Legacy of historic land cover changes on sediment provenance tracked with isotopic tracers in a Mediterranean agroforestry catchment

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ABSTRACT

A Compound Specific Stable Isotope (CSSI) sediment tracing approach is applied for the first time in a Mediterranean mountain agroforestry catchment subjected to intense land use changes in the past decades. Many Mediterranean mountain environments underwent conversion of rangelands into croplands during the previous centuries to increase agricultural production. Converted land has increased the risk of erosion and in some cases has led to loss of the entire fertile topsoil. After land abandonment the process was gradually reversed during the middle of the 20th century, allowing the recovery of natural land cover and reduction of soil erosion rates.

The $^{13}$C abundance of long chain fatty acids was used as tracer to assess the contribution of soil under different vegetation covers in complex landscapes subjected to land use changes after land abandonment in a medium-sized Mediterranean catchment. A Bayesian mixing model (MixSIAR) was used for estimating the contribution of different land use types to suspended sediments. To this purpose, composite samples were collected over the four main land covers existing in the study area: cropland, Mediterranean forest, pine forest, scrubland, and two main geomorphic elements: highly disturbed areas such as exposed subsoil and channel banks. Suspended sediment traps were installed at three locations in the catchment to assess the variability of source contributions from the headwaters to the outlet of the catchment. At every sampling point three replicating traps integrated the suspended sediment per climatologic season during a one hydrological year. The fatty acids (FAs) content was significantly higher at the catchment outlet than at the headwaters. The $\delta^{13}$C signatures of the FAs were successful in discriminating between Mediterranean forest, scrubland, pine forest and both geomorphic elements. Overall, the model identified agricultural land as the largest contributing source for most of the sampled seasons. The inclusion of prior information
with different informativeness produced variations in the model outputs and could represent an advantage as much as a disadvantage if priors are not used with caution and supported by robust evidence. The results of this study suggest that CSSI tracers are needed to correctly assess land use related sediment sources, while channel bank and subsoil contributions require geochemical tracers. The high agricultural apportionment despite its small coverage (16%) point out to the impact of human activities and the agriculture cycle on soil loss in these mountain agroforestry systems.

**Keywords:** Compound Specific Stable Isotope (CSSI), fatty acids (FAs), sediment source fingerprinting, concentration dependence, land cover changes

### 1. Introduction

The significant increase in fine sediment transport to water bodies has been confirmed as one of the most prevalent contaminants in aquatic biomes, compromising human water supplies and being a major cause of reservoir siltation (Navas et al., 2004). In Mediterranean mountains, the early stages of land abandonment have been widely recognized to promote erosion and increase sediment supply to water bodies (García-Ruiz, 2010). Large areas in the Southern Pyreanean region have experienced socio-economic changes that produced a decline in traditional farming and converted mountain agriculture fields into abandoned land. These practices, together with the abandonment of the countryside produced during the 60s progressively led to the replacement of part of the cultivated fields by natural revegetated areas (Nadal-Romero et al., 2016).

Soil is a valuable natural resource that performs crucial ecosystem functions and is vital to meet the food needs for the growing world population (Costanza et al., 1997). At present, soil formation is estimated to be 10 to 40 times less than soil erosion rates what represents a main threat because the loss of fertile topsoil leads to the subsequent
reduction in agricultural productivity. In turn, soil losses are directly related with increases in sediment export rates (Borrelli et al., 2017).

In order to mitigate the impacts of soil loss and the associated sediment exports to water bodies, reliable quantitative information on fine-grained sediment sources (typically <63 μm) is required (Owens et al., 2016; Collins et al., 2017). However, determining the sediment provenance in catchments is often difficult and requires expensive monitoring stations challenging to install in remote areas. In this regard, preliminary studies by Klages and Hsieh (1975) tracked the source of sediments based on mineralogical and grain size characterisation developing a technique known as fingerprinting. The initial fingerprinting investigations were essentially qualitative in their result, but the introduction of Frequentist and Bayesian (e.g. FingerPro (Lizaga et al., 2020a), SIFT (Pulley et al., 2018) and MixSIAR (Stock et al., 2018) mixing models enabled to estimate the relative contribution from different sediment sources and facilitate the implementation of the technique (Owens et al., 2016). One of the main characteristics when applying unmixing models in a Bayesian framework is that information from an independent source such as field assessment or additional evidence can be included via informative prior distributions as an input during the unmixing process (Moore & Semmens, 2008). However, choosing a prior requires explicit consideration of how much weight the prior should have in any analysis. Nowadays, only few studies have implemented informative priors in sediment fingerprinting. Recently, Wynants et al. (2020) included information from RUSLE sediment delivery and Uphadyay et al. (2020) incorporated information from a modified connectivity index.

The increasing complexity of the fingerprinting studies promoted including additional tracers to fulfil the requirements of the technique. To date, there are several studies assessing source apportions using fingerprinting techniques (e.g. Gruszowski et al., 2003;
Clarke, 2014; Palazón et al., 2015a; Szalińska et al., 2021). A wide range of sediment-properties has been implemented as fingerprinting tracers such as radionuclides (Evrard et al., 2013; Palazón et al., 2015a), geochemical properties (Smith et al., 2013; Mabit et al., 2014) and magnetic properties (Ramon et al., 2020; Zhang et al., 2020). While these tracers can provide accurate estimates of source apportionment as was proved by Gaspar et al. (2019a), they are restricted in their capability to discriminate between different land uses especially those with vegetation cover in some specific ecosystems. This is particularly evident in areas where the lithology is homogenous, and most of the variability of the sources is introduced by the type of vegetation (Gellis and Walling, 2013; Hancock and Revill, 2013; Chen et al., 2016).

In the last decades, plant-specific isotopic signature of organic molecules such as Fatty acids (FA’s), that exist in sediment, have been proposed as a new effective isotopic fingerprinting approach for land-use-specific sediment source identification (Gibbs, 2008; Gibbs, 2013; Glaser, 2015; Upadhayay et al., 2017; Mabit et al., 2018). To this purpose, the use of compound-specific stable isotope (CSSI) of very long-chain fatty acids (VLCFAs) represents an emerging alternative to previously analysed tracers (Reiffarth et al., 2016, 2019). Recent research use CSSI (Blake et al., 2012; Cooper et al., 2015; Alewell et al., 2016; Bravo-Linares et al., 2018; Lavrieux et al., 2019) to obtain the sediment export apportionments from various land uses.

The land use is usually defined by the plants growing on its surface. These plants tend to modify soil properties and exude different molecules in the soil, which can be used as biomarkers (Reiffarth et al., 2016). Most plant species produce a similar range of organic compounds but with different isotopic signatures δ¹³C (Tolosa et al., 2013). Thus, for fingerprinting studies, the CSSI technique relies on the determination of the δ¹³C signatures of particular soil organic compounds (i.e. FAs) (Mabit et al., 2018). The CSSI
technique exploits differences in the stable isotope signature of individual biotracers to recognise the areas that export high quantities of sediment to water supplies (Reiffarth et al., 2016).

The likely limited capabilities of traditionally implemented tracers to effectively discriminate between different land covers growing on similar substrates was detected in a Mediterranean agroecosystem by Lizaga et al. (2019a). Thus, the low geochemical discrimination by the same shared lithology for pine afforestation and Mediterranean forest forced merging both sources. In this context, the present paper aims to validate the utility of CSSI as an improvement in the discrimination of land covers developed on similar lithology in an agroforestry mountain catchment subjected to highly dynamic changes in land cover and land uses.

We hypothesise that the use of CSSI will increase the discrimination capacity of the different land uses in comparison with previous implemented tracers such as radionuclides and stable elements what could be relevant to assess processes in changing landscapes. Furthermore, despite the potential of the technique, no previous research has assessed the influence of different prior weights in sediment unmixing results.

To study the sediment dynamic of these agroforestry systems, we apply state-of-the-art techniques implemented for the use of CSSI in fingerprinting studies in a representative catchment that has undergone land abandonment of marginal fields and nowadays holds 84% of mixed forests and 16% of croplands.

To this purpose, we evaluate the capability of $\delta^{13}$C of fatty acids as fingerprinting tracers in a concentration dependence fingerprinting model. Furthermore, we assess the sensitivity to prior weights in sediment unmixing by considering different prior informativeness to understand the influence on the primary apportion results.
Our results will contribute to gain knowledge on the main factors leading to sediment export and will demonstrate the capability of CSSI as fingerprinting tracers to identify sediment provenance in complex and highly dynamic landscapes.

2. METHODOLOGY

2.1 Study Area

The study catchment with a total area of 23 km² is located in western Sierra de Santo Domingo and drained by an ephemeral stream tributary of the Arba River (Fig. 1). The hydrological system of the study catchment is composed of two subcatchments, the right-bank tributary (SBC1) and the left-bank tributary (SBC2) that drain the headwaters and merge in the middle part of the catchment in the main tributary draining the lowlands until the catchment outlet (CO). The catchment structure is dominated by the low angle dip sandstones of the Uncastillo Miocene formation bedding and the presence of a Quaternary glacis located at the Middle Eastern part. The climate is characterised by cold winters and hot and dry summers. The rainfall periods are mainly concentrated in the spring and autumn-winter seasons while the droughts take place in summer. The area is subjected to intense and localised storms during the second half of the summer period. The mean annual rainfall is nearly 650 mm and the mean maximum and minimum temperatures are between 30°C and -6°C, respectively (recorded since 1929 at the Yesa reservoir; AEMET).

At the start of the twentieth century, most of the catchment was cultivated. During the 1960s nearly 60% of the area remained as agricultural land. Currently, ~16% of the catchment is still cultivated while rangeland which is composed of Mediterranean open forest and scrubland along with pine forest occupies the remaining 83.5% (Lizaga et al., 2018a).
At present, the main land uses are cropland, Mediterranean forest, pine forest and scrubland. Besides, most croplands are located on a Quaternary glacis and fluvial terraces with gentle slopes covering the valley floors. Agricultural land use predominates in the lower part of the catchment while Mediterranean forest and scrubland occupy the East and West parts, and pine afforestation dominates in the headwaters (Fig.1). The abandonment of croplands during the recent decades was substantially greater at the headwaters due to the existence of shallow soils and more steep slopes that hinder the use of machinery (Navas et al., 2017).

Specific geomorphic features are the presence of interspersed patches of highly eroded areas where subsoil is exposed. Subsoil patches are dispersed across the catchment though is more abundant on steep slopes with low vegetation cover density. Another characteristic is the stream valley floor infilled by eroded sediment from the surrounding slopes, which is deeply incised. The stream channel banks are mainly composed by silt-dominated colluvium sediment characterised by steep banks without vegetation cover especially in the middle-low part of the catchment where thickness reaches its maximum up to 6 m.

2.2. Soil sampling, analysis and clearcutting monitoring

The precipitation amount was recorded with a resolution of one minute at the study site with a tipping bucket rain gauge connected to an Em50 Decagon data logger. Furthermore, to monitor the strip clearcutting in the catchment, satellite imagery data was analysed with digital image processing methods. A multitemporal Sentinel 2 satellite dataset formed the basis for monitoring the areas affected by clearcutting of the afforested pine during the study seasons. Satellite images were selected to track the beginning of the strip clearcutting and the dates when the forest recovered in terms of density cover.
Selected images with no cloud-coverage correspond to the following dates 2016-01-05, 2016-05-24, 2016-06-23 and 2016-10-21.

The potential sediment sources and sediment sampling locations established in this study were selected following the information of reconnaissance surveys, connectivity maps (Lizaga et al., 2018a), soil properties (Lizaga et al., 2019b) and spatial soil redistribution rates (Lizaga et al., 2018b).

Our research evaluates the sediment provenance in a representative agroforestry catchment during one hydrological year (June 2016 to June 2017) from the headwaters to the catchment outlet. To this purpose, a total of 66 samples, including 30 sediment sources and 36 suspended sediment mixtures were collected to characterize the system. Source samples were collected from four land use classes; agricultural land (AG), Mediterranean forest (MF), pine afforestation (PI), scrubland (SC), and two main geomorphic elements: eroded subsoil (SS) and channel bank (CB). A total of 30 sampling points (5 for each land use class) were selected to clearly represent each sediment source based on geochemical and radionuclides data from previous studies (Lizaga et al., 2018; Lizaga et al., 2019; Lizaga et al., 2020b). The samples were collected with a 2 cm cylindrical sampler with a total surface area of 127 cm². At each sampling location four composite samples collected around a central point were pooled to create a representative composite sample following Owens et al. (2016).

Suspended sediment samples (SSC) were collected following the methodology proposed by Phillips et al. (2000) in the middle part of the channel bed at the outlet of SBC1, SBC2 and CO with three parallel samplers at each point. Suspended sediments samples were integrated per three months during one entire hydrological year, from June 2016 to June 2017 corresponding to the climatological seasons. The SSC were retrieved as close as possible to the end of each season: summer (collection date 21 September),
autumn (collection date 21 December), winter (collection date 31 March) and spring (collection date 27 June). The objective of the sampling schedule was to provide a close replication of sediments transported during each season for evaluating both seasonality and intraseasonal effects of different crop practices such as sowing, fertilising and harvesting in the sediment contribution to the streams.

Samples were air-dried, weighted, ground, homogenised and sieved to ≤63µm following common methodologies (Palazón et al., 2015b; Owens et al., 2016; Collins et al., 2017). Besides, the selection of the ≤63µm particle size for sources and mixtures was related to the predominant silt texture of soils in the catchment (Lizaga et al., 2019a).

Lipids were extracted from the soil (source) and sediment (sink mixture) samples using accelerated solvent extraction (Dionex ASE 350, Thermo Scientific, Bremen Germany) with dichloromethane (DCM): MeOH (9:1 v/v) at 100ºC and 13 MPa for three cycles of 5 min (30 mL cells, 60% flush volume). For this c.a. 3 g of dried and 63 µm sieved sample was weighed in 22 mL stainless steel cells to which a recovery standard was added (12.5 ng C17:0FA, dissolved in 50 µL ethyl acetate). The recovered C17:0 was used to compute the FA content of the soils and sediments. The lipid extract was dried using rotary evaporation (CentriVap, Labconco, Kansas City, USA) at 60ºC and 20 mbar. Lipid fraction was re-dissolved in DCM/Isopropanol (2:1 v/v) before being separated in neutral and acid fraction using aminopropyl solid-phase extraction columns (Bond Elute, 500mg, 6mL, Agilent Technologies) according to Blake et al. (2012). Neutral fraction was removed with DCM/Isopropanol after which the acid fraction was eluted using 2 % acetic acid in diethyl ether (Russell and Werne, 2007). After taking the acid fraction to dryness by rotary evaporation, the Fatty acids were methylated using Methanolic BF₃ (14 %, 20 min at 60 ºC).
The obtained fatty acid methyl esters (FAME) were quantified, after addition of an internal standard (C19:0 FAME), using capillary gas chromatography (GC Trace Ultra, Thermo scientific) with flame ionisation detection (FID) equipped with a 5% Phenyl Polysilphenylene-siloxane column (BPX5, 30 m x 0.25 mm x 0.25 μm, Trajan). After adapting the solvent volume for optimal concentration for compound-specific stable isotope (CSSI) analysis, the $^{13}$C abundance of the individual FAME was determined using GC-isotope ratio mass spectroscopy (GC-IRMS). The GC-IRMS system used consisted out of a Trace 1310 GC equipped with the same GC column as for GC-FID connected to an ISOLINK II through a CongFlo IV to a Delta-V advantage IRMS detector (All Thermo scientific). Normalisation of the $^{13}$C signal on the Vienna Pee Dee belemnite (VPDB) scale was performed by injecting a mixture of C14:0, C16:0, C18:0 C20:0 and C30 FAME, and C14:0, C16:0, C18:0 C20:0 Fatty acid ethyl ester provided by Arndt Schimmelmann (Indiana University), calibrated using NBS 19, and L-SVEC defined as exactly +1.95 and -46.6 ‰, on the VPDB scale, respectively, every five samples. Additionally, mixtures of Fatty acids (C16, C17, C19 and C20) were methylated together with the samples to correct for the contribution of the methyl group of the FAME in order to obtain the $\delta^{13}$C of the FA.

2.3. Data processing and MixSIAR formulation

The estimation of the relative contribution of each potential sediment source to the sediment mixtures was assessed with the commonly used MixSIAR framework (Stock et al., 2018) for unmixing compound-specific stable isotopes (CSSI) of very-long-chain fatty acids (VLCFAs: C22-C32). To test the discrimination capacity of the selected tracers, an LDA (Linear Discriminant Analysis), an Euclidian distance matrix and a cluster analysis using the ward.D2 method were performed. Furthermore, an analysis of
variance was performed to assess whether the means of VLCFAs significantly differed between sources.

A crucial requirement in fingerprint assessment is the implementation of previous statistical tests to identify individual fingerprint properties, which discriminate between potential sources to select the optimum set of fingerprint properties (Yu and Oldfield, 1989; Walling and Woodward, 1995; Collins et al., 1996; Palazón and Navas, 2017). As the use of one mixture or another likely modifies which tracers are suitable for unmixing, different tracers were used as input for each of the sediment mixtures unmixed at the specific sampling locations.

MixSIAR is a Bayesian tracer mixing model, implemented as an open-source R package, based on JAGS library for Bayesian data analysis using Gibbs sampling Markov chain Monte Carlo (MCMC) algorithm (Plummer, 2003). MixSIAR framework permits the incorporation of informative priors which represent previous knowledge or measured data that could be used to help the model estimate the different source contributions. A detailed description of the package can be found in Stock et al. (2018).

Before unmixing the samples, the conservativeness of the tracers was tested for each mixture using the mixing polygon approach (Alewell et al., 2016; Upadhayay et al., 2017; Bravo-Linares et al., 2018). The method states that each mixture sample must be within a polygon bounding the signatures of the sources as a requirement of conservativeness. Thus, obtaining an optimum set of tracers for each mixture. Concentration of FA was not used directly as a tracer in the mixing model but was used as input in the isotopic mixing model using the concentration dependence option of the MixSIAR framework as used by Upadhayay et al. (2018) in a Nepal catchment.

From a geomorphological assessment and previous fingerprinting studies pursued in the study catchment by Gaspar et al. (2019b) and Lizaga et al. (2019a) using radionuclides and stable elements, CB, SS and AG were known to have a high proportional contribution
to the sediment flux in the catchment. Results from Lizaga et al. (2020b) were incorporated in six additional simulations that include as ‘prior information’ apportionings of 24%, 44%, 1% + 7%, and 24% for AG, CB, RG + PI and SS, respectively. These simulations were run by considering different prior informativeness defined in this research as the sum of the prior input into the model. The input priors ranged from low informative priors in which the sum of the priors input was 1, medium informative priors in which the weight of prior was set as the number of sources, to very informative priors in which the sum of the priors correspond to 100.

The Markov Chain Monte Carlo (MCMC) parameters in MixSIAR were set as follows: number of chains = 3, chain length = 3,000,000 (extreme), burn = 1,500,000, thin = 500. The convergence of mixing models was evaluated using the Gelman-Rubin diagnostic, rejecting the model output if any variable was above 1.0, in which case the chain length was increased. Furthermore, a diagnostic matrix plot of the posterior source contribution was used to evaluate the quality of source discrimination. Density plots of the proportional source contributions are reported along with the mean, median and standard deviation.

3. Results

3.1. Sediment source discrimination

Significant discrimination between the five sources was found by using the $\delta^{13}$C isotopic signatures of the VLCFAs (P-value < 0.01). The analytical results, the LDA plot and the cluster analysis evidenced the discrimination capacity of the $\delta^{13}$C-FAs (Fig. 2, Table S1). The LDA plots discriminated the four land uses, Agricultural (AG) and pine afforestation (PI) and the two geomorphic elements were clearly separated though Mediterranean forest (MF) and scrubland (SC) had a small overlap. Considering the
results from the LDA and cluster analyses the two natural vegetation covers (MF and SC) were merged into one source termed as rangeland (RG). After merging, the LDA plot showed significant discrimination between the five potential sediment sources. There were differences in the VLCFAs concentrations between the sediment sources (Table 1). The dominant FA in all source samples was C26, whereas C32 had the lowest concentration. For all analysed FAs the highest concentrations were found in MF while the lowest were in SS. The concentrations in the suspended sediment mixtures ranged between a minimum of 0.5 µg g⁻¹ soil for C32 and a maximum of 16.2 µg g⁻¹ soil for C24 (Fig. S1).

3.2. Spatio - Temporal variation of FAs in the suspended sediment mixtures

The sediment mass of the suspended sediment captured by the samplers varied with the accumulated rainfall (Fig. 3). A decreasing trend in the mixture sample mass was recorded from summer to spring seasons in SBC1 and in the catchment outlet, while the sediment mass in SBC2 remained constant during summer, autumn and winter. However, a slight increase in the sample mass was recorded during spring for all three subcatchments (Fig. 3). The mean contents of all FAs were higher in the catchment outlet than in the headwaters subcatchments being significantly higher (p<0.05) for C22, C24 and C30 (Fig. S1). The mean FA content of the suspended sediments in the three subcatchments had different seasonal trends displaying similar seasonal variation in all FAs (from C22 to C30) except for C32 (Fig. S1). Overall, the lowest content was recorded in autumn in all subcatchments.

\[ \delta^{13}C - \text{FAs} \] values were similar in SBC1 and in the catchment outlet but differed slightly in SBC2 (Fig. 4). The timeline of \[ \delta^{13}C - \text{FAs} \] showed two different trends for C22 to C28 and for C30 to C32 (Fig. 4). Contrary to the FA concentrations, the mean \[ \delta^{13}C - \text{FA} \] values
were similar in SBC1 and in the catchment outlet that in turn had similar trends during the study hydrological year with a positive and significant correlation for all FA except C22. However, this pattern was not observed in SBC2. In all subcatchments, $\delta^{13}$C-FA of C22 to C30 were lowest in autumn and highest in winter. Overall, $\delta^{13}$C-FA values from C26 and C28 were the most conservative while C32 was the less conservative.

### 3.3. Source discrimination and sediment source contributions

For most sediment mixtures, good source discrimination was achieved since a good number of tracers met the requirements of the within a polygon approach. However, due to the low $\delta^{13}$C values in the summer mixture samples in SBC2 were out of the mixing polygon for all tracers. These low values could be likely due to a disturbance of the channel bed by wild pigs when looking for water during dry periods. In order to avoid the inclusion of erroneous results and accomplishing the assumption of n-1 prerequisite in fingerprint studies, the summer mixture was not unmixed. All selected tracers from the autumn sampling in SBC1 were close to the borders limit of the mixing polygon suggesting special care when interpreting the results of this mixture.

The optimum set of tracers selected for each mixture is displayed in Table S2. The MixSIAR output indicated that overall, AG was the predominant source for the whole year (Table 3). The catchment outlet was estimated to have the highest AG (84.5% - 74.3%) contribution while SBC1 (69.2% - 33.4%) showed the lowest ($p=0.05$). On the other hand, CB contributed around 10% and 20% to SBC1 and SBC2 mixtures, respectively, but their contribution was much less ($p=0.05$) in the lower part at the catchment outlet. Despite the general high contribution from AG along the year, a higher ($p=0.05$) contribution of PI was found in SBC1 during summer and autumn seasons but during the spring season a lower AG contribution was recorded ($p=0.05$) in SBC2.
After the inclusion of the low informativeness prior, the results varied, increasing AG apportions while decreasing contributions from the other sources except for CB that remained almost equal (Table 3). The PI and SS contributions decreased slightly, being the PI contribution significant only during the summer period in SBC1. Despite the inclusion of informative priors suggesting high CB and SS apportions, neither CB nor SS increased their relative contributions. However, the escalation of prior weight could substantially modify the model results as shown in Fig. 6. Once we increased the informativeness of the priors the model results tend to fit the prior information reducing the informativeness of the input tracers.

4. Discussion

4.1 δ^{13}C-FA signature for land use discrimination

The content and δ^{13}C of FA under each land cover type and for the two geomorphic elements in this study show the extent of source discrimination that might be expected from the literature. The small differences between MF and SC are linked to their origins. Most scrubs and forests were previous croplands few decades before, and the signal of the agricultural lands likely remains in soil increasing the complexity to discriminate between land covers (Lizaga et al. 2019a). For this reason, Mediterranean forest that is the final phase of the successional stages of natural revegetation, in the transition to Mediterranean forest presents similar isotopic values to that of SC.

However, δ^{13}C-FAs has the ability to discriminate between the different land covers such as AG, PI and RG (Fig. 2), which implies that δ^{13}C-FAs signatures extracted from the soil surface were not extremely influenced by the past crops that occupied most of the area during the previous century.
4.2 FAs data for catchment assessment

The larger amount of sediment capture in the samplers during the summer period when most croplands are bare together with the lower sediment mass collected in SBC2 pinpoint the agricultural cycle as the main driver of the variability of sediment export in the catchment. The greatest sediment sample was collected after summer, with only 88 mm of accumulated precipitation, of which 54 mm were recorded during a 4 days storm event between 2016-09-13 and 2016-09-17 (Fig. 3). Thus, localised storms after long dry periods cause severe erosion of both, dry soils and bare fields before crops planting in autumn. These results are in agreement with previous findings by Gaspar et al. (2019b) and Lizaga et al. (2019b) during an exceptional storm event. These interacting factors likely increase the sediment supply to streams and subsequently, the mass of the suspended sediment collected.

The reduction of the suspended sediment mass collected after the summer campaign is likely affected by the gradual growing of crops. Thus, as the growth of natural vegetation progresses favoured by more available water in soil after summer, the soil is more protected. The different behaviour observed in SBC2 is likely due to higher presence of natural covers decreasing connectivity along with lower presence of AG land use reducing soil disturbances that increase soil erosion.

The headwaters, i.e. subcatchments SBC1 and SBC2, show higher proportion of land uses with high FAs content such as PI, SC and MF. Interestingly, the sediment in SBC1 and SBC2 has lower FA content than the catchment outlet (CO). Thus, a difference between the three sampling points in terms of content can only be attributable to the higher presence of croplands in the catchment outlet (CO) that increases the sediment apportions. However, the variation in the FAs concentrations through the four seasons shows a similar trend for SBC1 and the catchment outlet indicating similar influencing
factors in both sub-catchments. Besides, SBC2 shows a different temporal trend and also
different sediment mass compared to SBC1 and the catchment outlet likely due to greater
surfaces occupied by natural vegetation covers. Moreover, most cultivated fields in SBC2
are located at the headwaters instead of surrounding the main stream as in SBC1 and at
the catchment outlet. Such configuration would probably limit connectivity delaying the
supply of sediments reaching the streams; thus, AG contributions would spread along the
year.

Despite the similar content for different FAs, C32 shows the lowest content and a
different temporal trend than the other FAs which is most evident in the catchment outlet
(Figure S1). Furthermore, δ13C-C32 in the sediment mixtures was often outside the range
measured in the sources, and consequently, it might not be considered as a conservative
tracer in this Mediterranean environment.

The high fluctuations found in isotope values during and between seasons are in
agreement with previous results by Reiffarth et al. (2019) who attribute such fluctuations
to continuously variable environmental conditions that lead to the variation of the δ13C
isotopic values in the sediment sources.

4.3 Source sediment contributions

The good discrimination of vegetation covers from CSSI allows identifying pine forest
as the main contributing source among the land uses with permanent vegetation cover
(SC, MF and PI). The nearly 40% contribution of PI in SBC1 during summer is likely
associated with the strip clearcutting also favoured by the intense rainfall on dry soil
conditions (Fig. 3; Fig. 5). Hence, bare soil left during clearcutting and traffic of heavy
machinery lead to increase the sediment supply from clear cut areas of harvested pine
forest. After the summer period the contribution of PI decreases gradually throughout the
year to be negligible by the next spring. The latter is in good agreement with the low soil redistribution rates in undisturbed pine forest estimated using $^{137}$Cs in previous studies (Lizaga et al., 2018b; Scarciglia et al., 2020).

The low contribution of RGs is determined by the protecting capacity of the vegetation cover. Only extreme storm events have the capability to mobilise surface soil sediment from these well-protected lands to the streams. However, during exceptional storm events there are substantial rises of AG, CB and SS contributions compared to almost negligible amount of sediment exported from RGs (Lizaga et al., 2019b). Overall, mature and undisturbed vegetation cover show small contribution to total sediment load, what agrees with records in other environments (Gibbs et al. 2008; Bravo-Linares et al., 2019).

Despite $\delta^{13}$C-FAs clearly discriminate the different sediment sources, it appears that geomorphic elements such as channel banks and subsoil with high sediment contributions as found by Gaspar et al. (2019b), and Lizaga et al. (2019b, 2020b) and from the geomorphological assessment during fieldwork campaigns are probably underestimated. Hence, due to the constant high AG apportionment it cannot be totally discarded an anchoring problem of the model as reported by Davis et al. (2015) when using the SIAR model.

Furthermore, while the low informative prior effectively removes the PI contribution of autumn and spring seasons when no clear-cutting works occurred and the pine forest has recovered most of the lost plant density and shrub cover (Fig. 5); prior mainly affected contributions from land covers with permanent vegetation, reducing its apportionment while not significantly modifying the other source apportionments (Table 2). However, though the implementation of prior information could lead the model to likely better results it can also modify and mislead the unmix of the analytical tracers. As seen in Fig. 6, overall prior inclusion does not modify the results before increasing their
informativeness. However, by providing informativeness/weight to the priors, the model is neglecting the information delivered by the analytical tracers used as input and likely biasing model results. Despite in mathematic terms the inclusion of objective estimations as informative priors does not lead to additional model uncertainty, the inclusion of non-objective information could mislead the model results. As explained by Stock et al. (2018) it is unclear how much weight it should be given to a prior as it depends on the reliability the existing information. For example, in an attempt to downsize or reduce the informativeness of the prior information, Stock et al. (2018) rescaled the priors to have a total weight equal to the number of sources, which is the same weight as the “uninformative” prior; thus, having the same mean but different variance reduced its informativeness. The priors created in our research following the above methodology do not significantly modify the output of the model regarding the uninformative priors.

Another issue emerges in relation to the method for selecting CSSI tracers to unmix sediment mixtures. Several authors have implemented the mixing polygon approach as a guide in the tracer selection process which in this case is visual and relies on the observer's criteria or could be affected by outliers that will determine the polygon boundaries (e.g. Alewell et al., 2016; Bravo-Linares et al., 2018; Upadhayay et al., 2020). In spite of the potential of CSSI as efficient fingerprinting tracers, care must be taken when using the mixing polygon approach to select suitable tracers for unmixing, especially when tracers are neighbouring the borders of the unmixing polygon or even out of the polygon though close to the borders.

In geomorphological active landscapes it might be needed to complement the CSSI approach for improving the detection of channel bank and subsoil. In this regard, radionuclides offer great potential due to their distinctive soil content for different substrate mineralogies (Navas et al., 2005). Accordingly, to further confirm the results
obtained from δ13C-FA and following the recommendation by Reiffarth et al. (2016) it would be needed to implement other additional tracing methods including geochemistry along with CSSI.

Furthermore, concerns on the scarcity of suitable tracers for unmixing were reported in an agricultural catchment by (Smith and Blake, 2014). For this reason, when using CSSI, additional tools for tracer selection should be developed in the future to improve the tracer selection.

5. Conclusions

The use of δ13C-FA as tracers increased the discrimination between the different land uses which allows to elucidate the soil mobilisation dynamics from the different land uses in comparison with previous implemented tracers. We found that exported sediments are mainly originated from agricultural lands; thus, efforts should be focused to control soil erosion in croplands. The unmixing results also highlight the significant impact of afforestation practices. The application of CSSI in conjunction with other fingerprinting tools may offer a greater advantage for discriminating both vegetated and highly mineral substrates with absence of plant cover.

As δ13C-FA is mainly discriminating sediment sources based on land cover, it is likely to miss or underestimate the contribution of specific geomorphic features. Combining δ13C-FA with tracers such as radionuclides and stable elements will probably give a most complete picture of the sources supplying sediments in severely dissected landscapes, with exposed substrates drained by energetic streams that are also affected by intense rainfalls and present high sediment export dynamics as in this representative catchment of Mediterranean agroforestry systems.
The inclusion of prior information in fingerprinting studies could represent an advantage as much as a disadvantage if priors are not supported by robust evidence. Based in our results, if prior information is used, special consideration should be paid to the weight attributed to it. For this reason, we advise that until strong argumentation for deviating from this, the weight of prior should not exceed the number of sources.

The role of agricultural rotation and vegetation cover in the sediment delivery to the water courses is in agreement with weather data, sediment loads and the satellite images collected during the hydrological year studied. Therefore, conservation practices, especially in periods of absence of vegetation cover, should be promoted to prevent the loss of fertile topsoil. These findings report the benefits of applying CSSI for tracking sediment derived from agricultural practices, shed new light about the impacts of clearcutting in Mediterranean mountains and underline the benefits of natural covers to prevent soil loss.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2021.112291.

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References


Figure captions

Fig.1. Location of the Barués catchment in the central part of the Ebro Basin (NE Spain). 3D map of the two tributary subcatchments, SBC1 and SBC2, the catchment outlet (CO) and the land covers: (a) cropland (AG) and Mediterranean forest (MF); (b) pine afforestation (PI); (c) scrubland (SC) developed over abandoned cropland fields; (d) heavily degraded area termed as subsoil (SS); (e) channel banks (CB), deeply incised stream and landslides (topples), and (f) view of topples in a channel bank (CB) section.
Fig. 2. Linear discrimination analysis (LDA) plot of the sediment sources in the Barués catchment for a) six sources: agricultural (AG), channel bank (CB), Mediterranean Forest (MF), pine afforested forest (PI), scrubland (SC) and subsoil (SS), b) five sources; the combination of MF and SC in one source named rangeland (RG), and c) cluster analysis of the six sediment sources.

Fig. 3. Line graph of the sediment mixture mass for each subcatchment and the accumulated rainfall for the four seasonal sampling campaigns.
Fig. 4. Boxplots of $\delta^{13}$C-FAs for agricultural (AG), rangeland (RG), pine afforestation (PI), subsoil (SS), channel bank (CB) and the mixture samples in subcatchments SBC1, SBC2 and at the catchment outlet (CO).

Fig. 5. Sentinel 2 satellite images comparison from different months evidencing a clearcutting area: a) Location of the pine afforestation submitted to strip clearcutting in SBC1; b) pine afforestation harvest start; c) end of the clearcutting, and d) rapid recovery of the shrub vegetation removed during strip clearcutting and pine growth increase.
Fig. 6. Mean sediment source contributions and standard deviation of the 12 suspended sediment mixtures modelled with MixSIAR by using six different prior weights. Dashed lines represent the prior distribution 24%, 44%, 1%, 7% and 24% for agricultural (AG), channel bank (CB), rangeland (RG), pine forest (PI) and subsoil (SS), respectively, using different prior weights.
Fig. S1 and S2. a) Boxplots of FA concentration and $\delta^{13}$C-FAs in SBC1, SBC2 and CO;
b) timeline of FAs concentration for four sampling seasons.
Table 1. Mean and standard deviation (sd) of the FAs concentration (22 to 32 carbon chain length, C22-C32) for agricultural (AG), Mediterranean forest (MF), scrubland (SC), pine afforestation (PI), subsoil (SS) and channel bank (CB) sediment sources and mixture samples.

<table>
<thead>
<tr>
<th>Sources</th>
<th>C22</th>
<th>C24</th>
<th>C26</th>
<th>C28</th>
<th>C30</th>
<th>C32</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
<td>Mean</td>
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<td></td>
<td>(µg g⁻¹ soil)</td>
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<td>(µg g⁻¹ soil)</td>
<td>(µg g⁻¹ soil)</td>
<td>(µg g⁻¹ soil)</td>
</tr>
<tr>
<td>AG</td>
<td>3.28 ± 0.78</td>
<td>3.64 ± 0.78</td>
<td>4.45 ± 1.58</td>
<td>4.11 ± 1.61</td>
<td>2.79 ± 0.78</td>
<td>1.43 ± 0.25</td>
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<tr>
<td>CB</td>
<td>1.93 ± 0.61</td>
<td>3.13 ± 1.52</td>
<td>2.87 ± 1.36</td>
<td>2.87 ± 1.14</td>
<td>2.66 ± 0.75</td>
<td>1.47 ± 0.36</td>
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<tr>
<td>MF</td>
<td>7.38 ± 3.12</td>
<td>9.96 ± 4.61</td>
<td>14.8 ± 7.63</td>
<td>12.6 ± 7.32</td>
<td>12.9 ± 7.22</td>
<td>5.52 ± 3.15</td>
</tr>
<tr>
<td>PI</td>
<td>10.5 ± 6.32</td>
<td>12.7 ± 7.36</td>
<td>19.0 ± 14.9</td>
<td>11.9 ± 7.82</td>
<td>11.2 ± 7.93</td>
<td>5.33 ± 3.58</td>
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<tr>
<td>SC</td>
<td>8.38 ± 2.92</td>
<td>11.2 ± 4.66</td>
<td>17.4 ± 8.36</td>
<td>10.7 ± 6.10</td>
<td>10.2 ± 5.31</td>
<td>4.54 ± 2.70</td>
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<tr>
<td>SS</td>
<td>0.84 ± 0.34</td>
<td>0.74 ± 0.34</td>
<td>0.60 ± 0.25</td>
<td>0.84 ± 0.35</td>
<td>0.85 ± 0.38</td>
<td>0.49 ± 0.21</td>
</tr>
</tbody>
</table>

Table 2. Mean sediment source contributions and sd to the sediment mixtures modelled with MixSIAR by implementing: a) uninformative priors and b) informative priors. Agricultural (AG), channel bank (CB), rangeland (RG), pine forest (PI) and subsoil (SS).

<table>
<thead>
<tr>
<th>Mixture</th>
<th>AG</th>
<th>CB</th>
<th>RG</th>
<th>PI</th>
<th>SS</th>
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<td>a) Mixture</td>
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<td>Mean</td>
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<td></td>
<td>(µg g⁻¹ soil)</td>
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<td>(µg g⁻¹ soil)</td>
<td>(µg g⁻¹ soil)</td>
</tr>
<tr>
<td>CO - summer</td>
<td>74.3 ± 10.2</td>
<td>3.5 ± 3.1</td>
<td>4.8 ± 3.9</td>
<td>9.6 ± 8.3</td>
<td>7.9 ± 7.3</td>
</tr>
<tr>
<td>SBC2 - summer</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SBC1 - summer</td>
<td>33.4 ± 26.3</td>
<td>7.5 ± 6.5</td>
<td>4 ± 3.3</td>
<td>38.1 ± 23.8</td>
<td>17 ± 14.9</td>
</tr>
<tr>
<td>CO - autumn</td>
<td>82.2 ± 13.6</td>
<td>2.8 ± 2.6</td>
<td>1.3 ± 1.4</td>
<td>7.5 ± 9.5</td>
<td>6.1 ± 8.2</td>
</tr>
<tr>
<td>SBC2 - autumn</td>
<td>82.2 ± 10.3</td>
<td>4.2 ± 4.1</td>
<td>1.5 ± 1.5</td>
<td>3.7 ± 6.6</td>
<td>8.5 ± 8</td>
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<tr>
<td>SBC1 - autumn</td>
<td>48.9 ± 27.7</td>
<td>4.8 ± 4.2</td>
<td>2.9 ± 2.5</td>
<td>25.4 ± 24.4</td>
<td>18 ± 16.6</td>
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<tr>
<td>CO - winter</td>
<td>75.3 ± 18.8</td>
<td>4.2 ± 4.2</td>
<td>4.6 ± 3.7</td>
<td>3.2 ± 3</td>
<td>12.8 ± 19.5</td>
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<tr>
<td>SBC2 - winter</td>
<td>86.6 ± 8.6</td>
<td>3.4 ± 3.2</td>
<td>1.7 ± 1.8</td>
<td>2.7 ± 2.7</td>
<td>5.5 ± 7.5</td>
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<tr>
<td>SBC1 - winter</td>
<td>36.4 ± 15.7</td>
<td>16.3 ± 12.8</td>
<td>19.5 ± 12.9</td>
<td>6.8 ± 7.4</td>
<td>21.1 ± 17.5</td>
</tr>
<tr>
<td>CO - spring</td>
<td>84.5 ± 9.1</td>
<td>4 ± 3.7</td>
<td>2.4 ± 2.3</td>
<td>2.7 ± 2.7</td>
<td>6.4 ± 8.3</td>
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<tr>
<td>SBC2 - spring</td>
<td>35.2 ± 20.7</td>
<td>11.7 ± 9.4</td>
<td>4.9 ± 4.2</td>
<td>28.5 ± 17.9</td>
<td>19.7 ± 14.5</td>
</tr>
<tr>
<td></td>
<td>AG</td>
<td>CB</td>
<td>RG</td>
<td>PI</td>
<td>SS</td>
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<tr>
<td><strong>SBC1 - spring</strong></td>
<td>69.2 ± 18.7</td>
<td>5.1 ± 4.7</td>
<td>4.4 ± 3.4</td>
<td>2.9 ± 3.4</td>
<td>18.4 ± 19.6</td>
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<tr>
<td><strong>b) Mixture</strong></td>
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<tr>
<td>CO - summer</td>
<td>90.9 ± 9</td>
<td>2.7 ± 3.3</td>
<td>0.9 ± 2.4</td>
<td>2.1 ± 5.9</td>
<td>3.4 ± 6.2</td>
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<tr>
<td>SBC2 - summer</td>
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<tr>
<td>SBC1 - summer</td>
<td>61.9 ± 36</td>
<td>8.5 ± 8.7</td>
<td>0.5 ± 1.6</td>
<td>20 ± 32.8</td>
<td>9.2 ± 15.4</td>
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<tr>
<td>CO - autumn</td>
<td>96.7 ± 3.9</td>
<td>1.4 ± 2</td>
<td>0 ± 0.2</td>
<td>0.3 ± 1.6</td>
<td>1.6 ± 3.1</td>
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<tr>
<td>SBC2 - autumn</td>
<td>93.3 ± 7.7</td>
<td>2.6 ± 3.6</td>
<td>0.1 ± 0.4</td>
<td>0.2 ± 2.6</td>
<td>3.7 ± 6.7</td>
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<tr>
<td>SBC1 - autumn</td>
<td>83 ± 20.1</td>
<td>4.1 ± 5</td>
<td>0.2 ± 0.9</td>
<td>2.8 ± 13.2</td>
<td>9.9 ± 15.4</td>
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<tr>
<td>CO - winter</td>
<td>88.6 ± 18.1</td>
<td>3.2 ± 4.4</td>
<td>0.6 ± 1.9</td>
<td>0.2 ± 1</td>
<td>7.3 ± 18.2</td>
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<tr>
<td>SBC2 - winter</td>
<td>96.4 ± 4.9</td>
<td>1.8 ± 2.7</td>
<td>0.1 ± 0.4</td>
<td>0.1 ± 0.6</td>
<td>1.6 ± 4.1</td>
</tr>
<tr>
<td>SBC1 - winter</td>
<td>42.1 ± 17</td>
<td>29.8 ± 19.4</td>
<td>5.7 ± 12.5</td>
<td>0.4 ± 2.2</td>
<td>22 ± 27</td>
</tr>
<tr>
<td>CO - spring</td>
<td>94.4 ± 7.8</td>
<td>2.7 ± 3.8</td>
<td>0.2 ± 0.7</td>
<td>0.2 ± 0.6</td>
<td>2.5 ± 7</td>
</tr>
<tr>
<td>SBC2 - spring</td>
<td>63.3 ± 24.3</td>
<td>14.1 ± 11.9</td>
<td>0.5 ± 1.7</td>
<td>6.9 ± 17.6</td>
<td>15.3 ± 18.7</td>
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<tr>
<td>SBC1 - spring</td>
<td>81.1 ± 20.6</td>
<td>4.7 ± 5.9</td>
<td>0.5 ± 1.7</td>
<td>0.1 ± 0.6</td>
<td>13.5 ± 21.4</td>
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</table>