

1 FRONTIERS IN SOILS AND SEDIMENTS

2

3 **Methodological perspectives on the application of compound-specific stable isotope fingerprinting**
4 **for sediment source apportionment**

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30 **Abstract**

31 *Purpose* Compound-specific stable isotope (CSSI) fingerprinting of sediment sources is a
32 recently introduced tool to overcome some limitations of conventional approaches for sediment
33 source apportionment. The technique uses the ^{13}C CSSI signature of plant-derived fatty acids
34 ($\delta^{13}\text{C}$ -FAs) associated with soil minerals as a tracer. This paper provides methodological
35 perspectives to advance the use of CSSI fingerprinting in combination with stable isotope mixing
36 models (SIMMs) to apportion the relative contributions of different sediment sources (i.e. land
37 uses) to sediments.

38 *Results and discussion* CSSI fingerprinting allows quantitative estimation of the relative
39 contribution of sediment sources within a catchment at a spatio-temporal resolution taking into
40 account the following approaches. First, application of CSSI fingerprinting techniques to
41 complex catchments presents particular challenges and calls for well-designed sampling
42 strategies and data handling. Hereby, it is essential to balance the effort required for representative
43 sample collection and analyses against the need to accurately quantify the variability within the
44 system. Second, robustness of the CSSI approach depends on the specificity and conservativeness
45 of the $\delta^{13}\text{C}$ -FA fingerprint. Therefore, saturated long-chain (>20 carbon atoms) FAs, which are
46 biosynthesised exclusively by higher plants and are more stable than the more commonly used
47 short-chain FAs should be used. Third, given that FA concentrations can vary largely between
48 sources, concentration-dependent SIMMs that are also able to incorporate $\delta^{13}\text{C}$ -FA variability
49 should be standard operation procedures to correctly assess the contribution of sediment sources
50 via SIMMs.

51 *Conclusions* This paper reflects on the use of $\delta^{13}\text{C}$ -FAs in erosion studies and provides
52 recommendations for its application. We strongly advise the use of saturated long-chain (>20
53 carbon atoms) FAs as tracers and concentration-dependent Bayesian SIMMs. We anticipate
54 progress in CSSI sediment fingerprinting from two current developments: (i) development of

55 hierarchical Bayesian SIMMs to better address catchment complexity and (ii) incorporation of
56 dual isotope approaches ($\delta^{13}\text{C}$ - and $\delta^2\text{H}$ -FA) to improve estimates of sediment sources.

57

58 **Keywords** Compound-specific stable isotope (CSSI) analysis • Biotracers • Erosion • Fatty acids
59 (FAs) • Sediment fingerprinting • Stable isotope mixing models (SIMMs)

60

61 **1 Environmental and ecological impact of water erosion**

62 Water erosion is considered to be the gravest threat to soil security globally, leading to lower
63 crop yields and contamination of freshwater and estuaries (Koch et al. 2013; Montanarella et al.
64 2016). Soil loss and the associated loss of nutrients and organic carbon (OC) can have serious
65 on-site impacts, particularly for arable land, reducing soil productivity and threatening
66 sustainable agricultural production. This is especially problematic in hilly landscapes (Pimentel
67 2006; Zuazo and Pleguezuelo 2008; Pimentel and Burgess 2013; Rickson et al. 2015). The
68 transfer of fine sediment from cropland to water bodies is considered to be the world's largest
69 non-point pollution source and creates detrimental off-site effects (Vörösmarty et al. 2010). Fine
70 sediment (hereafter sediment) is defined as well mixed suspended mineral and organic
71 particulates with diameter less than 2 mm that have been moved from their site of origin by water.
72 The most serious environmental effect of sediment loss to water bodies is the contamination of
73 water with nutrients, pesticides and other toxic chemicals, which in turn adversely affects aquatic
74 habitat quality (Gardner and Gerrard 2003; Owens et al. 2005; Sanchez-Chardi et al. 2009; Urban
75 et al. 2009; Bunzel et al. 2015). Moreover, siltation significantly reduces water storage capacity
76 of lakes and reservoirs, decreasing their economic lifespan. The average annual storage capacity
77 loss in the world's reservoirs has been estimated to be around 0.5-1%, although losses as high as
78 4-5% have been reported for individual reservoirs (Smith et al. 2002; Haregeweyn et al. 2012;
79 Wisser et al. 2013). The relationship between soil erosion and siltation in floodplains and
80 reservoirs is not straightforward (Montanarella et al. 2016) as it is controlled by complex
81 mechanisms resulting from the specific hydro-sedimentological behaviour of each catchment.
82 Nevertheless, the costs associated with these processes can be high: In the USA and the European
83 Union, on-site economic costs of water erosion has been estimated at \$15 and 20 billion (US) per
84 year, respectively (Troeh et al. 2004; Panagos et al. 2015). The off-site annual cost of human-
85 induced sediment influx to rivers and streams ranges from \$20 to 50 billion in North America

86 alone (Mukundan et al. 2012). Given these ecological and social costs, erosion and associated
87 sedimentation issues have become a major part of the international environmental agenda and are
88 identified as major causes of catchment, freshwater and estuary degradation.

89 Without proper soil conservation practices, sediment transfer from key sediment sources
90 (hotspots defined by land use type or sub-catchment) are projected to intensify, particularly if
91 climate change increases the frequency of heavy rainfall events, drought periods, freezing-
92 thawing of soil and land use change (Nearing et al. 2004; Zhang et al. 2005; Boardman 2006;
93 Thothong et al. 2011; Ulén et al. 2012; Sun et al. 2013; Bollasina 2014). Consequently,
94 understanding the main sediment sources (hereafter sources) can make soil conservation
95 management strategies more efficient (Mukundan et al. 2012). Sediment fingerprinting
96 techniques offer methods of identifying sources using soil/sediment properties and the application
97 of mixing models (Collins et al. 1998; Walling 2013). A wide range of sediment-associated
98 properties have been used for this purpose, including geochemical properties, radionuclides,
99 mineral magnetism, bulk stable isotopes and colour (Martinez-Carreras et al. 2010; Collins et al.
100 2013; Walling et al. 2013). While these robust and highly transferable fingerprints can provide
101 accurate estimates of source apportionment for a range of agro-ecosystems, they are typically
102 limited in their ability to discriminate between sources in cases where agricultural land use types
103 span geological boundaries or where geological variations in the landscape are small (Gellis and
104 Walling 2011; Blake et al. 2012; Hancock and Revill 2013; Chen et al. 2016). In addition to
105 inorganic properties, plant-specific organic molecules (biotracers) found in the sediment can also
106 be used for fingerprinting and are more specific to discriminate between different land uses. The
107 use of compound-specific stable isotope (CSSI) signatures (Fig. 1), for example, is emerging as
108 a promising sediment fingerprinting technique for this purpose. The isotopic signature of
109 individual compounds in a complex mixture is hereafter referred to as a CSSI signature, as
110 opposed to the bulk stable isotopic signature, which is the isotopic signature of the entire soil or

111 sediment. The CSSI technique exploits differences in the stable isotope signature of individual
112 biotracers to identify and apportion the contribution of specific land uses to the sediment load
113 (Gibbs 2008; Blake et al. 2012; Gibbs 2013; Cooper et al. 2015; Alewell et al. 2016).

114 Fatty acids (FAs) and alkanes are commonly used as biotracers in CSSI-based source
115 apportionment techniques (Table 1). A key characteristic of these compounds is that their CSSI
116 signatures vary across sources and survive deposition in soil and sediment in a recognizable form
117 (Rosell-Melé and McClymont 2007). Fatty acids are well suited to water erosion studies because
118 of their high abundances in soils (universal biotracers) and their polarity, which allows them to
119 disperse and adsorb to soil particles (Gibbs 2008; Feakins et al. 2016).

120 Many biological, environmental and analytical factors contribute to FA carbon and hydrogen
121 isotopic variability and uncertainty in soil and sediments (reviewed by Reiffarth et al. (2016) for
122 carbon). The source of the sediment is therefore not the only factor contributing to biotracer
123 variability in mixture signatures. While some of this variability can be addressed by improving
124 sampling and analysis strategies, even the best methods will result in more CSSI variability than
125 can be explained by the mixture of source signatures alone. Fortunately, recent advances in
126 Bayesian stable isotope mixing models (SIMMs) have established robust methods to address
127 CSSI variability in biotracers and uncertainty in the estimation of proportional source
128 contributions (Moore and Semmens 2008; Semmens et al. 2009; Parnell et al. 2013; Stock and
129 Semmens 2016).

130 In this paper we provide a comprehensive methodological perspective on the application of
131 FA isotope signatures for the apportionment of sediment sources. We focus on the following
132 topics: (i) the concept of CSSI sediment fingerprinting (section 2), (ii) variability in CSSI of FAs
133 (section 3), (iii) soil and sediment sampling strategies (section 4), (iv) FA extraction and CSSI
134 measurement (section 5) and finally (v) challenges and opportunities associated with using the

135 CSSI signature of sources and sediments in Bayesian mixing models to obtain source
136 contributions to sediments (section 6).

137

138 **2 Concept behind the CSSI sediment fingerprinting approach**

139 Different properties of biotracers, such as abundance, composition and isotopic signature,
140 provide a powerful means to identify and apportion the sources of deposited and suspended
141 sediments across a range of aquatic environments (Table 1). Biotracer abundance and
142 composition has mostly been used to differentiate between terrestrial and aquatic organic matter
143 sources in river, lake and estuarine sediments (Ouyang et al. 2015). Many biotracers are neither
144 land use-specific nor conservative because they degrade quickly in the sediment. On the other
145 hand, the stable isotopic signatures of plant-derived FAs have the potential to differentiate
146 between sediments originating from different land uses, since their isotopic signatures record
147 ecological and hydrological conditions during their biosynthesis. Additionally, plant-derived FAs
148 are less influenced by diagenesis and are stable over long timescales in soil and sediments
149 (Sinninghe Damsté and Schouten 2006; Drenzek et al. 2007; Gibbs 2008; Cooper et al. 2015).
150 For these reasons, CSSI signatures of plant-derived FAs are appropriate biotracers for the
151 identification and estimation of source contribution to sediment using SIMM_S (Table 1). Most
152 CSSI studies use C ($\delta^{13}\text{C}$) and/or H ($\delta^2\text{H}$) isotopes of biotracers to identify and assess sources and
153 delivery processes of soil and terrestrial organic matter to aquatic ecosystems. The focus of this
154 paper is on sediment source apportionment i.e. relative contributions of source soils to sediment
155 mixture, and not on the differentiation between terrestrial versus aquatic organic matter inputs.

156 CSSI sediment fingerprinting using $\delta^{13}\text{C}$ of fatty acids ($\delta^{13}\text{C}$ -FAs) was first successfully
157 applied by Gibbs (2008) in New Zealand to assess the relative contribution of sources associated
158 with different land uses to estuarine sediment. The following steps were taken to implement this
159 technique: (i) definition and sampling of potential sources (e.g. cropland, forest, pasture) within

160 a catchment and collection of sediment mixture samples from a target area, (ii) measurement of
161 FA isotopic signatures from both the potential sources and sediment, (iii) selection of a subset of
162 FAs whose carbon isotopic signatures are apparently conserved and well-separated across
163 sources, and (iv) estimation of proportional source contributions to the sediment using SIMMs
164 based on $\delta^{13}\text{C}$ -FA values of the sediments and sources (Fig. 1). Using CSSI signatures of FAs to
165 apportion sources of sediment by land use assumes that (i) the land use categories under
166 consideration (n-potential sources in Fig.1), have plant communities producing FAs with distinct
167 isotopic signature, and that these FAs label the soil with CSSI signatures that reflect land uses
168 (Gibbs 2008, 2013) and (ii) when soil is eroded and transported to the aquatic system, the FAs
169 label is transported together with the soil particles, through the system. In the transport process,
170 particles originating from different land uses, and therefore bearing their specific CSSI labels, are
171 mixed (e.g. three sources in Fig. 1) such that the sediment represents a mixture of contributing
172 upstream sources. To obtain CSSI values, FAs are extracted from soil and sediments, purified,
173 and derivatised for measurement by gas chromatography - isotope ratio mass spectrometry (GC-
174 IRMS). FAs used as inputs for mixing models should be present in all sources and sediment
175 samples at a concentration that allows precise isotopic measurement. Mixing models assume that
176 the stable isotopic composition of each FA in the mixture (the sediment sample) is a linear
177 combination of the isotopic compositions of that specific FA in all contributing sources. The
178 SIMMs estimate the probability distribution of each source's proportional contribution (land use
179 types) to the measured mixture (sediment sample).

180

181 **3 Fatty acids as biotracers**

182 Plants synthesize FAs containing different numbers of carbon atoms. These FAs are
183 commonly classified as either short-chain (≤ 20 carbon atoms, i.e. low molecular weight) or long-
184 chain (> 20 carbon atoms, i.e. high molecular weight). While short-chain FAs are found in the

185 cellular membranes of various organisms, long-chain FAs are found predominantly in the
186 cuticular waxes of vascular plant leaves, allowing them to be used as specific tracers for plant-
187 derived organic matter (Naraoka et al. 1995; Matsumoto et al. 2007; Galy and Eglinton 2011).
188 Therefore, the analysis of long-chain FAs in soils offers the possibility to specifically trace
189 organic matter that is plant-derived (Amblés et al. 1998; Bull et al. 1998; Matsumoto et al. 2007;
190 Tuo et al. 2011; Jandl et al. 2013).

191

192 **3.1 Isotopic signatures of fatty acids in plants**

193 *3.1.1 Carbon isotopes ($\delta^{13}\text{C}$)*

194 It is generally known that the CO_2 fixation pathways of the plant (C_3 , C_4 or CAM) induce
195 different isotopic fractionations, leading to different $\delta^{13}\text{C}$ -FA values (e.g. Chikaraishi 2014;
196 Reiffarth et al. 2016). Other processes in the biosynthesis of FA can also induce differences in
197 isotopic fractionation, and hence $\delta^{13}\text{C}$ -FA values, within each plant type (C_3 , C_4 or CAM).
198 Chikaraishi (2014) and Reiffarth et al. (2016) provide a comprehensive review of the biological
199 and environmental sources of $\delta^{13}\text{C}$ -FAs variability in plants. Briefly, decarboxylation (e.g. of
200 pyruvate to form acetyl-CoA) appears to be an important and potentially species-specific process
201 driving isotopic discrimination during FA biosynthesis (Dungait et al. 2010; Chikaraishi 2014
202 and references therein). As a result of this, ^{13}C depletion of long-chain FAs can be as high as
203 10‰ relative to glucose (Chikaraishi et al. 2004b; Hobbie and Werner 2004; Badeck et al. 2005;
204 Dungait et al. 2008; Chikaraishi 2014). However, the effect is more pronounced for C_4 compared
205 to C_3 plants, with an average 9.5 and 3.5‰ depletion relative to bulk plant tissue, respectively
206 (Agrawal et al. 2014). A significant difference in $\delta^{13}\text{C}$ also exists between C_3 angiosperms and
207 gymnosperms, where gymnosperm $\delta^{13}\text{C}$ -FA values are on average 3‰ more enriched compared
208 to that of angiosperms (Chikaraishi et al. 2004a). The isotopic signature of individual FA
209 homologues in C_3 plants are characterized by a gradual depletion with increasing carbon number

210 (e.g. from C₂₄ to C₃₂ depletion can be up to -2.7‰), whereas in C₄ plants the $\delta^{13}\text{C}$ -FA values stay
211 constant or are slightly enriched (up to +0.7 ‰ for C₂₄ to C₃₂) (Agrawal et al. 2014 and references
212 therein). Depending on external parameters such as soil water availability, temperature and
213 sunlight, the extent of isotope fractionation may differ even for the same pathway, especially for
214 C₃ plants (Heaton 1999; Chikaraishi et al. 2004a). In addition, altitude, slope and aspect are
215 topographical factors indirectly affecting carbon isotopic ratios through their effect on climatic
216 (e.g. atmospheric pressure, temperature and precipitation) and edaphic factors (e.g. soil age, soil
217 depth, nutrient status and water holding capacity) (Warren et al. 2001). Altogether, carbon
218 isotopic variation in plant FAs is partially explained at the spatio-temporal, interspecies and even
219 intra-species levels (Dungait et al. 2008, 2010). However, the influence of topography on FA
220 isotopic signatures of different land cover is still not clear and requires further research.

221

222 3.1.2 Hydrogen isotopes ($\delta^2\text{H}$)

223 The hydrogen isotopic composition of FAs ($\delta^2\text{H}$ -FAs) is used as a tracer in biogeochemical
224 and paleo-environmental studies (Jones et al. 2008; Seki et al. 2012). The hydrogen isotopic
225 signature of plant FAs and alkanes originates from a common precursor and depends ultimately
226 on the $\delta^2\text{H}$ value of leaf water (Sachse et al. 2012; Ponton et al. 2014; Feakins et al. 2016). The
227 signature of FAs and alkanes are related: C_n-FAs (e.g. C₃₀ FA) are the biosynthetic precursors of
228 the C_{n-1}-alkanes (e.g. C₂₉ alkanes) but, due to a biosynthetic isotopic fractionation during the
229 decarboxylation process, there is an offset in $\delta^2\text{H}$ value between C_{n-1}-alkanes and C_n-FAs pairs.
230 Nevertheless, Feakins et al. (2016) observed a lack of overall consistency in decarboxylation-
231 associated ^2H fractionation between pairs of FAs and alkanes (e.g. C₃₀ and C₂₉ pairs) among plant
232 species. As a consequence, overall compound class offset (i.e. between FAs and alkanes) is
233 insignificant at the plant community level where sample size is large enough. As a result, this
234 offset is also insignificant on the land use level, since plant community, which integrates FAs

235 biosynthesised from a multitude of plants over a large area and time scale, defines land use.
236 Therefore, $\delta^2\text{H}$ -FAs are likely to be similar to those of alkanes in terms of their usefulness for
237 discriminating between soils developed under different plant ecotypes (i.e. grass, shrubs or wood)
238 (Liu et al. 2006; Hou et al. 2007; Liu and Yang 2008) and recording elevation gradients defined
239 by the isotopic signature of precipitation (Ponton et al. 2014; Feakins et al. 2016). However, very
240 limited $\delta^2\text{H}$ -FA data exists from living plants, while data of soils and sediments are in line with
241 those of alkanes.

242 In addition to biosynthetic fractionation, climatic and plant morphological characteristics can
243 affect the $\delta^2\text{H}$ values of FAs due to differences in plant water sources, temperature, precipitation,
244 evapotranspiration and root or leaf morphology. Only a few studies have investigated factors
245 affecting leaf $\delta^2\text{H}$ values of FAs (Huang et al. 2004; Chikaraishi and Naraoka 2007; Hou et al.
246 2007; Feakins et al. 2016). Hydrogen in FAs is derived from leaf water during photosynthesis.
247 Leaf water is itself controlled by soil water, which originates from rainfall or snowmelt in
248 temperate climates. Besides fractionation during photosynthesis and FA biosynthesis, $\delta^2\text{H}$ values
249 will be controlled by the isotopic signature of leaf water at the time they are biosynthesised
250 (Chikaraishi and Naraoka 2003; Seki et al. 2010; Seki et al. 2012; Liu et al. 2015). In moisture
251 limited areas or seasons, hydrogen isotope values of leaf water can be directly enriched in
252 deuterium by transpiration and/or indirectly enriched by evaporation of soil water. It is generally
253 accepted that the uptake of soil water by plants is not associated with discernible isotopic
254 fractionation (Dawson et al. 2002). However, fundamental differences can be observed in terms
255 of the water use of different ecological life forms (e.g. woody plants vs. grasses) at different
256 depths due to their root systems. Grasses and herbs take up water from the surface soil, whereas
257 deep rooted trees and shrubs use water from deeper soil layers. Since soil water $\delta^2\text{H}$ usually
258 increases with depth (Grieu et al. 2001), this may result in higher $\delta^2\text{H}$ value of leaf FAs and
259 alkanes of trees compared to those of grasses and herbs (Liu et al. 2006; Liu et al. 2015).

260

261 **3.2 Isotopic signatures of fatty acids in soils and sediment**

262 In agricultural land uses with patchwork fields and a wide spectrum of crop and soil
263 management practices, each agricultural system/rotation may have distinct FA isotopic
264 signatures. Additionally, if crops are planted on land that once was forest, the subsoil is likely to
265 have different CSSI values (related to forest) than the surface soil (growing crops) (Wiesenberg
266 et al. 2004). Fatty acids in soil derive principally from growing vegetation, vegetation from
267 previous rotations, and crop residues (VanBergen et al. 1997; Mueller et al. 2012). Root exudation
268 and decomposition of organic matter in soil can vary the proportions and isotope signatures of
269 FAs (Wiesenberg et al. 2004; Wiesenberg and Schwark 2006; Dungait et al. 2008; Jandl et al.
270 2013), but the exact effect of these processes is difficult to quantify. In essence, the combination
271 of past and present FAs at a particular site provides an isotopic fingerprint for the specific land
272 use. Monoculture or similar vegetation composition over years will result in low variability of
273 FA isotopic signatures in the source soil (Wiesenberg et al. 2004). In contrast, agro-ecosystems
274 and natural systems often involve a mixture or rotation of C₃ and C₄ plants seasonally or annually.
275 Generally, rotation and/or mixing of different crops in one field on a seasonal and/or annual basis
276 will blend the FA isotopic signatures of each crop into a ‘new’ mixture of FA isotopic signatures
277 that lies between the FA isotopic signatures of the individual crops.

278 The adsorption and complexation of FAs to soil and their persistence for long periods of time
279 in the sediment make them unique tracers (Bianchi and Canuel 2011; Bergamino et al. 2014).
280 Fatty acids are partially water soluble at the pH of most natural waters and can therefore be carried
281 down into the soil profile with infiltrating water. Along their flow path, FAs are adsorbed onto
282 soil particles or trapped in the internal voids of fine soil particles, especially clay and silt, from
283 which they hardly re-diffuse, thereby preserving the isotopic signature of the plant FAs in the soil
284 (Jandl et al. 2005; Bayrak 2006; Gibbs 2008; Blake et al. 2012). Short-chain FAs are more

285 hydrophilic and are thus more easily mobilized and leached down the soil profile (Matsumoto et
286 al. 2007). In contrast, long-chain FAs (solubility decreases with increasing carbon chain length)
287 are more likely to be retained on the upper erodible soil layers (Amblés et al. 1994). Fatty acid
288 concentrations in soils and sediment may change over time due to degradation by microorganisms
289 via oxidation and re-synthesis, volatilization, dilution, and dispersion (Dinel et al. 1990;
290 Banowetz et al. 2006; Matsumoto et al. 2007), but degradation is believed to have little effect on
291 $\delta^{13}\text{C}$ -FA values (Chikaraishi and Naraoka 2005; Blessing et al. 2008; Gibbs 2008). Canuel and
292 Martens (1996) observed that the concentration of C₁₄ to C₁₈ FAs degraded at a faster rate in
293 sediment than longer chain FAs, which had lower or insignificant concentration reduction rates
294 over a five month period after deposition. Furthermore, unsaturated FAs degrade faster than
295 saturated FAs due to their higher vulnerability to biological and chemical degradation
296 (Niggemann and Schubert 2006).

297 Presently, very limited effort has been directed at understanding the $\delta^2\text{H}$ of FAs transported
298 from source to sediment via water erosion. However, hydrogen in FAs is covalently linked to C
299 by a strong and nonpolar bond requiring high activation energy for exchange, making it the most
300 isotopically conservative H moiety (Radke et al. 2005) and thus a good (conserved) isotope signal
301 of water used by plants (Sachse et al. 2012). To the best of our knowledge, there is currently no
302 published study that has used $\delta^2\text{H}$ -FA values for sediment source apportionment, although $\delta^2\text{H}$
303 of long-chain FAs (e.g. C₂₈) was utilized to differentiate sediment particulate organic matter
304 between different source areas defined by the isotopic signature of precipitation (Wilkie et al.
305 2013; Ponton et al. 2014).

306 In conclusion, based on the information currently available in the literature and our
307 experience, $\delta^{13}\text{C}$ values of long-chain saturated FAs are advised to be used for sediment source
308 discrimination and apportionment, in contrast to short-chain and unsaturated FAs, which are less
309 useful for this purpose. Reasons include the fact that long-chain FAs are produced almost

310 exclusively by vascular plants and therefore avoid contamination by microorganisms and algae
311 at the deposition site and that they are more resistant to degradation in soil and sediment
312 environments, which reduces the risk of isotopic fractionation (Hu et al. 2006; Bourgeois et al.
313 2011; Fang et al. 2014; Alewell et al. 2016; Reiffarth et al. 2016). Furthermore, data on δ^2H -FAs
314 might allow for an improved discrimination between land use types, mainly based on plant
315 ecotypes (e.g. grasses, shrubs and trees). $\delta^{13}C$ and δ^2H values in plants are controlled by largely
316 independent mechanisms, though both are present in the same molecule and thus follow exactly
317 the same transit through the catchment. Therefore, compound-specific dual isotopes ($\delta^{13}C$ and
318 δ^2H) of FAs could provide better source/land use information on FAs than single isotopic
319 analyses (Krull et al. 2006; Seki et al. 2010; Cooper et al. 2015).

320

321 **4. Sources and sediment sampling strategies**

322 **4.1 Sources**

323 In the CSSI approach, a catchment should be subdivided into spatial sources (i.e. sub-
324 catchments (Fig. 2) or land use types (Fig.3a)) using a reconnaissance survey and topographic or
325 drainage maps as background information. Source soil sampling should provide FA isotope
326 signatures encompassing the local spatial variability (within sediment sources); in other words,
327 every land use should be represented by a stratified random sampling design that accounts for
328 factors such as field size and patchy agriculture practices. Particular attention should be paid to
329 the collection of erodible topsoil within a land use, as that soil is sensitive to erosion and thus
330 connected to the stream network (Olley and Caitcheon 2000; Hancock and Revill 2013; Tiecher
331 et al. 2015). Collection of transported sediment from the lowest point of a single land use site can
332 integrate the variation within that site, thus providing an integrated signal of erodible soil from
333 that source. Beyond land use types, other important sources include unpaved roads, eroded
334 riverbanks, river channels containing sediment from earlier erosion events and any other site-

335 specific secondary sources along the river channel. Currently, analytical cost is one of the most
336 important factors influencing the sampling intensity and number of samples. The question of
337 whether to use spatially-integrated random composite samples (i.e. soil samples obtained
338 randomly from different positions within the land use that are then combined to make composite
339 samples) is therefore a trade-off between analytical cost saving and the need to determine the
340 degree of $\delta^{13}\text{C}$ -FA spatial variability (Brandt et al. 2016): a question which can only be answered
341 in terms of specific research objectives. Spatially-integrated samples integrate larger spatial and
342 temporal scales and are therefore less susceptible to potential sampling bias caused by
343 annual/seasonal variation in isotopic fractionation during FA production. Importantly, the
344 complexity of a larger catchment can be better captured by integrating various sub-catchments
345 (Fig. 2). Here, a primary consideration is to account for sediment contribution from sub-
346 catchments to the main river system that drains the larger catchment (Rhoton et al. 2008; Vale et
347 al. 2016). Therefore, sediment from the tributaries upstream of confluence become sources for
348 downstream sediments (Fig. 2; I, II, III and IV), and sediment traps should be located accordingly.
349 It is important to collect sediment samples downstream of the confluence at distances sufficient
350 to allow for the complete mixing of upstream sources.

351 When designing sampling strategies, it is important to consider the relative timeframes
352 represented by source and sediment samples. For instance, bulk and FA stable carbon isotopic
353 signatures of source soils might not be constant over multiple years (Fox and Martin 2015), and
354 it is thus advised to resample the sources for every sediment sampling campaign. Otherwise, bias
355 can be introduced when older source samples are used to apportion more recent sediment
356 samples.

357

358 **4.2 Sediment**

359 Different types of sediment samples can be selected depending on the timeframe and flux of
360 interest and may range from event based samples collected during a specific event to suspended
361 sediment deposited within a given time frame. Examples of the latter include sediment collected
362 using time-integrated mass-flux samplers (TIMS) or samples of deposited sediment from a flood
363 plain, which may contain sediment from the last flood event or that which has been accumulated
364 over a long time period (e.g. sediment core). Event based samples can be collected during flood
365 events by filtration or by sedimentation after pumping water out of the stream. Time-integrated
366 mass-flux samplers (also known as Phillips samplers) effectively trap suspended sediments by
367 reducing flow velocity when water enters the sampler (Phillips et al. 2000; Perks et al. 2014;
368 Smith and Owens 2014). Multiple TIMS should be installed at different locations (easy to reach
369 throughout the year) with similar water depths and well-mixed uniform flow. Sediment samples
370 can be retrieved at different time intervals for apportioning sediment sources according to specific
371 temporal resolutions.

372 Sediment is delivered to the aquatic environment as primary and aggregated particles but the
373 aggregates break down during transport due to abrasion and disaggregation as a result of
374 turbulence (Droppo 2001). In general, eroded material is enriched in clay- and silt-sized particles
375 relative to the original soil. Sorting within the fluvial system, however, could lead to mixtures of
376 coarse and fine material from a range of sources due to contrasting transport times of different
377 fractions and proximity to sediment sources (Fletcher and Muda 1999; Miller and Miller 2007).
378 It is important to note that the concentration of suspended sediment tends to increase with
379 increasing distance from the bank due to an increase in sand-sized materials (Walling et al. 2011).
380 For the same reason, vertical concentrations of suspended sediment in fluvial systems tends to
381 increase with increasing depth. Nevertheless, the choice of sediment size fraction depends on the
382 characteristics of the sediment transported out of the catchment and the fraction responsible for
383 any environmental issues (e.g. siltation of salmonid spawning gravels) in question (Bartley et al.

384 2014; Collins et al. 2016). Therefore, appropriate sediment sampling site selection is
385 recommended, with samples taken at the outlet of the catchment and/or at key locations across
386 the catchment, to provide a representative sediment.

387

388 **5 FA extraction and carbon and hydrogen isotope measurement**

389 FAs are typically extracted using a combination of solvents such as chloroform, methanol
390 (MeOH), hexane and dichloromethane (DCM). Wiesenberg and Gocke (2017) provides helpful
391 insights into the common procedures of FA extraction and purification for CSSI analyses. To
392 minimize analytical variability in $\delta^{13}\text{C}$ -FA values from sample handling to isotope measurement,
393 the reader is referred to the recommendations made by Reiffarth et al. (2016). It is highly
394 advisable to derive a total lipid extract (TLE) from the same size fractions for both sediment and
395 source soils to ensure comparison of like-with-like, since FA concentrations and their $\delta^{13}\text{C}$ values
396 differ between soil fractions (Griepentrog et al. 2015).

397 The choice of extraction method depends on the availability of instrumentation (e.g.
398 accelerated solvent extraction). Fatty acids must be further purified from the complex TLE to
399 minimise the risk of co-eluting contaminants during CSSI analysis. It is also important to use
400 halogen-resistant plastic or glass solid phase extraction (SPE) columns due to the nature of the
401 applied solvents. Fatty acids must be derivatised to fatty acid methyl esters (FAMES) prior to
402 CSSI analysis, and, to that end, several derivatisation procedures have been proposed in the
403 literature (de la Fuente et al. 2006; Milinsk et al. 2008; Ichihara and Fukubayashi 2010).
404 Depending on the applied purification, FAs can either consist of free extractable FAs and/or ester
405 bound FAs. Isotopic signatures of individual FAs can be measured using gas chromatograph-
406 combustion-isotope ratio mass spectrometry (GC-C-IRMS) and gas chromatograph-thermal
407 conversion-isotope ratio mass spectrometry (GC-TC-IRMS) for carbon and hydrogen,
408 respectively. The addition of a methyl group to produce FAMES alters the C and H isotopic

409 signature of FAs, which has to be corrected in order to obtain the isotopic signature of the original
410 FAs (Chikaraishi et al. 2004b). To obtain the highest possible accuracy, it is preferable to compare
411 sample and standard within each chromatogram after handling them as similarly as possible
412 according to the principle of identical treatment (Werner and Brand 2001). The GC-C-IRMS or
413 GC-TC-IRMS does not provide structural information, and identification is solely based on
414 retention time. It is therefore advisable to confirm the identity of individual FAs and to check for
415 chromatographic peak purity during previous gas chromatography-mass spectrometry (GC-MS).

416

417 **6 Data analysis using Bayesian mixing models**

418 **6.1 Overview and current practice**

419 Stable isotope mixing models use stable isotope data of FAs in sources and mixture
420 (sediment) to provide quantitative estimates of the proportional contribution of each source to the
421 sediment. Mixing models originated in the ecological literature, where they are used, for instance,
422 to quantify proportions of different food sources in consumer diets (mixture), typically using bulk
423 stable isotope data but increasingly using other tracers such as amino acids and FAs (Boecklen
424 et al. 2011; Parnell et al. 2013; Phillips et al. 2014). At their core, mixing models are mass balance
425 equations, where the tracer values of the mixtures are a convex combination of the mean tracer
426 values of the sources after correcting for non-conservative processes (modification of the tracer
427 values in the mixture, “trophic discrimination factor” in the case of diet studies). In this section,
428 we highlight characteristics of mixing models pertinent to their application for CSSI sediment
429 fingerprinting, as thorough reviews of the development and advantages of Bayesian mixing
430 models can be found elsewhere (Hopkins and Ferguson 2012; Parnell et al. 2013; Semmens et al.
431 in review).

432 IsoSource (Phillips and Gregg 2003) is currently the most commonly applied mixing model
433 for sediment fingerprinting using $\delta^{13}\text{C}$ -FAs values (Gibbs 2008; Blake et al. 2012; Hancock and

434 Revill 2013; Alewell et al. 2016). IsoSource requires a minimum of three sources and two tracers
435 and cannot accept more than five tracers. It uses a resampling algorithm and a tolerance term to
436 identify several possible analytical solutions to the mixing system (given a tolerance) and
437 provides a range of possible proportional contributions. Because each solution is feasible and
438 might be multimodal, researchers are encouraged to report the range of proportional contributions
439 of each source rather than simply reporting the mean or median (Phillips and Gregg 2003; Gibbs
440 2008). The original version of IsoSource does not take differences in concentration into account,
441 but a modified version has been developed to overcome these shortcomings (Granek et al. 2009).
442 However, one of the limitations of IsoSource is that it models mean values of source and sediment
443 isotopic signature rather than the distribution of actual values. Additionally, it does not measure
444 uncertainty quantitatively (Moore and Semmens 2008). Bayesian modelling approaches are
445 becoming more popular as a result of recently proposed improvements to linear (e.g. IsoSource)
446 and Bayesian SIMMs, such as the inclusion of variability, prior information and sensitivity
447 analyses (e.g. MixSIAR, Stock and Semmens 2013; IsotopeR, Hopkins and Ferguson 2012).

448 Bayesian implementations of SIMMs (e.g. MixSIR, Moore and Semmens 2008; SIAR,
449 Parnell et al. 2010) have seen increased use in both ecology and sediment fingerprinting recently
450 since they use a flexible and more statistically sound likelihood framework (Semmens et al. 2013;
451 Cooper et al. 2014). Most important mixing model improvements developed since MixSIR/SIAR
452 have been incorporated into MixSIAR, an open-source R package (Stock and Semmens 2013;
453 Semmens et al. in review). Furthermore, these Bayesian SIMMs provide the opportunity to
454 implement a hierarchical structure to the data, which might prove to be particularly useful in
455 catchments with high complexity. Below, we focus on considerations for using Bayesian SIMMs
456 to perform sediment fingerprinting that is specific to $\delta^{13}\text{C}$ -FA data.

457

458 **6.2. Concentration-dependent SIMMs**

459 The mixing models applied in the majority of previous CSSI sediment fingerprinting studies
 460 did not consider the difference in relative FA concentrations between the sources (i.e.
 461 concentration-independent models), instead applying a post unmixing correction for total tracer
 462 concentrations (using the cumulative tracer i.e. total FAs concentration, Alewell et al. 2016, or
 463 total organic carbon content as a proxy, Gibbs 2008).

464 The unmixing of sediment samples to determine the proportional contribution of the sources
 465 using a SIMM (linear or Bayesian) is always based on a simple isotopic mixing model. For one
 466 tracer's isotope and S sources the mixing model can be written as follows:

467

$$468 \quad \beta = \sum_{s=1}^S \delta_s \pi_s \quad (1)$$

469

470 where β is the isotopic composition of the mixture, δ_s is the isotopic composition of source s and
 471 π_s is the proportional contribution of the isotopic tracer of source s .

472 For multiple tracers this equation can be generalized as:

473

$$474 \quad \beta_i = \sum_{s=1}^S \delta_{n,s} \pi_{n,s}, \text{ for } n = 1, \dots, N \quad (2) \text{ and}$$

$$475 \quad \sum_{s=1}^S \pi_{n,s} = 1, \text{ for } n = 1, \dots, N \quad (3)$$

476

477 where the subscript n denotes the different tracers (i.e. different FAs) and the subscript s denotes
 478 the different sources. This results in N x 2 equations that have to be solved for S x N unknowns
 479 ($\pi_{n,s}$). The proportional contribution of the tracer n ($\pi_{n,s}$) can be written as a function of the
 480 proportional contributions of the sources (f_s).

481

$$482 \quad \pi_{n,s} = \frac{f_{s \times C_{n,s}}}{\sum_{s=1}^S f_{s \times C_{n,s}}} \quad (4)$$

483

484 where $C_{n,s}$ is the concentration of tracer n in source s .

485 In a concentration-independent mixing model, the N $\pi_{n,s}$ are assumed to be a random
486 distribution of a common π_s . This assumption, however, is only correct if the isotopic tracer
487 composition (i.e. relative concentration of FAs in our case) is identical for all sources (i.e.
488 $\frac{C_{n,1}}{\sum_{n=1}^N C_{n,1}} = \frac{C_{n,2}}{\sum_{n=1}^N C_{n,2}} = \dots = \frac{C_{n,S}}{\sum_{n=1}^N C_{n,S}}$ for all n), which is actually rather an exception than the
489 rule. In a concentration-dependent model, $\pi_{n,s}$ in equation (2) is replaced by equation (4), leading
490 to $N + 1$ (i. e. $\sum_{s=1}^S f_s = 1$) equations for S unknowns (f_s).

491 Although widely used in the CSSI erosion study community, concentration-independent
492 models are, in essence, not correct. We argue that the use of concentration-dependent models
493 should be mandatory for future use of CSSI tracers in erosion studies. The magnitude of the error
494 introduced by using a concentration-independent SIMM followed by post mixing correction will
495 vary, and might be small in some cases (e.g. when relative FA concentrations do not vary much
496 between sources) (Fig. 3c). Nevertheless, we strongly advocate for the inclusion of readily-
497 available FA concentration data during mixing model formulation. Ignoring FA concentrations
498 during this process leads to distortion of the source contributions (Phillips and Koch 2002;
499 Phillips et al. 2014).

500

501 **6.3 Recommendations for CSSI sediment fingerprinting**

502 *6.3.1 Selection of FAs to use in mixing models*

503 In order for mixing models to successfully apportion source contributions, the input tracer
504 data needs to be (i) conservative (i.e. either no isotopic fractionation during transport from source
505 to sink or predictable isotope fractionation) and (ii) informative (e.g. they must differentiate
506 between the sources). The first and most important method of selecting FAs is, logically, based
507 on their biochemistry (i.e. which organisms produce it? how recalcitrant is it?) and behaviour in
508 the soil and sediment environment (i.e. how will it bind to the sediment particle?). These premises

509 clearly call for the use of saturated, long chain, FAs (see above). After careful consideration of
510 their biochemistry and behaviour, the simple tests described below can provide additional
511 guidance on whether to include or exclude specific FAs.

512 Mixing models assume that sediment is a homogeneous mixture of the contributing sources.
513 Therefore, the isotopic composition of each FA in the sediment should fall within the range of
514 credibility intervals found for the source soils' isotopic composition. A bracketing test is a
515 common way of evaluating this assumption for isotopic compositions measured in sediment
516 samples (Benstead et al. 2006; Smith et al. 2013; Wilkinson et al. 2013; Brandt et al. 2016).
517 However, a bracketing test only evaluates extreme values based on the assumption that any
518 intermediate data points are represented by the extremes. It does not determine conservative
519 behaviour, but it does identify samples that are outliers.

520 Bracketing tests with more than one dimension can be visualized by mixing polygons. For
521 example, the mixing space of three sources defined by two $\delta^{13}\text{C}$ -FAs can be plotted as vertices
522 of a polygon (although the concentration-dependent model may make the edges somewhat curved
523 rather than straight) and all sediment samples should ideally be bound within the polygon
524 (Phillips and Koch 2002; Hopkins and Ferguson 2012). Sediment samples that are not bound
525 within the polygon indicate either a missing source or non-conservative transport. Additionally,
526 the mixing space geometry (in two- or three-isotope systems) can be quantitatively evaluated
527 using a Monte Carlo simulation of mixing polygons for the point-in-polygon assumption test
528 (Smith et al. 2013) and have been used in CSSI sediment fingerprinting (Brandt et al. 2016).
529 Convex hulls (mixing polygons) can be iterated using the distributions of the $\delta^{13}\text{C}$ -FA values of
530 the intended sources. The proportion of polygons which provide a solution (i.e. meet the point-
531 in-polygon assumption) is then calculated, providing the quantitative basis for validating mixing
532 space geometry (Smith et al. 2013; Brandt et al. 2016). When there are more than three tracers,
533 this polygon generalizes to an n-dimensional hyper ellipse (Blonder et al. 2014). Transformation

534 of such an ellipse into the perfect circle, centred around the origin, by linear matrix algebra using
535 the covariance matrix of the data (the same data that defines the ellipse) and projection of
536 sediment data (after transformation in the same way like ellipse) into the circles helps to test the
537 point-in-polygon assumption at higher dimensions (Jackson 2016). However, these approaches
538 still neglect the concentration effect on the geometry of the mixing space and thus warrants
539 further research.

540 Once visualization of the mixing space or bracketing testing is complete, Tukey's HSD test
541 can be used to identify FAs that allow for significant differentiation of sources. Optionally, best
542 FA subsets for differentiation among sources can also be obtained using the Simulated Annealing
543 Algorithm (SAA). Using this method, the selected subset (e.g. C₂₂, C₂₆, C₃₂) can provide the same
544 level of discrimination (Fig 3b) as all variables (e.g. C₂₂, C₂₄, C₂₆, C₂₈, C₃₀, C₃₂) do. Detailed
545 explanations of the SAA are available elsewhere (Silva 2001; Brusco 2014; Cerdeira et al. 2015).
546 Selection of variables helps to minimize co-linear $\delta^{13}\text{C}$ -FAs and reduce multiple and conflicting
547 solutions. When a selected set of FAs fails to discriminate potential sources, the sources can be
548 re-defined either by lumping or splitting them to produce sufficient heterogeneity in the isotopic
549 values of FAs among sources (D'Haen et al. 2012; Sherriff et al. 2015).

550

551 *6.3.2 Inclusion of prior information and covariates*

552 In general, there is a demand for knowledge on relevant soil erosion processes in the
553 landscape and the fate of sediment in the catchment environment (Fox and Papanicolaou 2008;
554 Ulén et al. 2012). Soil does not erode uniformly across the entire soil surface due to the
555 'patchiness' of rainfall and episodic nature of water erosion, which can make substantial
556 differences in soil erosion severity between different land uses and between locations within a
557 land use. Additionally, land use characteristics (e.g. land cover, area) of the catchment will
558 theoretically have a direct impact on the relative contributions to sediment. This fact can be used

559 as prior information in Bayesian mixing models. Prior information is unmeasured data that is not
560 directly involved in tracing the sources and originates mainly from catchment characteristics,
561 expert knowledge and literature on the proportions of land use. The incorporation of logical and
562 appropriate prior information into the Bayesian SIMM helps to account for the full range of
563 source variability and reduces the uncertainty of the estimates as much as possible. Furthermore,
564 by incorporating a residual error term in the Bayesian SIMM (e.g. MixSIAR), the additional
565 unquantified variation in isotopic signatures between individual sediments can be represented
566 (i.e. deviation of the observed value from the true value) and the variability of the isotopic mixing
567 system in the sediment can be captured (Semmens et al. 2009; Stock and Semmens 2016).
568 Therefore, CSSI sediment fingerprinting can be improved by formulating mixing models that
569 take prior information and residual error into account and incorporate covariates and covariance
570 from the sources and sediment samples (e.g. base flow vs. episodic runoff sediment, seasonal
571 differences in erosion and sediment generation due to rainfall intensity and land cover change)
572 (Table 2). The cross-isotopic tracer covariance is parameterised within Bayesian mixing model
573 through a single correlation parameter for each source (Hopkins and Ferguson 2012; Parnell et
574 al. 2013). Moreover, MixSIAR can incorporate covariates as random or fixed effects and we
575 recommend their use when there is reason to believe that the inclusion of covariates will influence
576 the outcome of sediment source apportionment.

577

578 **6.4 Research needs**

579 The issue of how to statistically select tracers for inclusion in mixing models is still unsettled.
580 Bracketing tests can identify non-conservative tracers, but it is possible for a tracer to be non-
581 conservative and still pass the test. Simulation studies should shed light on the impact of including
582 more or fewer tracers that may or may not be conservative or informative. Rainfall simulation
583 experimental tests can provide information on the conservativeness of CSSI tracers during the

584 sediment generation process. However, it is critical to understand the effects that residence time
585 and storage of different sediments size fractions have on the $\delta^{13}\text{C}$ -FAs in the catchment.

586 Another future direction for Bayesian mixing models is to deal with larger and more complex
587 catchments through the estimation of sediment mixing at the sub-catchment level (Fig. 2). We
588 envision extended mixing models that are able to distinguish the source contributions within each
589 sub-catchment, contributions of each sub-catchment to the overall catchment, and the source
590 contributions to the overall catchment. In this type of hierarchical network model, the
591 geographical location of potential sediment sources with respect to sediment sampling sites
592 should always be considered when designing sampling plans and interpreting the model results.

593

594 **7 Conclusions and perspectives**

595 Stable carbon isotopic composition of plant-derived FAs associated with soil and sediment
596 are a powerful tool for providing detailed insights into the contribution of specific land uses to
597 sediment loads at the catchment scale. However, the wider adoption of CSSI fingerprinting for
598 sediment source apportionment is hampered by the fact that clear guidelines that deal with a
599 number of methodological constraints are missing: (i) source and sediment sampling strategies,
600 (ii) FA extraction and selection and (iii) formulation of SIMM inputs.

601 First, it must be noted that efforts in analytics or modelling cannot overcome poor and/or
602 non-representative sampling. Therefore, the collection of spatially integrated random composite
603 samples to obtain representative sources and the installation of TIMS in streams at multiple
604 locations across a catchment to collect suspended sediment are essential to maximize the
605 effectiveness of CSSI fingerprinting approaches. Second, we particularly recommend the use of
606 saturated, long-chain (>20 carbon atoms) FAs from the same size fraction of source soil and
607 sediment due to their exclusive plant origin, conservativeness, strong interaction with soil
608 minerals and ensuring comparison of “like-with-like”. Third, stable isotope mixing models

609 cannot estimate reliable contributions of sediment sources if the model applied does not account
610 for differences in FA concentrations among sources. Therefore the use of concentration-
611 dependent mixing models should be mandatory in sediment fingerprinting studies. In addition,
612 we strongly advise the use of Bayesian mixing models (e.g. MixSIAR) over more basic models
613 such as IsoSource due to their greater flexibility through the use of informative priors and their
614 ability to incorporate a residual error term, which enables them to better cope with CSSI
615 variability.

616 CSSI fingerprinting can provide key information for targeted erosion management, but there
617 is a need for further improvement in source discrimination and SIMM formulation. There exists
618 no robust statistical approach to formally test for missing sources and conservativeness of tracers.
619 Indeed, even if the $\delta^{13}\text{C}$ -FAs fall within the source mixing space, it is still possible that $\delta^{13}\text{C}$ -FA
620 of sediment may be biased by missing sources or non-conservative transport. Therefore, it is
621 equally important to have adequate information on (i) (hillslope) system under investigation (i.e.
622 expert decision on potential erosion sources, covariates effect on the relative contributions of
623 sediment source), (ii) sediment cascade connectivity and (iii) assumptions and limitations of
624 Bayesian SIMMs. Sediment fingerprinting might be further strengthened by adding the $\delta^2\text{H}$ of
625 FAs as complementary isotope tracer capable of discrimination among sources in high resolution.
626 Therefore, coupling of Bayesian SIMMs and dual isotopes ($\delta^{13}\text{C}$ and $\delta^2\text{H}$) of FAs could be an
627 extremely useful addition to the rapidly growing roster of techniques available for sediment
628 fingerprinting. Additionally, as MixSIAR continues to advance, we anticipate the incorporation
629 of erosion processes (e.g. sheet, rill and gulley erosion) responsible for mobilizing sediment
630 within a single source and within hierarchical structures in the drainage basins. The CSSI
631 sediment fingerprinting methodology described in this paper, as well as the expanding number of
632 laboratories capable of CSSI analyses, will definitely contribute to the mitigation of erosion and
633 sediment related problems in the context of land use and climate change.

634

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645

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1037 **Table captions**

1038 **Table 1** Sediment fingerprinting techniques using different properties of biotracers

1039 **Table 2** MixSIAR terminology adapted for sediment fingerprinting

1040

1041 **Figure captions**

1042 **Fig. 1** Overview of the CSSI sediment fingerprinting concept: (i) sediment generating rainfall
1043 events produce sediment from different sources which are then mixed during delivery processes
1044 and end up in the sediment of rivers and lakes, (ii) biotracers (e.g. FAs) are extracted from the
1045 soil and sediments and their $\delta^{13}\text{C}$ values are measured and (iii) FAs are selected based on their
1046 biochemistry, behaviour (e.g. conservativeness, stability) and presence in sources and sediments.
1047 Source and sediment CSSI values are fed into a concentration-dependent Bayesian stable isotope
1048 mixing model. The model accounts for variability in CSSI values of sources and sediment to
1049 generate a proportional density distribution of source contributions to sediment.

1050

1051 **Fig. 2** Sediment sampling concept for dealing with the hierarchical structure of a complex
1052 drainage basin. The larger catchment can be broken up into sub-catchments, and each sub-
1053 catchment may contain different sediment sources to evaluate the sediment contributions from
1054 each sub-catchment or source (e.g. A, B, C, etc.). Hence, sediment from a tributary upstream of
1055 confluence becomes a sediment source for the downstream sediment sample (e.g. at confluence
1056 I (see inset) sediment samples 1 and 2 are the sources for sediment sample 3).

1057

1058 **Fig. 3** Coupling $\delta^{13}\text{C}$ -FAs and MixSIAR for catchment scale sediment source apportionment: (a)
1059 Land uses and sediment sampling locations in the Kunchal catchment of Nepal; (b) Discriminant
1060 function plot based on $\delta^{13}\text{C}$ of a subset of FAs (C_{22} , C_{26} , C_{32}) obtained via Simulated Annealing
1061 Algorithm (ellipsoid encompasses 95% of group range); (c) Box plots (dark red rhombus and

1062 error bar indicate mean and standard deviation, respectively) of relative contribution of sources
1063 (i.e. land uses) to sediment. Estimated mean contribution of each land use is significantly different
1064 ($p < 0.001$) among models types (see legend).