opportunity for the channel bank materials to be delivered to the catchment outlet
515 than material mobilized from more distal sources. This is further supported by the
516 findings of Haddadchi et al. (2015) and Rodrigues et al. (2018), who have suggested
517 that the closer a source is to the target sediment sampling site, the higher this source
518 contribution. Indeed, the importance of incision processes as a sediment generation
519 factor due to changes in upslope hydrological response has long been recognized in
520 many areas of the world. In Australia, for example, channel and gully incision has been
521 documented to contribute as high as 90% of the sediment yield (Caitcheon et al., 2012;
522 Krause et al., 2003; Olley et al., 2013) often triggered by conversion of native forest
523 vegetation to agriculture. Similarly, considerable contributions from channel
524 banks/subsurface sources have also been determined in some European catchments
525 although relative importance of land management changes is quite catchment-specific

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

527 Cropland areas represented a less important source of suspended sediment in
528 this catchment at the time of sampling compared to the channel banks. This coheres
529 with most sloping cultivated land within this catchment having been converted into
530 terraces and paddy fields during the implementation of the 'State Key Soil and Water
531 Conservation Project in the Upper Yangtze River Basin' project since 1989.
532 Consequently, the remaining small area of steep cultivated slopes ($>15^\circ$), which have
533 potential to supply sediment to the catchment channel system, contributed less than
534 20% of the suspended sediment load.

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

539 **4.3 Management implications**

540 Source apportionment results suggest that a large proportion of the suspended
541 sediment reaching the catchment outlet originated from well-developed and active
542 eroding channel banks that are effectively reworking stored valley fill material
543 deposited in the past. This finding implies that future sediment management
544 strategies should direct particular attention to channel bank stability in areas with
545 similar environmental settings and furthermore identify the root cause of channel
546 incision (Gellis and Sanisaca, 2018). While soil conservation strategies reduce
547 dramatically the influence of agricultural activities on sediment flux and reduce on-site

548 food security challenges of soil erosion, reworking of valley fill materials by runoff can
549 act to maintain the downstream delivery of sediment during catchment recovery
550 (Trimble, 1999). This would appear to be the case in this system where a gradual
551 relaxation to equilibrium of the sediment continuum after the implementation of
552 conservation measures may temper downstream benefits in terms of catchment
553 sediment yield. Herein it is inferred that valley sediment storage was augmented by
554 historic upslope soil erosion in the past and the contemporary sediment output of the
555 system still carries this legacy with downstream consequences for water and energy
556 security. This is an important message for policy makers.

557 Although steep cultivated slopes in this region have high rates of soil erosion
558 (Zhang et al., 2003), the area of steep sloping cultivated land is relatively small
559 especially in the Lower Jinsha River Basin (Valentin et al., 2015). Natural factors
560 including topography, climate and lithology are key potential contributing factors to
561 soil erosion in this particular area (Valentin et al., 2015). With the continuous
562 investments in ecological conservation and restoration by the Chinese government,
563 diverse soil conservation practices (e.g. reforestation, terracing) have been
564 implemented in the Upper Yangtze River Basin, which further reduced soil loss and
565 sediment production. Perhaps more importantly, rapid urbanization characterized by
566 the migration of the rural population to cities in recent years has led to a significant
567 increase in abandoned farmland in many agricultural catchments in China (Tang et al.,
568 2019). In this context, decreasing sediment contribution from cultivated land and
569 therefore an increased proportion of the river sediment load originating from channel

570 erosion due to incision processes can be expected in such catchments. The progressive
571 refinement of the sediment source fingerprinting techniques offers considerable
572 potential for decision makers in developing targeted sediment control strategies and
573 testing their effectiveness once implemented (e.g. Chen et al., 2016).

574 **4.4 Limitations**

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

587 **5. Conclusions**

588 This study has reported the application of a geochemical fingerprinting to
589 determine the sediment provenance in a small agricultural catchment in the Upper
590 Yangtze River basin, southwestern China. Eroding channel banks were demonstrated

591 to be the dominant sediment source, suggesting that future management works
592 should be focused on this particular source type in such catchments. While measures
593 such as improving the integrity of the valley bottom vegetation and reducing
594 contributions of excess runoff to the channel will be important, this challenge needs
595 to be considered within the wider context of reworking of legacy valley fill deposits
596 from the pre-soil conservation eras. This presents a formidable management challenge
597 to mitigate the downstream impacts of enhanced sediment flux. The positive is that
598 intensive agricultural land in this system, where there has been widespread
599 implementation of soil conservation techniques, does not make a substantial
600 contribution to downstream sediment flux confirming the long-term benefit of the
601 regional policies for soil resource retention and food security.

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

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

613 investigations.

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794 **Figure captions**

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

799 **Figure 2** Particle size distribution (mean $\pm 1\sigma$) of the suspended sediment samples
800 collected at the catchment outlet.

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

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

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

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

810 **Table 1** Artificial mixtures with known source proportions used for model validation

811 for each size fraction

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

812

813 **Table 2** Results of applying the minimum-maximum range test to the potential

814 fingerprint properties for different size fraction associated with real sediments

815

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

816

817 **Table 3** Results of applying the minimum-maximum range test to the potential
 818 fingerprint properties for different size fraction associated with the artificial mixtures
 819

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

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

823

Grain size <63 μm			Grain size <125 μm		
Tracer	<i>H</i> value	<i>P</i> value	Tracer	<i>H</i> value	<i>P</i> 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*

824 * Statistically significant values at $p < 0.05$

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

827

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*			

828 * Statistically significant values at $p < 0.05$

829 **Table 6** The results of applying the stepwise Discrimination Function Analysis to select
 830 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

831

832 **Table 7** Comparison between predicted median source contributions and known
 833 proportions (in parentheses) for artificial mixtures associated with different grain size
 834 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

835

836 **Table 8** Unmixing model results of estimated proportional source contributions (%) to
 837 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

838