

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

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Abstract

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

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Results and discussion CSSI fingerprinting allows quantitative estimation of the relative contribution of sediment sources within a catchment at a spatio-temporal resolution, taking into account the following approaches. First, application of CSSI fingerprinting techniques to complex catchments presents particular challenges and calls for well-designed sampling strategies and data handling. Hereby, it is essential to balance the effort required for representative sample collection and analyses against the need to accurately quantify the variability within the system. Second, robustness of the CSSI approach depends on the specificity and conservativeness of the $\delta^{13}\text{C}$ -FA fingerprint. Therefore, saturated long-chain (>20 carbon atoms) FAs, which are biosynthesised exclusively by higher plants and are more stable than the more commonly used short-chain FAs, should be used. Third, given that FA concentrations can vary largely between sources, concentration-dependent SIMMs that are also able to incorporate $\delta^{13}\text{C}$ -FA variability should be standard operation procedures to correctly assess the contribution of sediment sources via SIMMs. **Conclusions** This paper reflects on the use of $\delta^{13}\text{C}$ -FAs in erosion studies and provides recommendations for its application. We strongly advise the use of saturated long-chain (>20 carbon atoms) FAs as tracers and concentration-dependent Bayesian SIMMs. We anticipate progress in CSSI sediment fingerprinting from two current developments: (i) development of hierarchical Bayesian SIMMs to better address catchment complexity and (ii) incorporation of dual isotope approaches ($\delta^{13}\text{C}$ - and $\delta^2\text{H}$ -FA) to improve estimates of sediment sources.

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

1 Environmental and ecological impact of water erosion

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

Without proper soil conservation practices, sediment transfer from key sediment sources (hotspots defined by land use type or sub-catchment) is projected to intensify, particularly if climate change increases the frequency of heavy rainfall events, drought periods, freezing-thawing of soil and land use change (Nearing et al. 2004; Zhang et al. 2005; Boardman 2006; Thothong et al. 2011; Ulén et al. 2012; Sun et al. 2013; Bollasina 2014). Consequently, understanding the

main sediment sources (hereafter sources) can make soil conservation management strategies more efficient (Mukundan et al. 2012). Sediment fingerprinting techniques offer methods of identifying sources using soil/sediment properties and the application of mixing models (Collins et al. 1998; Walling 2013). A wide range of sediment-associated properties have been used for this purpose, including geochemical properties, radionuclides, mineral magnetism, bulk stable isotopes and colour (Martinez-Carreras et al. 2010; Collins et al. 2013; Walling et al. 2013). While these robust and highly transferable fingerprints can provide accurate estimates of source apportionment for a range of agro-ecosystems, they are typically limited in their ability to discriminate between sources in cases where agricultural land use types span geological boundaries or where geological variations in the landscape are small (Gellis and Walling 2011; Blake et al. 2012; Hancock and Revill 2013; Chen et al. 2016). In addition to inorganic properties, plant-specific organic molecules (biotracers) found in the sediment can also be used for fingerprinting and are more specific to discriminate between different land uses. The use of compound-specific stable isotope (CSSI) signatures (Fig. 1), for example, is emerging as a promising sediment fingerprinting technique for this purpose. The isotopic signature of individual compounds in a complex mixture is hereafter referred to as a CSSI signature, as opposed to the bulk stable isotopic signature, which is the isotopic signature of the entire soil or sediment. The CSSI technique exploits differences in the stable isotope signature of individual biotracers to identify and apportion the contribution of specific land uses to the sediment load (Gibbs 2008; Blake et al. 2012; Gibbs 2013; Cooper et al. 2015; Alewell et al. 2016).

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

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

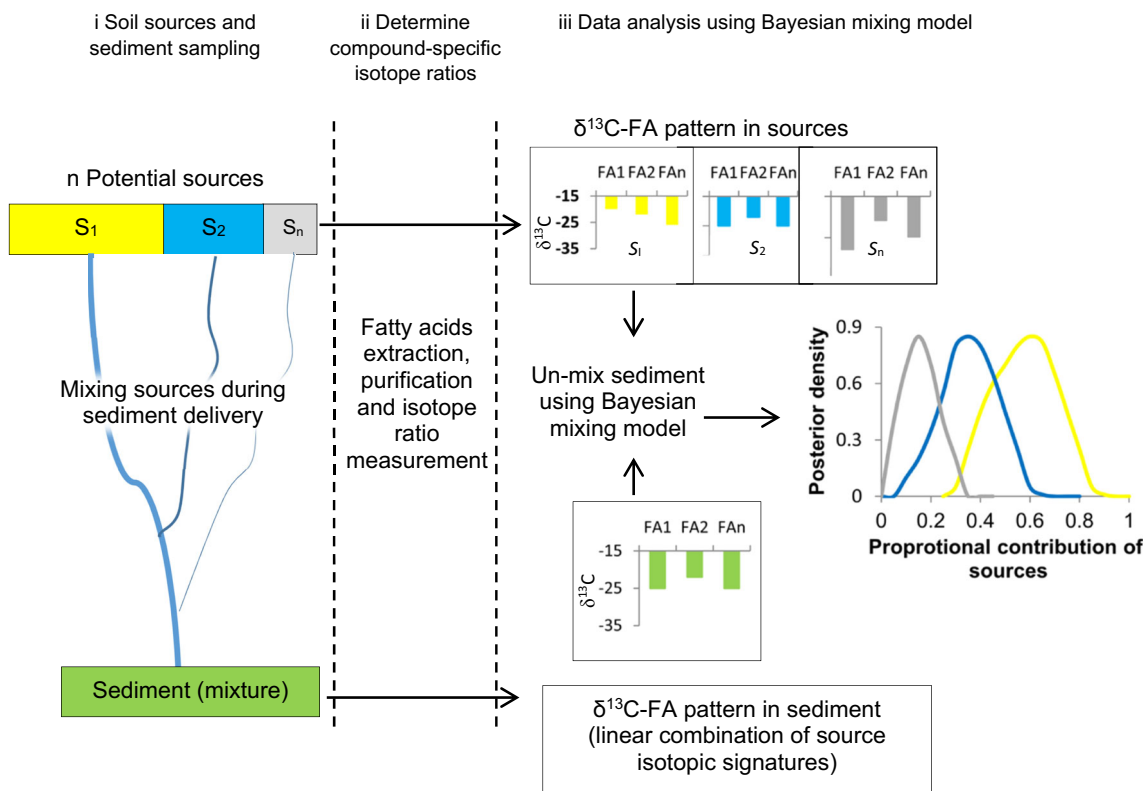


Fig. 1 Overview of the CSSI sediment fingerprinting concept: (i) Sediment generating rainfall events produce sediment from different sources which are then mixed during delivery processes and end up in the sediment of rivers and lakes, (ii) biotracers (e.g. FAs) are extracted from the soil and sediments and their $\delta^{13}\text{C}$ values are measured and (iii) FAs are selected based on their biochemistry, behaviour (e.g.

conservativeness, stability) and presence in sources and sediments. Source and sediment CSSI values are fed into a concentration-dependent Bayesian-stable isotope mixing model. The model accounts for variability in CSSI values of sources and sediment to generate a proportional density distribution of source contributions to sediment

Semmens 2008; Semmens et al. 2009; Parnell et al. 2013; Stock and Semmens 2016).

In this paper, we provide a comprehensive methodological perspective on the application of FA isotope signatures for the apportionment of sediment sources. We focus on the following topics: (i) the concept of CSSI sediment fingerprinting (Section 2), (ii) variability in CSSI of FAs (Section 3), (iii) soil and sediment sampling strategies (Section 4), (iv) FA extraction and CSSI measurement (Section 5) and finally (v) challenges and opportunities associated with using the CSSI signature of sources and sediments in Bayesian mixing models to obtain source contributions to sediments (Section 6).

2 Concept behind the CSSI sediment fingerprinting approach

Different properties of biotracers, such as abundance, composition and isotopic signature, provide a powerful means to identify and apportion the sources of deposited and suspended sediments across a range of aquatic environments (Table 1). Biotracer abundance and composition have mostly been used

to differentiate between terrestrial and aquatic organic matter sources in river, lake and estuarine sediments (Ouyang et al. 2015). Many biotracers are neither land use-specific nor conservative because they degrade quickly in the sediment. On the other hand, the stable isotopic signatures of plant-derived FAs have the potential to differentiate between sediments originating from different land uses, since their isotopic signatures record ecological and hydrological conditions during their biosynthesis. Additionally, plant-derived FAs are less influenced by diagenesis and are stable over long timescales in soil and sediments (Sinninghe Damsté and Schouten 2006; Drenzek et al. 2007; Gibbs 2008; Cooper et al. 2015). For these reasons, CSSI signatures of plant-derived FAs are appropriate biotracers for the identification and estimation of source contribution to sediment using SIMM_S (Table 1). Most CSSI studies use C ($\delta^{13}\text{C}$) and/or H ($\delta^2\text{H}$) isotopes of biotracers to identify and assess sources and delivery processes of soil and terrestrial organic matter to aquatic ecosystems. The focus of this paper is on sediment source apportionment, i.e. relative contributions of source soils to sediment mixture, and not on the differentiation between terrestrial versus aquatic organic matter inputs.

Table 1 Sediment fingerprinting techniques using different properties of biotracers

Biotracers	Data analysis and modelling	Advantages	Disadvantages
Molecular concentration sediment fingerprinting^a			
Fatty acids (Hu et al. 2006; Dai and Sun 2007; Tuo et al. 2011; Zocatelli et al. 2012; Bergamino et al. 2014)	Principle component analysis (PCA) or multivariate analysis of variance (MANOVA) of normalized fatty acids concentrations of sediment sources and sediments, ratio of (C ₂₆₊ C ₂₈)/ΣC _{even} FAs, C ₂₂ /C ₂₄ di-FAs and C ₂₀ /C ₂₀₊ ω-hydroxy FAs, isotopic mixing models (SIAR)	i. Unique distribution in different plants ii. Structural features provide information about organic matter (OM) sources and cycling in soil and sediments iii. Spatial and temporal changes	i. Lack of land use specificity ii. Qualitative information about sediment sources iii. Content changes in sediments iv. Present in trace level v. Difficult to link with soil (mineral) sources
Alkanes (Seki et al. 2010; Tuo et al. 2011; Chen et al. 2016)	PCA alkanes content from sediment source as well as sediments, odd-numbered n-alkanes in the range of C ₂₇ –C ₃₁ indicate input from terrigenous OM, relative chain length ratio and SIAR		
Lignin phenolic component (Goni et al. 1998; Loh et al. 2012)	Syringyl/vanillyl (S/V) ratio and cinnamyl/vanillyl (C/V) ratio provide information angiosperm vs. gymnosperm origin Woody vs. non-woody		
Compound-specific stable isotope (CSSI) sediment fingerprinting^b			
Fatty acids (Gibbs 2008; Blake et al. 2012; Hancock and Revill 2013; Alewell et al. 2016; Brandt et al. 2016)	Subset of δ ¹³ C-FAs from the sediment sources are compared with a sediment via isotopic mixing models (IsoSource and SIAR)	i. Assessment of spatial and temporal changes of sediment/OM possible in lake, river and estuarine ii. Sediment routing accounted iii. Robust information about relative contribution of land use in the sediment	i. Requires sophisticated analytical facility ii. No generic guide to select number of samples required and subset of CSSI iii. Presence at trace concentration (e.g. in subsoil) does not allow to measure isotopic signature accurately
Alkanes (Seki et al. 2010; Cooper et al. 2015)	Long-chain alkanes δ ¹³ C and δ ² H from OC from sources and sediment compared via multivariate extension of isotopic mixing model (SIAR) and molecular distribution		

^a Composition and abundance of biotracers are used

^b Isotopic signatures of biotracers are used

CSSI sediment fingerprinting using δ¹³C of fatty acids (δ¹³C-FAs) was first successfully applied by Gibbs (2008) in New Zealand to assess the relative contribution of sources associated with different land uses to estuarine sediment. The following steps were taken to implement this technique: (i) definition and sampling of potential sources (e.g. cropland, forest and pasture) within a catchment and collection of sediment mixture samples from a target area, (ii) measurement of FA isotopic signatures from both the potential sources and sediment, (iii) selection of a subset of FAs whose carbon isotopic signatures are apparently conserved and well-separated across sources and (iv) estimation of proportional source contributions to the sediment using SIMM_S based on δ¹³C-FA values of the sediments and sources (Fig. 1). Using CSSI signatures of FAs to apportion sources of sediment by land use assumes that (i) the land use categories under consideration (n-potential sources in Fig. 1) have plant communities producing FAs with distinct isotopic signature and that these FAs label the soil with CSSI signatures that reflect land uses (Gibbs 2008, 2013), and (ii) when soil is eroded and transported to the aquatic system, the FA label is transported together with the soil particles through the system. In the

transport process, particles originating from different land uses, and therefore bearing their specific CSSI labels, are mixed (e.g. three sources in Fig. 1) such that the sediment represents a mixture of contributing upstream sources. To obtain CSSI values, FAs are extracted from soil and sediments, purified and derivatised for measurement by gas chromatography-isotope ratio mass spectrometry. FAs used as inputs for mixing models should be present in all sources and sediment samples at a concentration that allows precise isotopic measurement. Mixing models assume that the stable isotopic composition of each FA in the mixture (the sediment sample) is a linear combination of the isotopic compositions of that specific FA in all contributing sources. The SIMMs estimate the probability distribution of each source's proportional contribution (land use types) to the measured mixture (sediment sample).

3 Fatty acids as biotracers

Plants synthesize FAs containing different numbers of carbon atoms. These FAs are commonly classified as either short-

chain (≤ 20 carbon atoms, i.e. low molecular weight) or long-chain (> 20 carbon atoms, i.e. high molecular weight). While short-chain FAs are found in the cellular membranes of various organisms, long-chain FAs are found predominantly in the cuticular waxes of vascular plant leaves, allowing them to be used as specific tracers for plant-derived organic matter (Naraoka et al. 1995; Matsumoto et al. 2007; Galy and Eglinton 2011). Therefore, the analysis of long-chain FAs in soils offers the possibility to specifically trace organic matter that is plant-derived (Amblés et al. 1998; Bull et al. 1998; Matsumoto et al. 2007; Tuo et al. 2011; Jandl et al. 2013).

3.1 Isotopic signatures of fatty acids in plants

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

It is generally known that the CO_2 fixation pathways of the plant (C_3 , C_4 or CAM) induce different isotopic fractionations, leading to different $\delta^{13}\text{C}$ -FA values (e.g. Chikaraishi 2014; Reiffarth et al. 2016). Other processes in the biosynthesis of FA can also induce differences in isotopic fractionation, and hence $\delta^{13}\text{C}$ -FA values, within each plant type (C_3 , C_4 or CAM). Chikaraishi (2014) and Reiffarth et al. (2016) provide a comprehensive review of the biological and environmental sources of $\delta^{13}\text{C}$ -FAs variability in plants. Briefly, decarboxylation (e.g. of pyruvate to form acetyl-CoA) appears to be an important and potentially species-specific process driving isotopic discrimination during FA biosynthesis (Dungait et al. 2010; Chikaraishi 2014 and references therein). As a result of this, ^{13}C depletion of long-chain FAs can be as high as 10‰ relative to glucose (Chikaraishi et al. 2004b; Hobbie and Werner 2004; Badeck et al. 2005; Dungait et al. 2008; Chikaraishi 2014). However, the effect is more pronounced for C_4 compared to C_3 plants, with an average 9.5 and 3.5‰ depletion relative to bulk plant tissue, respectively (Agrawal et al. 2014). A significant difference in $\delta^{13}\text{C}$ also exists between C_3 angiosperms and gymnosperms, where gymnosperm $\delta^{13}\text{C}$ -FA values are on average 3‰ more enriched compared to that of angiosperms (Chikaraishi et al. 2004a). The isotopic signature of individual FA homologues in C_3 plants is characterized by a gradual depletion with increasing carbon number (e.g. from C_{24} to C_{32} depletion can be up to -2.7%), whereas in C_4 plants the $\delta^{13}\text{C}$ -FA values stay constant or are slightly enriched (up to $+0.7\%$ for C_{24} to C_{32}) (Agrawal et al. 2014 and references therein). Depending on external parameters such as soil water availability, temperature and sunlight, the extent of isotope fractionation may differ even for the same pathway, especially for C_3 plants (Heaton 1999; Chikaraishi et al. 2004a). In addition, altitude, slope and aspect are topographical factors indirectly affecting carbon isotopic ratios through their effect on climatic (e.g. atmospheric pressure, temperature and precipitation) and edaphic factors (e.g. soil age, soil depth, nutrient status and water holding capacity)

(Warren et al. 2001). Altogether, carbon isotopic variation in plant FAs is partially explained at the spatio-temporal, inter-species and even intra-species levels (Dungait et al. 2008, 2010). However, the influence of topography on FA isotopic signatures of different land cover is still not clear and requires further research.

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

The hydrogen isotopic composition of FAs ($\delta^2\text{H}$ -FAs) is used as a tracer in biogeochemical and paleo-environmental studies (Jones et al. 2008; Seki et al. 2012). The hydrogen isotopic signature of plant FAs and alkanes originates from a common precursor and depends ultimately on the $\delta^2\text{H}$ value of leaf water (Sachse et al. 2012; Ponton et al. 2014; Feakins et al. 2016). The signature of FAs and alkanes are related: C_n -FAs (e.g. C_{30} FA) are the biosynthetic precursors of the C_{n-1} -alkanes (e.g. C_{29} alkanes), but due to a biosynthetic isotopic fractionation during the decarboxylation process, there is an offset in $\delta^2\text{H}$ value between C_{n-1} -alkanes and C_n -FAs pairs. Nevertheless, Feakins et al. (2016) observed a lack of overall consistency in decarboxylation-associated ^2H fractionation between pairs of FAs and alkanes (e.g. C_{30} and C_{29} pairs) among plant species. As a consequence, overall compound class offset (i.e. between FAs and alkanes) is insignificant at the plant community level where sample size is large enough. As a result, this offset is also insignificant on the land use level, since plant community, which integrates FAs biosynthesised from a multitude of plants over a large area and time scale, defines land use. Therefore, $\delta^2\text{H}$ -FAs are likely to be similar to those of alkanes in terms of their usefulness for discriminating between soils developed under different plant ecotypes (i.e. grass, shrubs or wood) (Liu et al. 2006; Hou et al. 2007; Liu and Yang 2008) and recording elevation gradients defined by the isotopic signature of precipitation (Ponton et al. 2014; Feakins et al. 2016). However, very limited $\delta^2\text{H}$ -FA data exists from living plants, while data of soils and sediments are in line with those of alkanes.

In addition to biosynthetic fractionation, climatic and plant morphological characteristics can affect the $\delta^2\text{H}$ values of FAs due to differences in plant water sources, temperature, precipitation, evapotranspiration and root or leaf morphology. Only a few studies have investigated factors affecting leaf $\delta^2\text{H}$ values of FAs (Huang et al. 2004; Chikaraishi and Naraoka 2007; Hou et al. 2007; Feakins et al. 2016). Hydrogen in FAs is derived from leaf water during photosynthesis. Leaf water is itself controlled by soil water, which originates from rainfall or snowmelt in temperate climates. Besides fractionation during photosynthesis and FA biosynthesis, $\delta^2\text{H}$ values will be controlled by the isotopic signature of leaf water at the time they are biosynthesised (Chikaraishi and Naraoka 2003; Seki et al. 2010; Seki et al. 2012; Liu et al. 2015). In moisture-limited areas or seasons, hydrogen isotope values of leaf water can be

directly enriched in deuterium by transpiration and/or indirectly enriched by evaporation of soil water. It is generally accepted that the uptake of soil water by plants is not associated with discernible isotopic fractionation (Dawson et al. 2002). However, fundamental differences can be observed in terms of the water use of different ecological life forms (e.g. woody plants vs. grasses) at different depths due to their root systems. Grasses and herbs take up water from the surface soil, whereas deep rooted trees and shrubs use water from deeper soil layers. Since soil water $\delta^2\text{H}$ usually increases with depth (Grieu et al. 2001), this may result in higher $\delta^2\text{H}$ value of leaf FAs and alkanes of trees compared to those of grasses and herbs (Liu et al. 2006; Liu et al. 2015).

3.2 Isotopic signatures of fatty acids in soils and sediment

In agricultural land uses with patchwork fields and a wide spectrum of crop and soil management practices, each agricultural system/rotation may have distinct FA isotopic signatures. Additionally, if crops are planted on land that once was forest, the subsoil is likely to have different CSSI values (related to forest) than the surface soil (growing crops) (Wiesenberg et al. 2004). Fatty acids in soil derive principally from growing vegetation, vegetation from previous rotations and crop residues (VanBergen et al. 1997; Mueller et al. 2012). Root exudation and decomposition of organic matter in soil can vary the proportions and isotope signatures of FAs (Wiesenberg et al. 2004; Wiesenberg and Schwark 2006; Dungait et al. 2008; Jandl et al. 2013), but the exact effect of these processes is difficult to quantify. In essence, the combination of past and present FAs at a particular site provides an isotopic fingerprint for the specific land use. Monoculture or similar vegetation composition over years will result in low variability of FA isotopic signatures in the source soil (Wiesenberg et al. 2004). In contrast, agro-ecosystems and natural systems often involve a mixture or rotation of C_3 and C_4 plants seasonally or annually. Generally, rotation and/or mixing of different crops in one field on a seasonal and/or annual basis will blend the FA isotopic signatures of each crop into a ‘new’ mixture of FA isotopic signatures that lies between the FA isotopic signatures of the individual crops.

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

soil profile (Matsumoto et al. 2007). In contrast, long-chain FAs (solubility decreases with increasing carbon chain length) are more likely to be retained on the upper erodible soil layers (Amblés et al. 1994). Fatty acid concentrations in soils and sediment may change over time due to degradation by microorganisms via oxidation and re-synthesis, volatilization, dilution and dispersion (Dinel et al. 1990; Banowetz et al. 2006; Matsumoto et al. 2007), but degradation is believed to have little effect on $\delta^{13}\text{C}$ -FA values (Chikaraishi and Naraoka 2005; Blessing et al. 2008; Gibbs 2008). Canuel and Martens (1996) observed that the concentration of C_{14} to C_{18} FAs degraded at a faster rate in sediment than longer chain FAs, which had lower or insignificant concentration reduction rates over a 5-month period after deposition. Furthermore, unsaturated FAs degrade faster than saturated FAs due to their higher vulnerability to biological and chemical degradation (Niggemann and Schubert 2006).

Presently, very limited effort has been directed at understanding the $\delta^2\text{H}$ of FAs transported from source to sediment via water erosion. However, hydrogen in FAs is covalently linked to C by a strong and non-polar bond requiring high activation energy for exchange, making it the most isotopically conservative H moiety (Radke et al. 2005) and thus a good (conserved) isotope signal of water used by plants (Sachse et al. 2012). To the best of our knowledge, there is currently no published study that has used $\delta^2\text{H}$ -FA values for sediment source apportionment, although $\delta^2\text{H}$ of long-chain FAs (e.g. C_{28}) was utilized to differentiate sediment particulate organic matter between different source areas defined by the isotopic signature of precipitation (Wilkie et al. 2013; Ponton et al. 2014).

In conclusion, based on the information currently available in the literature and our experience, $\delta^{13}\text{C}$ values of long-chain saturated FAs are advised to be used for sediment source discrimination and apportionment, in contrast to short-chain and unsaturated FAs, which are less useful for this purpose. Reasons include the fact that long-chain FAs are produced almost exclusively by vascular plants and therefore avoid contamination by microorganisms and algae at the deposition site and that they are more resistant to degradation in soil and sediment environments, which reduces the risk of isotopic fractionation (Hu et al. 2006; Bourgeois et al. 2011; Fang et al. 2014; Alewell et al. 2016; Reiffarth et al. 2016). Furthermore, data on $\delta^2\text{H}$ -FAs might allow for an improved discrimination between land use types, mainly based on plant ecotypes (e.g. grasses, shrubs and trees). $\delta^{13}\text{C}$ and $\delta^2\text{H}$ values in plants are controlled by largely independent mechanisms, though both are present in the same molecule and thus follow exactly the same transit through the catchment. Therefore, compound-specific dual isotopes ($\delta^{13}\text{C}$ and $\delta^2\text{H}$) of FAs could provide better source/land use information on FAs than single isotopic analyses (Krull et al. 2006; Seki et al. 2010; Cooper et al. 2015).

4 Sources and sediment sampling strategies

4.1 Sources

In the CSSI approach, a catchment should be subdivided into spatial sources (i.e. sub-catchments (Fig. 2) or land use types (Fig.3a)) using a reconnaissance survey and topographic or drainage maps as background information. Source soil sampling should provide FA isotope signatures encompassing the local spatial variability (within sediment sources); in other words, every land use should be represented by a stratified random sampling design that accounts for factors such as field size and patchy agriculture practices. Particular attention should be paid to the collection of erodible topsoil within a land use, as soil is sensitive to erosion and thus connected to the stream network (Olley and Caitcheon 2000; Hancock and Revill 2013; Tiecher et al. 2015). Collection of transported

sediment from the lowest point of a single land use site can integrate the variation within that site, thus providing an integrated signal of erodible soil from that source. Beyond land use types, other important sources include unpaved roads, eroded riverbanks, river channels containing sediment from earlier erosion events and any other site-specific secondary sources along the river channel. Currently, analytical cost is one of the most important factors influencing the sampling intensity and number of samples. The question of whether to use spatially integrated random composite samples (i.e. soil samples obtained randomly from different positions within the land use that are then combined to make composite samples) is therefore a tradeoff between analytical cost saving and the need to determine the degree of $\delta^{13}\text{C}\text{-FA}$ spatial variability (Brandt et al. 2016): a question which can only be answered in terms of specific research objectives. Spatially integrated samples integrate larger spatial and temporal scales and are

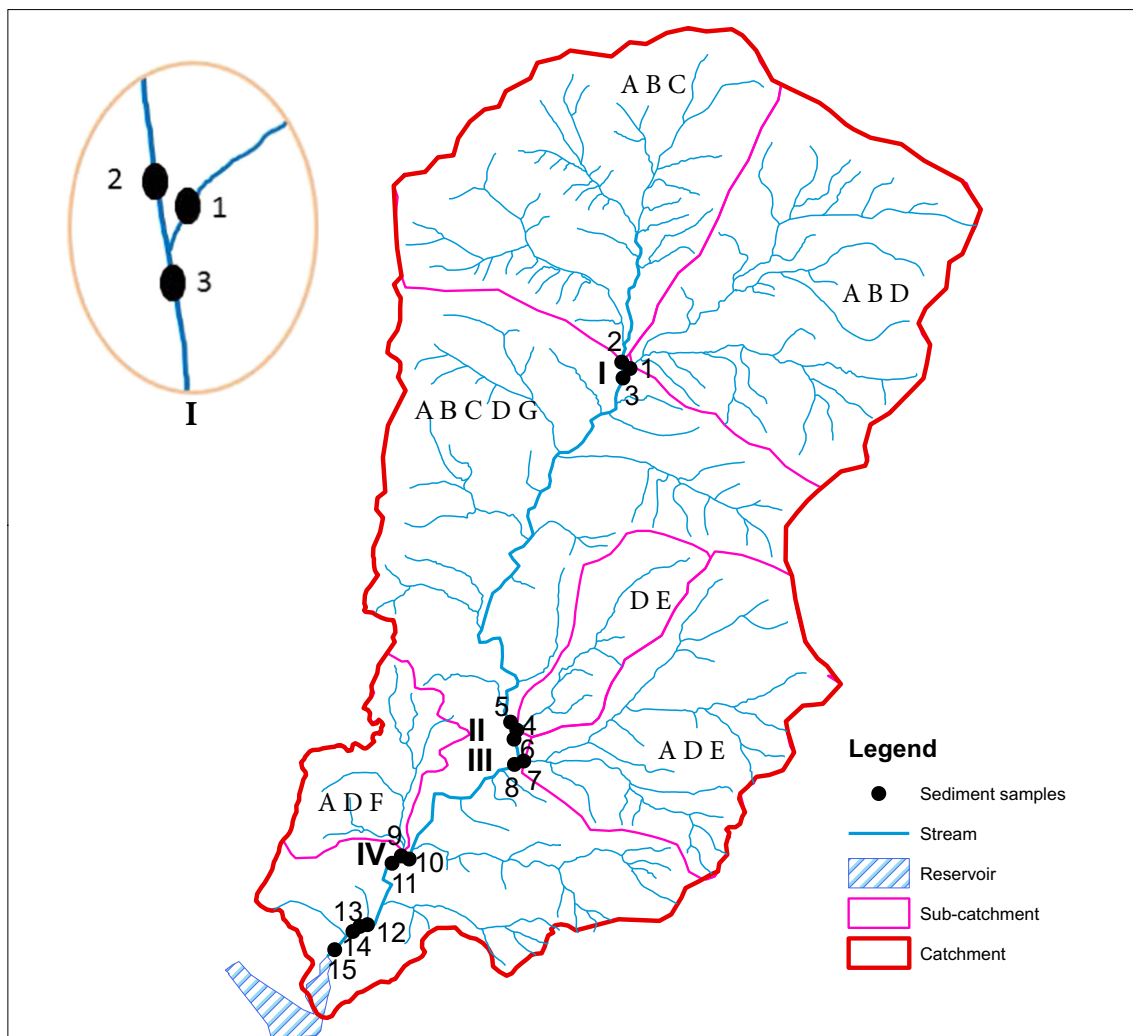


Fig. 2 Sediment sampling concept for dealing with the hierarchical structure of a complex drainage basin. The larger catchment can be broken up into sub-catchments, and each sub-catchment may contain different sediment sources to evaluate the sediment contributions from

each sub-catchment or source (e.g. A, B, C, etc.). Hence, sediment from a tributary upstream of confluence becomes a sediment source for the downstream sediment sample (e.g. at confluence I (see inset), sediment samples 1 and 2 are the sources for sediment sample 3)

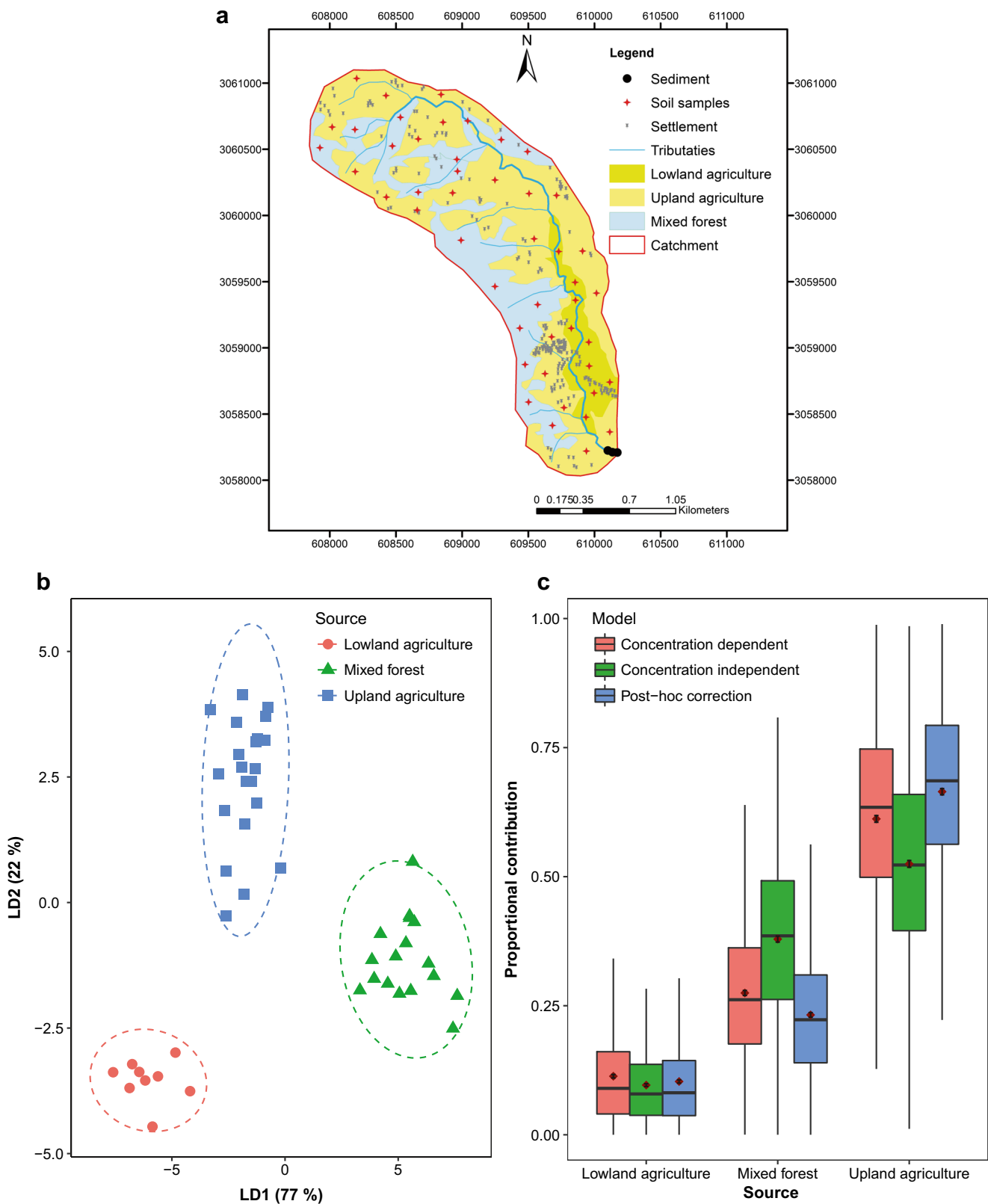


Fig. 3 Coupling $\delta^{13}\text{C}$ -FAs and MixSIAR for catchment scale sediment source apportionment: **a** land uses and sediment sampling locations in the Kunchal catchment of Nepal; **b** discriminant function plot based on $\delta^{13}\text{C}$ of a subset of FAs (C_{22} , C_{26} , C_{32}) obtained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

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

therefore less susceptible to potential sampling bias caused by annual/seasonal variation in isotopic fractionation during FA production. Importantly, the complexity of a larger catchment can be better captured by integrating various sub-catchments (Fig. 2). Here, a primary consideration is to account for sediment contribution from sub-catchments to the main river system that drains the larger catchment (Rhoton et al. 2008; Vale et al. 2016). Therefore, sediment from the tributaries upstream of confluence becomes sources for downstream sediments (Fig. 2 I, II, III and IV), and sediment traps should be located accordingly. It is important to collect sediment samples downstream of the confluence at distances sufficient to allow for the complete mixing of upstream sources.

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

4.2 Sediment

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

Sediment is delivered to the aquatic environment as primary and aggregated particles, but the aggregates break down during transport due to abrasion and disaggregation as a result of turbulence (Droppo 2001). In general, eroded material is enriched in clay- and silt-sized particles relative to the original soil. Sorting within the fluvial system, however, could lead to mixtures of coarse and fine material from a range of sources due

to contrasting transport times of different fractions and proximity to sediment sources (Fletcher and Muda 1999; Miller and Miller 2007). It is important to note that the concentration of suspended sediment tends to increase with increasing distance from the bank due to an increase in sand-sized materials (Walling et al. 2011). For the same reason, vertical concentrations of suspended sediment in fluvial systems tend to increase with increasing depth. Nevertheless, the choice of sediment size fraction depends on the characteristics of the sediment transported out of the catchment and the fraction responsible for any environmental issues (e.g. siltation of salmonid spawning gravels) in question (Bartley et al. 2014; Collins et al. 2016). Therefore, appropriate sediment sampling site selection is recommended, with samples taken at the outlet of the catchment and/or at key locations across the catchment, to provide a representative sediment.

5 FA extraction and carbon and hydrogen isotope measurement

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

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

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

6 Data analysis using Bayesian mixing models

6.1 Overview and current practice

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

IsoSource (Phillips and Gregg 2003) is currently the most commonly applied mixing model for sediment fingerprinting using $\delta^{13}\text{C}$ -FAs values (Gibbs 2008; Blake et al. 2012; Hancock and Revill 2013; Alewell et al. 2016). IsoSource requires a minimum of three sources and two tracers and cannot accept more than five tracers. It uses a resampling algorithm and a tolerance term to identify several possible analytical solutions to the mixing system (given a tolerance) and provides a range of possible proportional contributions. Because each solution is feasible and might be multimodal, researchers are encouraged to report the range of proportional contributions of each source rather than simply reporting the mean or median (Phillips and Gregg 2003; Gibbs 2008). The original version of IsoSource does not take differences in concentration into account, but a modified version has been developed to overcome

these shortcomings (Granek et al. 2009). However, one of the limitations of IsoSource is that it models mean values of source and sediment isotopic signature rather than the distribution of actual values. Additionally, it does not measure uncertainty quantitatively (Moore and Semmens 2008). Bayesian modeling approaches are becoming more popular as a result of recently proposed improvements to linear (e.g. IsoSource) and Bayesian SIMMs, such as the inclusion of variability, prior information and sensitivity analyses (e.g. MixSIAR, Stock and Semmens 2013; IsotopeR, Hopkins and Ferguson 2012).

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

6.2 Concentration-dependent SIMMs

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

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

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

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

For multiple tracers, this equation can be generalized as:

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

and

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

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

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

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

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

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

6.3 Recommendations for CSSI sediment fingerprinting

6.3.1 Selection of FAs to use in mixing models

In order for mixing models to successfully apportion source contributions, the input tracer data needs to be (i) conservative (i.e. either no isotopic fractionation during transport from source to sink or predictable isotope fractionation) and (ii) informative (e.g. they must differentiate between the sources). The first and most important method of selecting FAs is, logically, based on their biochemistry (i.e. Which organisms produce it? How recalcitrant is it?) and behaviour in the soil and sediment environment (i.e. How will it bind to the sediment particle?). These premises clearly call for the use of saturated long-chain FAs (see above). After careful consideration of their biochemistry and behaviour, the simple tests described

below can provide additional guidance on whether to include or exclude specific FAs.

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

Bracketing tests with more than one dimension can be visualized by mixing polygons. For example, the mixing space of three sources defined by two $\delta^{13}\text{C}$ -FAs can be plotted as vertices of a polygon (although the concentration-dependent model may make the edges somewhat curved rather than straight) and all sediment samples should ideally be bound within the polygon (Phillips and Koch 2002; Hopkins and Ferguson 2012). Sediment samples that are not bound within the polygon indicate either a missing source or non-conservative transport. Additionally, the mixing space geometry (in two- or three-isotope systems) can be quantitatively evaluated using a Monte Carlo simulation of mixing polygons for the point-in-polygon assumption test (Smith et al. 2013) and has been used in CSSI sediment fingerprinting (Brandt et al. 2016). Convex hulls (mixing polygons) can be iterated using the distributions of the $\delta^{13}\text{C}$ -FA values of the intended sources. The proportion of polygons which provides a solution (i.e. meet the point-in-polygon assumption) is then calculated, providing the quantitative basis for validating mixing space geometry (Smith et al. 2013; Brandt et al. 2016). When there are more than three tracers, this polygon generalizes to an n -dimensional hyper ellipse (Blonder et al. 2014). Transformation of such an ellipse into the perfect circle, centred around the origin, by linear matrix algebra using the covariance matrix of the data (the same data that defines the ellipse) and projection of sediment data (after transformation in the same way like ellipse) into the circles helps to test the point-in-polygon assumption at higher dimensions (Jackson 2016). However, these approaches still neglect the concentration effect on the geometry of the mixing space and thus warrant further research.

Once visualization of the mixing space or bracketing testing is complete, Tukey's HSD test can be used to identify FAs that allow for significant differentiation of sources. Optionally, best FA subsets for differentiation among sources can also be obtained using the Simulated Annealing Algorithm (SAA). Using this method, the selected subset (e.g. C_{22} , C_{26} , C_{32}) can provide the same level of discrimination (Fig. 3b) as all variables (e.g. C_{22} , C_{24} , C_{26} , C_{28} , C_{30} , C_{32}) do. Detailed explanations of the SAA are available elsewhere (Silva 2001;

Brusco 2014; Cerdeira et al. 2015). Selection of variables helps to minimize co-linear $\delta^{13}\text{C}$ -FAs and reduce multiple and conflicting solutions. When a selected set of FAs fails to discriminate potential sources, the sources can be re-defined either by lumping or splitting them to produce sufficient heterogeneity in the isotopic values of FAs among sources (D'Haen et al. 2012; Sherriff et al. 2015).

6.3.2 Inclusion of prior information and covariates

In general, there is a demand for knowledge on relevant soil erosion processes in the landscape and the fate of sediment in the catchment environment (Fox and Papanicolaou 2008; Ulén et al. 2012). Soil does not erode uniformly across the entire soil surface due to the ‘patchiness’ of rainfall and episodic nature of water erosion, which can make substantial differences in soil erosion severity between different land uses and between locations within a land use. Additionally, land use characteristics (e.g. land cover, area) of the catchment will theoretically have a direct impact on the relative contributions to sediment. This fact can be used as prior information in Bayesian mixing models. Prior information is unmeasured data that is not directly involved in tracing the sources and originates mainly from catchment characteristics, expert knowledge and literature on the proportions of land use. The incorporation of logical and appropriate prior information into the Bayesian SIMM helps to account for the full range of source variability and reduces the uncertainty of the estimates as much as possible. Furthermore, by incorporating a residual error term in the Bayesian SIMM (e.g. MixSIAR), the additional unquantified variation in isotopic signatures between individual sediments can be represented (i.e. deviation of the observed value from the true value) and the variability of the isotopic mixing system in the sediment can be captured (Semmens et al. 2009; Stock and Semmens 2016). Therefore, CSSI sediment fingerprinting can be

improved by formulating mixing models that take prior information and residual error into account and incorporate covariates and covariance from the sources and sediment samples (e.g. base flow vs. episodic runoff sediment, seasonal differences in erosion and sediment generation due to rainfall intensity and land cover change) (Table 2). The cross-isotopic tracer covariance is parameterised within Bayesian mixing model through a single correlation parameter for each source (Hopkins and Ferguson 2012; Parnell et al. 2013). Moreover, MixSIAR can incorporate covariates as random or fixed effects, and we recommend their use when there is reason to believe that the inclusion of covariates will influence the outcome of sediment source apportionment.

6.4 Research needs

The issue of how to statistically select tracers for inclusion in mixing models is still unsettled. Bracketing tests can identify non-conservative tracers, but it is possible for a tracer to be non-conservative and still pass the test. Simulation studies should shed light on the impact of including more or fewer tracers that may or may not be conservative or informative. Rainfall simulation experimental tests can provide information on the conservativeness of CSSI tracers during the sediment generation process. However, it is critical to understand the effects that residence time and storage of different sediments size fractions have on the $\delta^{13}\text{C}$ -FAs in the catchment.

Another future direction for Bayesian mixing models is to deal with larger and more complex catchments through the estimation of sediment mixing at the sub-catchment level (Fig. 2). We envision extended mixing models that are able to distinguish the source contributions within each sub-catchment, contributions of each sub-catchment to the overall catchment and the source contributions to the overall catchment. In this type of hierarchical network model, the geographical location of potential sediment sources with respect

Table 2 MixSIAR terminology adapted for sediment fingerprinting

Term	Description
Process error	Within each source, tracer values of replicate samples may vary due to local differences in erosion rate, rainfall intensity, etc. Process error is the expected amount of variability in sediment tracer values that results from this within-source variability in tracer values
Residual error	Unexplained variability in sediment tracer values, beyond that accounted for by process error or covariates (fixed/random effects)
Fixed effect	Source proportions in the sediment deviate from their mean in a predictable way, by a categorical covariate. Examples: base vs. high flow events, seasonal differences in rainfall intensity and land cover
Random effect	As for fixed effects, the source proportions in the sediment deviate from their mean by a categorical covariate. However, the researcher is less interested in the proportions for each level and considers the covariate a ‘nuisance’ variable, but still wants to account for the variation in tracer values due to the covariate. Must have >3 levels and replicate sediment samples within level. Example: year

to sediment sampling sites should always be considered when designing sampling plans and interpreting the model results.

7 Conclusions and perspectives

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

First, it must be noted that efforts in analytics or modelling cannot overcome poor and/or non-representative sampling. Therefore, the collection of spatially integrated random composite samples to obtain representative sources and the installation of TIMS in streams at multiple locations across a catchment to collect suspended sediment are essential to maximize the effectiveness of CSSI fingerprinting approaches. Second, we particularly recommend the use of saturated, long-chain (>20 carbon atoms) FAs from the same size fraction of source soil and sediment due to their exclusive plant origin, conservativeness, strong interaction with soil minerals and ensuring comparison of ‘like-with-like’. Third, stable isotope mixing models cannot estimate reliable contributions of sediment sources if the model applied does not account for differences in FA concentrations among sources. Therefore, the use of concentration-dependent mixing models should be standard procedure in sediment fingerprinting studies. In addition, we strongly advise the use of Bayesian mixing models (e.g. MixSIAR) over more basic models such as IsoSource due to their greater flexibility through the use of informative priors and their ability to incorporate a residual error term, which enables them to better cope with CSSI variability.

CSSI fingerprinting can provide key information for targeted erosion management, but there is a need for further improvement in source discrimination and SIMM formulation. There exists no robust statistical approach to formally test for missing sources and conservativeness of tracers. 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 of sediment may be biased by missing sources or non-conservative transport. Therefore, it is equally important to have adequate information on (i) (hillslope) system under investigation (i.e. expert decision on potential erosion sources, covariates effect on the relative contributions of sediment source), (ii) sediment cascade connectivity and (iii) assumptions and limitations of Bayesian SIMMs. Sediment fingerprinting might be further strengthened by adding the $\delta^2\text{H}$ of FAs as complementary isotope tracer capable of discrimination among sources in high

resolution. Therefore, coupling of Bayesian SIMMs and dual isotopes ($\delta^{13}\text{C}$ and $\delta^2\text{H}$) of FAs could be an extremely useful addition to the rapidly growing roster of techniques available for sediment fingerprinting. Additionally, as MixSIAR continues to advance, we anticipate the incorporation of erosion processes (e.g. sheet, rill and gully erosion) responsible for mobilizing sediment within a single source and within hierarchical structures in the drainage basins. The CSSI sediment fingerprinting methodology described in this paper, as well as the expanding number of laboratories capable of CSSI analyses, will definitely contribute to the mitigation of erosion and sediment-related problems in the context of land use and climate change.

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References

- Agrawal S, Galy V, Sanyal P, Eglinton T (2014) C-4 plant expansion in the Ganga Plain during the last glacial cycle: insights from isotopic composition of vascular plant biomarkers. *Org Geochem* 67:58–71
- Alewell C, Birkholz A, Meusburger K, Schindler-Wildhaber Y, Mabit L (2016) Quantitative sediment source attribution with compound-specific isotope analysis in a C3 plant-dominated catchment (central Switzerland). *Biogeosciences* 13:1587–1596
- Amblés A, Colina-Tejada A, Jambu P, Lemeé L, Parlanti E (1998) Experimental leaching of podzol soil lipids. Nature and biological origin of water soluble components. *Agrochimica* 42:158–171
- Amblés A, Jambu P, Parlanti E, Joffe J, Riffe C (1994) Incorporation of natural monoacids from plant residues into an hydromorphic forest podzol. *Eur J Soil Sci* 45:175–182
- Badeck FW, Tcherkez G, Nogue S, Piel C, Ghashghaie J (2005) Post-photo synthetic fractionation of stable carbon isotopes between plant organs—a widespread phenomenon. *Rapid Commun Mass Spectrom* 19:1381–1391
- Banowetz GM, Whittaker GW, Dierksen KP, Azevedo MD, Kennedy AC, Griffith SM, Steiner JJ (2006) Fatty acid methyl ester analysis to identify sources of soil in surface water. *J Environ Qual* 35:133–140
- Bartley R, Bainbridge ZT, Lewis SE, Kroon FJ, Wilkinson SN, Brodie JE, Silburn DM (2014) Relating sediment impacts on coral reefs to watershed sources, processes and management: a review. *Sci Total Environ* 468:1138–1153
- Bayrak Y (2006) Application of Langmuir isotherm to saturated fatty acid adsorption. *Micropor Mesopor Mat* 87:203–206
- Benstead JP, March JG, Fry B, Ewel KC, Pringle CM (2006) Testing IsoSource: stable isotope analysis of a tropical fishery with diverse organic matter sources. *Ecology* 87:326–333

- Bergamino L, Dalu T, Richoux NB (2014) Evidence of spatial and temporal changes in sources of organic matter in estuarine sediments: stable isotope and fatty acid analyses. *Hydrobiologia* 732:133–145
- Bianchi TS, Canuel EA (2011) Chemical biomarkers in aquatic ecosystems. Princeton University Press, Princeton, New Jersey 417 pp
- Blake WH, Ficken KJ, Taylor P, Russell MA, Walling DE (2012) Tracing crop-specific sediment sources in agricultural catchments. *Geomorphology* 139:322–329
- Blessing M, Jochmann MA, Schmidt TC (2008) Pitfalls in compound-specific isotope analysis of environmental samples. *Anal Bioanal Chem* 390:591–603
- Blonder B, Lamanna C, Violle C, Enquist BJ (2014) The n-dimensional hypervolume. *Glob Ecol Biogeogr* 23:595–609
- Boardman J (2006) Soil erosion science: reflections on the limitations of current approaches. *Catena* 68:73–86
- Boecklen WJ, Yarnes CT, Cook BA, James AC (2011) On the use of stable isotopes in trophic ecology. *Annu Rev Ecol Syst* 42:411–440
- Bollasina MA (2014) Hydrology: probing the monsoon pulse. *Nat Clim Chang* 4:422–423
- Bourgeois S, Pruski AM, Sun MY, Buscail R, Lantoine F, Kerherve P, Vétion G, Riviere B, Charles F (2011) Distribution and lability of land-derived organic matter in the surface sediments of the Rhone prodelta and the adjacent shelf (Mediterranean Sea, France): a multi proxy study. *Biogeosciences* 8:3107–3125
- Brandt C, Cadisch G, Nguyen LT, Vien TD, Rasche F (2016) Compound-specific $\delta^{13}\text{C}$ isotopes and Bayesian inference for erosion estimates under different land use in Vietnam. *Geoderma Regional* 7:311–322
- Brusco MJ (2014) A comparison of simulated annealing algorithms for variable selection in principal component analysis and discriminant analysis. *Comput Stat Data Anal* 77:38–53
- Bull ID, van Bergen PF, Poulton R, Evershed RP (1998) Organic geochemical studies of soils from the Rothamsted classical experiments—II. Soils from the Hoosfield Spring Barley Experiment treated with different quantities of manure. *Org Geochem* 28:11–26
- Bunzel K, Schaefer RB, Thraen D, Kattwinkel M (2015) Pesticide runoff from energy crops: a threat to aquatic invertebrates? *Sci Total Environ* 537:187–196
- Canuel EA, Martens CS (1996) Reactivity of recently deposited organic matter: degradation of lipid compounds near the sediment-water interface. *Geochim Cosmochim Acta* 60:1793–1806
- Cerdeira JO, Silva PD, Cadima J, Minhoto M (2015) Subselect: selecting variables subsets. R package version 0.12–5. Web <http://CRAN.R-project.org/package=subselect>. Accessed. May 20, 2016
- Chen FX, Fang NF, Shi ZH (2016) Using biomarkers as fingerprint properties to identify sediment sources in a small catchment. *Sci Total Environ* 557:123–133
- Chikaraishi Y (2014) $^{13}\text{C}/^{12}\text{C}$ signatures in plants and algae. In: Holland HD, Turekian KK (eds) *Treatise on geochemistry*. Elsevier, Oxford, pp 95–123
- Chikaraishi Y, Naraoka H (2003) Compound-specific delta D-delta C-13 analyses of n-alkanes extracted from terrestrial and aquatic plants. *Phytochemistry* 63:361–371
- Chikaraishi Y, Naraoka H (2005) Delta C-13 and delta D identification of sources of lipid biomarkers in sediments of Lake Haruna (Japan). *Geochim Cosmochim Acta* 69:3285–3297
- Chikaraishi Y, Naraoka H (2007) Delta C-13 and delta D relationships among three n-alkyl compound classes (n-alkanoic acid, n-alkane and n-alkanol) of terrestrial higher plants. *Org Geochem* 38:198–215
- Chikaraishi Y, Naraoka H, Poulson SR (2004a) Carbon and hydrogen isotopic fractionation during lipid biosynthesis in a higher plant (*Cryptomeria japonica*). *Phytochemistry* 65:323–330
- Chikaraishi Y, Naraoka H, Poulson SR (2004b) Hydrogen and carbon isotopic fractionations of lipid biosynthesis among terrestrial (C3, C4 and CAM) and aquatic plants. *Phytochemistry* 65:1369–1381
- Collins AL, Pulley S, Foster IDL, Gellis A, Porto P, Horowitz AJ (2016) Sediment source fingerprinting as an aid to catchment management: a review of the current state of knowledge and a methodological decision-tree for end-users. *J Environ Manag*. doi:10.1016/j.jenvman.2016.09.075
- Collins AL, Walling DE, Leeks GJL (1998) Use of composite fingerprints to determine the provenance of the contemporary suspended sediment load transported by rivers. *Earth Surf Process Landf* 23:31–52
- Collins AL, Zhang YS, Duethmann D, Walling DE, Black KS (2013) Using a novel tracing-tracking framework to source fine-grained sediment loss to watercourses at sub-catchment scale. *Hydrol Process* 27:959–974
- Cooper RJ, Krueger T, Hiscock KM, Rawlins BG (2014) Sensitivity of fluvial sediment source apportionment to mixing model assumptions: a Bayesian model comparison. *Water Resour Res* 50:9031–9047
- Cooper RJ, Pedentchouk N, Hiscock KM, Disdle P, Krueger T, Rawlins BG (2015) Apportioning sources of organic matter in streambed sediments: an integrated molecular and compound-specific stable isotope approach. *Sci Total Environ* 520:187–197
- Dai JH, Sun MY (2007) Organic matter sources and their use by bacteria in the sediments of the Altamaha estuary during high and low discharge periods. *Org Geochem* 38:1–15
- Dawson TE, Mambelli S, Plamboeck AH, Templer PH, Tu KP (2002) Stable isotopes in plant ecology. *Annu Rev Ecol Syst* 33:507–559
- de la Fuente MA, Luna P, Juarez M (2006) Chromatographic techniques to determine conjugated linoleic acid isomers. *Trends Anal Chem* 25:917–926
- D'Haen K, Verstraeten G, Degryse P (2012) Fingerprinting historical fluvial sediment fluxes. *Prog Phys Geogr* 36:154–186
- Dinel H, Schnitzer M, Mehuys GR (1990) Soil lipids: origin, nature, content, decomposition, and effect on soil physical properties. In: Bollag JM, Stotzky G (eds) *Soil biochemistry*, vol 6. Marcel Dekker, New York, pp 397–429
- Drenzek NJ, Montlucon DB, Yunker MB, Macdonald RW, Eglinton TI (2007) Constraints on the origin of sedimentary organic carbon in the Beaufort Sea from coupled molecular C-13 and C-14 measurements. *Mar Chem* 103:146–162
- Droppo IG (2001) Rethinking what constitutes suspended sediment. *Hydrol Process* 15:1551–1564
- Dungait JAJ, Docherty G, Straker V, Evershed RP (2008) Interspecific variation in bulk tissue, fatty acid and monosaccharide delta(13)C values of leaves from a mesotrophic grassland plant community. *Phytochemistry* 69:2041–2051
- Dungait JAJ, Docherty G, Straker V, Evershed RP (2010) Seasonal variations in bulk tissue, fatty acid and monosaccharide delta C-13 values of leaves from mesotrophic grassland plant communities under different grazing managements. *Phytochemistry* 71:415–428
- Fang JD, Wu FC, Xiong YQ, Li FS, Du XM, An D, Wang LF (2014) Source characterization of sedimentary organic matter using molecular and stable carbon isotopic composition of n-alkanes and fatty acids in sediment core from Lake Dianchi, China. *Sci Total Environ* 473:410–421
- Feakins SJ, Bentley LP, Salinas N, Shenkin A, Blonder B, Goldsmith GR, Ponton C, Arvin LJ, Wu MS, Peters T, West AJ, Martin RE, Enquist BJ, Asner GP, Malhi Y (2016) Plant leaf wax biomarkers capture gradients in hydrogen isotopes of precipitation from the Andes and Amazon. *Geochim Cosmochim Acta* 182:155–172
- Fletcher WK, Muda J (1999) Influence of selective logging and sedimentological process on geochemistry of tropical rainforest streams. *J Geochem Explor* 67:211–222
- Fox JF, Martin DK (2015) Sediment fingerprinting for calibrating a soil erosion and sediment-yield model in mixed land-use watersheds. *J Hydrol Eng* 20:C4014002
- Fox JF, Papanicolaou AN (2008) An un-mixing model to study watershed erosion processes. *Adv Water Resour* 31:96–108

- Galy V, Eglinton T (2011) Protracted storage of biospheric carbon in the Ganges-Brahmaputra basin. *Nat Geosci* 4:843–847
- Gardner R, Gerrard A (2003) Runoff and soil erosion on cultivated rainfed terraces in the Middle Hills of Nepal. *Appl Geogr* 23:23–45
- Gellis AC, Walling DE (2011) Sediment source fingerprinting (tracing) and sediment budgets as tools in targeting river and watershed restoration programs. In: Simon A, Bennett SJ, Castro JM (eds) *Stream restoration in dynamic fluvial systems: scientific approaches, analyses, and tools*. American Geophysical Union, Washington, DC, pp 263–291
- Gibbs MM (2008) Identifying source soils in contemporary estuarine sediments: a new compound-specific isotope method. *Estuar Coasts* 31:344–359
- Gibbs MM (2013) Protocols on the use of the CSSI technique to identify and apportion soil sources from land use. Report no: HAM2013–106. National Institute of Water and Atmospheric Research Ltd, Hamilton, New Zealand
- Goni MA, Ruttenger KC, Eglinton TI (1998) A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochim Cosmochim Acta* 62:3055–3075
- Graney EF, Compton JE, Phillips DL (2009) Mangrove-exported nutrient incorporation by sessile coral reef invertebrates. *Ecosystems* 12:462–472
- Griepentrog M, Eglinton TI, Hagedorn F, Schmidt MWI, Wiesenberger GLB (2015) Interactive effects of elevated CO₂ and nitrogen deposition on fatty acid molecular and isotope composition of above- and belowground tree biomass and forest soil fractions. *Glob Chang Biol* 21:473–486
- Grieu P, Lucero DW, Ardiani R, Ehleringer JR (2001) The mean depth of soil water uptake by two temperate grassland species over time subjected to mild soil water deficit and competitive association. *Plant Soil* 230:197–209
- Hancock GJ, Revell AT (2013) Erosion source discrimination in a rural Australian catchment using compound-specific isotope analysis (CSIA). *Hydrol Process* 27:923–932
- Haregeweyn N, Melesse B, Tsunekawa A, Tsubo M, Meshesha D, Balana BB (2012) Reservoir sedimentation and its mitigating strategies: a case study of Angereb reservoir (NW Ethiopia). *J Soils Sediments* 12:291–305
- Heaton THE (1999) Spatial, species, and temporal variations in the C-13/C-12 ratios of C-3 plants: implications for palaeodiet studies. *J Archaeol Sci* 26:637–649
- Hobbie EA, Werner RA (2004) Intramolecular, compound-specific, and bulk carbon isotope patterns in C-3 and C-4 plants: a review and synthesis. *New Phytol* 161:371–385
- Hopkins JB, Ferguson JM (2012) Estimating the diets of animals using stable isotopes and a comprehensive Bayesian mixing model. *PLoS One* 7:e28478
- Hou J, D'Andrea WJ, MacDonald D, Huang Y (2007) Hydrogen isotopic variability in leaf waxes among terrestrial and aquatic plants around Blood Pond, Massachusetts (USA). *Org Geochem* 38:977–984
- Hu JF, Zhang HB, Peng PA (2006) Fatty acid composition of surface sediments in the subtropical Pearl River estuary and adjacent shelf, Southern China. *Estuar Coast Shelf Sci* 66:346–356
- Huang YS, Shuman B, Wang Y, Webb T (2004) Hydrogen isotope ratios of individual lipids in lake sediments as novel tracers of climatic and environmental change: a surface sediment test. *J Paleolimnol* 31:363–375
- Ichihara K, Fukubayashi Y (2010) Preparation of fatty acid methyl esters for gas-liquid chromatography. *J Lipid Res* 51:635–640
- Jackson A (2016) SIBER. Web <https://github.com/AndrewLJackson/SIBER>. Accessed. 15 July, 2016
- Jandl G, Baum C, Leinweber P (2013) Crop-specific differences in the concentrations of lipids in leachates from the root zone. *Arch Agron Soil Sci* 59:119–125
- Jandl G, Leinweber P, Schulten HR, Ekschmitt K (2005) Contribution of primary organic matter to the fatty acid pool in agricultural soils. *Soil Biol Biochem* 37:1033–1041
- Jones AA, Sessions AL, Campbell BJ, Li C, Valentine DL (2008) D/H ratios of fatty acids from marine particulate organic matter in the California Borderland Basins. *Org Geochem* 39:485–500
- Koch A, McBratney A, Adams M, Field D, Hill R, Crawford J, Minasny B, Lal R, Abbott L, O'Donnell A, Angers D, Baldock J, Barbier E, Binkley D, Parton W, Wall DH, Bird M, Bouma J, Chenu C, Flora CB, Goulding K, Grunwald S, Hempel J, Jastrow J, Lehmann J, Lorenz K, Morgan CL, Rice CW, Whitehead D, Young I, Zimmermann M (2013) Soil security: solving the global soil crisis. *Global Policy* 4:434–441
- Krull E, Sachse D, Muegler I, Thiele A, Gleixner G (2006) Compound-specific delta(13)C and delta(2)H analyses of plant and soil organic matter: a preliminary assessment of the effects of vegetation change on ecosystem hydrology. *Soil Biol Biochem* 38:3211–3221
- Liu JZ, Liu WG, An ZS (2015) Insight into the reasons of leaf wax delta D n-alkane values between grasses and woods. *Sci Bull* 60:549–555
- Liu WG, Yang H (2008) Multiple controls for the variability of hydrogen isotopic compositions in higher plant n-alkanes from modern ecosystems. *Glob Chang Biol* 14:2166–2177
- Liu WG, Yang H, Li LW (2006) Hydrogen isotopic compositions of n-alkanes from terrestrial plants correlate with their ecological life forms. *Oecologia* 150:330–338
- Loh PS, Chen CTA, Lou JY, Anshari GZ, Chen HY, Wang JT (2012) Comparing lignin-derived phenols, delta C-13 values, OC/N ratio and C-14 age between sediments in the Kaoping (Taiwan) and the Kapuas (Kalimantan, Indonesia) rivers. *Aquat Geochem* 18:141–158
- Martinez-Carreras N, Udelhoven T, Krein A, Gallart F, Iffly JF, Ziebel J, Hoffmann L, Pfister L, Walling DE (2010) The use of sediment colour measured by diffuse reflectance spectrometry to determine sediment sources: application to the Attert River catchment (Luxembourg). *J Hydro* 382:49–63
- Matsumoto K, Kawamura K, Uchida M, Shibata Y (2007) Radiocarbon content and stable carbon isotopic ratios of individual fatty acids in subsurface soil: implication for selective microbial degradation and modification of soil organic matter. *Geochem J* 41:483–492
- Milinsk MC, Matsushita M, Visentainer JV, de Oliveira CC, de Souza NE (2008) Comparative analysis of eight esterification methods in the quantitative determination of vegetable oil fatty acid methyl esters (FAME). *J Braz Chem Soc* 19:1475–1483
- Miller JR, Miller SMO (2007) *Contaminated rivers: a geomorphological-geochemical approach to site assessment and remediation*. Springer Science and Business Media, Dordrecht, The Netherlands **418 pp**
- Montanarella L, Pennock DJ, McKenzie N, Badraoui M, Chaude V, Bpatista I, Mamo T, Yemefack M, Aulakh MS, Yagi K, Hong SY, Vijamsorn P, Zhang GL, Arrouays D, Black H, Krasilnikov P, Sobocka J, Alegre J, Henriquez CR, Mendonca-Santos MDL, Taboada M, Espinosa-Victoria D, AlShankiti A, AlviPanah SK, Elskeikh EAEM, Hempel J, Arbestrain MC, Nachtergaele FRV (2016) World's soils are under threat. *Soil* 2:79–82
- Moore JW, Semmens BX (2008) Incorporating uncertainty and prior information into stable isotope mixing models. *Ecol Lett* 11:470–480
- Mueller KE, Polissar PJ, Oleksyn J, Freeman KH (2012) Differentiating temperate tree species and their organs using lipid biomarkers in leaves, roots and soil. *Org Geochem* 52:130–141
- Mukundan R, Walling DE, Gellis AC, Slattery MC, Radcliffe DE (2012) Sediment source fingerprinting: transforming from a research tool to a management tool. *J Am Water Resour Assoc* 48:1241–1257
- Naraoka H, Yamada K, Ishiwatari R (1995) Carbon isotopic difference of saturated long-chain n-fatty acids between a terrestrial and a marine sediment. *Geochem J* 29:189–195

- Nearing MA, Pruski FF, O'Neal MR (2004) Expected climate change impacts on soil erosion rates: a review. *J Soil Water Conserv* 59: 43–50
- Niggemann J, Schubert CJ (2006) Fatty acid biogeochemistry of sediments from the Chilean coastal upwelling region: sources and diagenetic changes. *Org Geochem* 37:626–647
- Olley J, Caitcheon G (2000) Major element chemistry of sediments from the Darling-Barwon River and its tributaries: implications for sediment and phosphorus sources. *Hydrol Process* 14:1159–1175
- Ouyang XG, Guo F, Bu HM (2015) Lipid biomarkers and pertinent indices from aquatic environment record paleoclimate and paleoenvironment changes. *Quat Sci Rev* 123:180–192
- Owens PN, Batalla RJ, Collins AJ, Gomez B, Hicks DM, Horowitz AJ, Kondolf GM, Marden M, Page MJ, Peacock DH, Petticrew EL, Salomons W, Trustrum NA (2005) Fine-grained sediment in river systems: environmental significance and management issues. *River Res Appl* 21:693–717
- Panagos P, Borrelli P, Poesen J, Ballabio C, Lugato E, Meusburger K, Montanarella L, Alewell C (2015) The new assessment of soil loss by water erosion in Europe. *Environ Sci Pol* 54:438–447
- Parnell AC, Inger R, Bearhop S, Jackson AL (2010) Source partitioning using stable isotopes: coping with too much variation. *PLoS One* 5: e9672
- Parnell AC, Phillips DL, Bearhop S, Semmens BX, Ward EJ, Moore JW, Jackson AL, Grey J, Kelly DJ, Inger R (2013) Bayesian stable isotope mixing models. *Environmetrics* 24:387–399
- Perks MT, Warburton J, Bracken L (2014) Critical assessment and validation of a time-integrating fluvial suspended sediment sampler. *Hydrol Process* 28:4795–4807
- Phillips DL, Gregg JW (2003) Source partitioning using stable isotopes: coping with too many sources. *Oecologia* 136:261–269
- Phillips DL, Inger R, Bearhop S, Jackson AL, Moore JW, Parnell AC, Semmens BX, Ward EJ (2014) Best practices for use of stable isotope mixing models in food-web studies. *Can J Zoolog* 92:823–835
- Phillips DL, Koch PL (2002) Incorporating concentration dependence in stable isotope mixing models. *Oecologia* 130:114–125
- Phillips JM, Russell MA, Walling DE (2000) Time-integrated sampling of fluvial suspended sediment: a simple methodology for small catchments. *Hydrol Process* 14:2589–2602
- Pimentel D (2006) Soil erosion: a food and environmental threat. *Environ Dev Sustainability* 8:119–137
- Pimentel D, Burgess M (2013) Soil erosion threatens food production. *Agriculture* 3:443–463
- Ponton C, West AJ, Feakins SJ, Galy V (2014) Leaf wax biomarkers in transit record river catchment composition. *Geophys Res Lett* 41: 6420–6427
- Radke J, Bechtel A, Gaupp R, Puttmann W, Schwark L, Sachse D, Gleixner G (2005) Correlation between hydrogen isotope ratios of lipid biomarkers and sediment maturity. *Geochim Cosmochim Acta* 69:5517–5530
- Reiffarth DG, Petticrew EL, Owens PN, Lobb DA (2016) Sources of variability in fatty acid (FA) biomarkers in the application of compound-specific stable isotopes (CSSIs) to soil and sediment fingerprinting and tracing: a review. *Sci Total Environ* 565:8–27
- Rhoton FE, Emmerich WE, DiCarlo DA, McChesney DS, Nearing MA, Ritchie JC (2008) Identification of suspended sediment sources using soil characteristics in a semiarid watershed. *Soil Sci Soc Am J* 72:1102–1112
- Rickson RJ, Deeks LK, Graves A, Harris JAH, Kibblewhite MG, Sakrabani R (2015) Input constraints to food production: the impact of soil degradation. *Food Sec* 7:351–364
- Rosell-Melé A, McClymont EL (2007) Biomarkers as paleoceanographic proxies. In: Hillaire-Marcel C, De Vernal A (eds) *Developments in marine geology*, Volume 1. Elsevier Science, Amsterdam, pp 441–490
- Sachse D, Billault I, Bowen GJ, Chikaraishi Y, Dawson TE, Feakins SJ, Freeman KH, Magill CR, McInerney FA, van der Meer MTJ, Polissar P, Robins RJ, Sachs JP, Schmidt HL, Sessions AL, White JWC, West JB, Kahmen A (2012) Molecular paleohydrology: interpreting the hydrogen-isotopic composition of lipid biomarkers from photosynthesizing organisms. *Annu Rev Earth Planet Sci* 40: 221–249
- Sanchez-Chardi A, Ribeiro CAO, Nadal J (2009) Metals in liver and kidneys and the effects of chronic exposure to pyrite mine pollution in the shrew *Crocidura russula* inhabiting the protected wetland of Donana. *Chemosphere* 76:387–394
- Seki O, Kawamura K, Ishiwatari R (2012) Assessment of hydrogen isotopic compositions of n-fatty acids as paleoclimate proxies in Lake Biwa sediments. *J Quat Sci* 27:884–890
- Seki O, Nakatsuka T, Shibata H, Kawamura K (2010) A compound-specific n-alkane delta C-13 and delta D approach for assessing source and delivery processes of terrestrial organic matter within a forested watershed in northern Japan. *Geochim Cosmochim Acta* 74:599–613
- Semmens BX, Ward EJ, Moore JW, Darimont CT (2009) Quantifying inter- and intra-population niche variability using hierarchical Bayesian stable isotope mixing models. *PLoS One* 4:e6187
- Semmens BX, Ward EJ, Parnell AC, Phillips DL, Bearhop S, Inger R, Jackson A, Moore JW (2013) Statistical basis and outputs of stable isotope mixing models: comment on Fry (2013). *Mar Ecol Prog Ser* 490:285–289
- Sherriff S, Franks S, Rowan J, Fenton O, Ó'hUallacháin D (2015) Uncertainty-based assessment of tracer selection, tracer non-conservativeness and multiple solutions in sediment fingerprinting using synthetic and field data. *J Soils Sediments* 15:2101–2116
- Silva APD (2001) Efficient variable screening for multivariate analysis. *J Multivar Anal* 76:35–62
- Sinninghe Damsté JS, Schouten S (2006) Biological markers for anoxia in the photic zone of the water column. In: Volkman JK (ed) *Marine organic matter: biomarkers, isotopes and DNA*. Springer, Berlin, Heidelberg, pp 127–163
- Smith JA, Mazumder D, Suthers IM, Taylor MD (2013) To fit or not to fit: evaluating stable isotope mixing models using simulated mixing polygons. *Methods Ecol Evol* 4:612–618
- Smith TB, Owens PN (2014) Flume- and field-based evaluation of a time-integrated suspended sediment sampler for the analysis of sediment properties. *Earth Surf Process Landf* 39:1197–1207
- Smith SV, Renwick WH, Bartley JD, Buddemeier RW (2002) Distribution and significance of small, artificial water bodies across the United States landscape. *Sci Total Environ* 299:21–36
- Stock BC, Semmens BX (2013) MixSIAR GUI User Manual. Version 3.1. Web <https://github.com/brianstock/MixSIAR/>. Accessed. 26 February, 2016
- Stock BC, Semmens BX (2016) Unifying error structures in commonly used biotracer mixing models. *Ecology* 97:2562–2569
- Sun WY, Shao QQ, Liu JY (2013) Soil erosion and its response to the changes of precipitation and vegetation cover on the Loess Plateau. *J Geogr Sci* 23:1091–1106
- Thothong W, Huon S, Janeau JL, Boonsaner A, de Rouw A, Planchon O, Bardoux G, Parkpian P (2011) Impact of land use change and rainfall on sediment and carbon accumulation in a water reservoir of North Thailand. *Agric Ecosyst Environ* 140:521–533
- Tiecher T, Caner L, Minella JPG, dos Santos DR (2015) Combining visible-based-color parameters and geochemical tracers to improve sediment source discrimination and apportionment. *Sci Total Environ* 527:135–149
- Troeh FR, Hobbs JA, Donahue RL (2004) *Soil and water conservation for productivity and environmental protection*. Prentice-Hall Inc., Upper Saddle River, New Jersey 672 pp
- Tuo JC, Wu CJ, Zhang MF, Chen R (2011) Distribution and carbon isotope composition of lipid biomarkers in Lake Erhai and Lake

- Gahai sediments on the Tibetan Plateau. *J Great Lakes Res* 37:447–455
- Ulén B, Bechmann M, Øygarden L, Kyllmar K (2012) Soil erosion in Nordic countries—future challenges and research needs. *Acta Agric Scand Sect B* 62:176–184
- Urban JD, Tachovsky JA, Haws LC, Staskal DW, Harris MA (2009) Assessment of human health risks posed by consumption of fish from the Lower Passaic River, New Jersey. *Sci Total Environ* 408:209–224
- Vale SS, Fuller IC, Procter JN, Basher LR, Smith IE (2016) Application of a confluence-based sediment-fingerprinting approach to a dynamic sedimentary catchment, New Zealand. *Hydrol Process* 30:812–829
- VanBergen PF, Bull ID, Poulton PR, Evershed RP (1997) Organic geochemical studies of soils from the Rothamsted classical experiments. 1. Total lipid extracts, solvent insoluble residues and humic acids from Broadbalk wilderness. *Org Geochem* 26:117–135
- Vörösmarty CJ, McIntyre PB, Gessner MO, Dudgeon D, Prusevich A, Green P, Glidden S, Bunn SE, Sullivan CA, Liermann CR, Davies PM (2010) Global threats to human water security and river biodiversity. *Nature* 467:555–561
- Walling DE (2013) The evolution of sediment source fingerprinting investigations in fluvial systems. *J Soils Sediments* 13:1658–1675
- Walling DE, Golosov V, Olley J (2013) Introduction to the special issue 'tracer applications in sediment research'. *Hydrol Process* 27:775–780
- Walling D, Wilkinson S, Horowitz A (2011) Catchment erosion, sediment delivery, and sediment quality. In: Rogers P, Uhlenbrook S, Frimmel F, Hanaki K, Tom V (eds) *Treatise on water science: the science of hydrology*. Elsevier, Amsterdam, pp 305–338
- Warren CR, McGrath JF, Adams MA (2001) Water availability and carbon isotope discrimination in conifers. *Oecologia* 127:476–486
- Werner RA, Brand WA (2001) Referencing strategies and techniques in stable isotope ratio analysis. *Rapid Commun Mass Spectrom* 15:501–519
- Wiesenberg GL, Gocke M (2017) Analysis of lipids and polycyclic aromatic hydrocarbons as indicators of past and present (micro)biological activity. In: McGenity T, Timmis K, Nogales B (eds) *Hydrocarbon and lipid microbiology protocols: petroleum, hydrocarbon and lipid analysis*. Springer, Berlin Heidelberg, pp 61–91
- Wiesenberg GLB, Schwark L (2006) Carboxylic acid distribution patterns of temperate C-3 and C-4 crops. *Org Geochem* 37:1973–1982
- Wiesenberg GLB, Schwarzbauer J, Schmidt MWI, Schwark L (2004) Source and turnover of organic matter in agricultural soils derived from n-alkane/n-carboxylic acid compositions and C-isotope signatures. *Org Geochem* 35:1371–1393
- Wilkie KMK, Chaplign B, Meyer H, Burns S, Petsch S, Brigham-Grette J (2013) Modern isotope hydrology and controls on delta D of plant leaf waxes at Lake El'gygytgyn, NE Russia. *Clim Past* 9:335–352
- Wilkinson SN, Hancock GJ, Bartley R, Hawdon AA, Keen RJ (2013) Using sediment tracing to assess processes and spatial patterns of erosion in grazed rangelands, Burdekin River basin, Australia. *Agric Ecosyst Environ* 180:90–102
- Wisser D, Frohling S, Hagen S, Bierkens MFP (2013) Beyond peak reservoir storage? A global estimate of declining water storage capacity in large reservoirs. *Water Resour Res* 49:5732–5739
- Zhang GH, Nearing MA, Liu BY (2005) Potential effects of climate change on rainfall erosivity in the Yellow River basin of China. *Trans Am Soc Agric Eng* 48:511–517
- Zocatelli R, Lavrieux M, Disnar J-R, Le Milbeau C, Jacob J, Breheret JG (2012) Free fatty acids in Lake Aydat catchment soils (French Massif Central): sources, distributions and potential use as sediment biomarkers. *J Soils Sediments* 12:734–748
- Zuazo VHD, Pleguezuelo CRR (2008) Soil-erosion and runoff prevention by plant covers. A review. *Agron Sustain Dev* 28:65–86