Fingerprinting changes of source apportionments from mixed land uses in stream sediments before and after an exceptional rainstorm event

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ABSTRACT

The loss of fertile topsoil is one of the principal soil degradation problems in mountain agroecosystems worldwide. Soil erosion rates reach their maximum during exceptional storm events that remove soil particles, especially from unprotected topsoil. In Mediterranean mountainous environments, several centuries of non-irrigated agriculture and the subsequent removal of natural vegetation for developing agriculture has increased the surface area prone to erosion. In addition, the irregularity in exceptional precipitation events results in a great loss of fertile soil, the subsequent siltation of reservoirs and a decrease in water quality. To analyse the soil response to exceptional events, 161 source samples were collected in a 23 km² catchment that was mostly cultivated at the beginning of the last century. Source samples were distributed over the five main land use/land covers such as agricultural land, pine afforestation, open forest, bare soil and channel bank areas. Furthermore, 20 channel bed sediment samples were collected along the main streams before and after the exceptional storm event to document

changes in the sediments. In addition, floodplain sediments were collected to provide a close replication of sediments deposited during regular storm events. Source apportionments were calculated using the FingerPro mixing model in the pre-event, regular events and post-event scenarios.

The unmixing outputs displayed a large variation of source apportionments from the upper part to the lower part of the catchment and from pre- to post-event sediments. After the event, a decrease of more than 70% of the clay fraction and its associated elements such as Fe, Al, K, Ba, Sr, Rb, Pb, Zn, V, ^{137}Cs , ^{40}K , ^{232}Th and SOC along with a rise in contents of elements associated with the coarse fraction (Si, Nb, Zr, Ti, P and ^{226}Ra) was recorded in the channel bed sediments. At the catchment outlet, the pre-event sediment showed substantial contributions from bare soil (29%) and from agriculture and channel banks, which both reached 35%, while the channel bank was the main source along the catchment ranging between 44 and 71%. The low contribution from soil under natural covers with a mean value less than 4% underlines the benefits of vegetation to prevent soil loss. In the post-event sediment, the channel bank contribution increased up to 63% at the catchment outlet. Our findings highlight the hazards of exceptional storm events on modifying sediment source contribution and exporting fine sediment.

1. Introduction

The impact of soil erosion on mountain agroecosystems has received increasing attention due to the vulnerability of shallow soil to erosion processes, which are the main cause of soil loss and subsequent land degradation. Very intense rainstorms after dry periods are relatively frequent in the Mediterranean region (Serrano-Notivol et al., 2017). Mediterranean agroecosystems are susceptible to degradation due to irregular space-time distribution of high-intensity rainfall and storm events, followed by long dry periods

(Mariani and Parisi, 2014). The importance of these exceptional rainstorms has been highlighted, and they have been found to be responsible for major geomorphological changes including piping, gully formation, landslides and subsequent soil loss (Grodek et al., 2012; Nadal-Romero et al., 2013). Thus, fragile soils with low nutrient contents existing in Mediterranean mountain agroecosystems, along with an absence of dense vegetation cover due to deforestation in the past century, have created areas prone to erosion (Navas et al., 2017). Soils without vegetation cover are easily erodible during exceptional storm events such as the three-day long exceptional rainstorm event that occurred in 2012 in northeastern Spain (Serrano-Muela et al., 2015).

Exceptional rainfall events accelerate soil and bedrock erosion on hillslopes, which commonly results in higher sediment mobilisation and variations in sediment sources released into the streams. Exported fine sediment produces an important indirect impact such as rapid siltation of downstream water bodies that reached a maximum in the Mediterranean mountains due to land abandonment in the mid-1950s (Navas et al., 2009). Since the 1950s, Mediterranean mountain agroecosystems were commercialised through technological progress and the EU Common Agricultural Policy (CAP), which favoured the expansion of certain management systems focused on more fertile and accessible land. These practices produced a decline in traditional farming methods and converted mountain agriculture into marginal agricultural land leading to the abandonment of the countryside (Lasanta et al., 2016; Quijano et al., 2016a; Borrelli et al., 2017). Subsequent natural vegetation regrowth (Navas et al., 2008) and afforestation during the 1960s and 1980s produced a large effect on reducing slope-channel coupling and runoff due to an increase in plant cover (Cavalli et al., 2013; Heckmann et al., 2018; Llena et al., 2019). Thus, Mediterranean agricultural soils suffered significant modifications due to land use/land cover changes (Romanya and Rovira, 2011). As a consequence of such changes,

cultivated Mediterranean fields show large variability in soil losses with average soil redistribution rates between -30 to $15 \text{ Mg ha}^{-1} \text{ yr}^{-1}$, while in other land uses that offer protection to the soil surface (such as open forest), rates are much more moderate, varying from -3 to $5 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ (Navas et al., 2014; Lizaga et al., 2018a).

Currently, soil erosion is an estimated 10–40 times greater than soil formation rates (Pimentel, 2006; Verheijen et al., 2009). Various approaches have been suggested for sediment yield monitoring and quantification of soil redistribution rates (Favis-Mortlock et al., 2008; Walling and Collins, 2008; Dutta, 2016; Wynants et al., 2018). However, erosion processes are mostly influenced by a variety of driving forces such as slope, land management, altitude, vegetation cover, land use, soil type and changing weather patterns and extremes under current climate (Renard et al., 2011; Lana-Renault et al., 2013; Lecce et al., 2013; Buendia et al., 2016; Nadal-Romero et al., 2019; Shang et al., 2019). Thus, to control soil erosion, it is important to recognise the most susceptible areas, soils or land uses exposed to erosion processes as these processes lead to the loss of soil nutrients.

Concerns about the nutrient loss associated with fine particles due to soil erosion have led to analysis methods for quantifying and predicting erosion rates of fine grain sediment. To this purpose geochemistry, magnetic properties, radiotracers and modelling approaches offer considerable potential for studying erosion processes and calculating soil redistribution rates (Navas et al., 2005; Gaspar et al., 2013; Quijano et al., 2016b; Masselink et al., 2017). In areas where rill erosion is dominant, studies at the slope scale have proven effective (Li et al., 2009). However, few studies quantify soil redistribution rates at catchment or river scale (Mabit et al., 2002; Porto et al., 2003; Navas et al., 2013; Lizaga et al., 2018a; Chen et al., 2019).

Large-scale erosion after exceptional rainstorm events has occurred irregularly in the northeastern part of the Spanish Peninsula (Gutiérrez et al., 1998; White et al., 1997; García-Ruiz et al., 2002). Exceptional storm events and the subsequent overflow of river banks typically increase sediment transfer and suspended sediment loads in river catchments triggering variations in sediment solute concentrations (Winston and Criss, 2002).

The large increase in fine grain sediment mobilised during exceptional storm events has been demonstrated to be one of the most widespread contaminants in aquatic ecosystems, compromising water quality and causing reservoir siltation (Navas et al., 2004). For these reasons, defining the sources of eroded fine-grained sediment is a fundamental requirement for catchment management as well as for understanding the evolution of landscapes and delineating the most sensitive areas to soil loss.

Determining sediment provenance in catchments using conventional monitoring techniques is often challenging, but in most environments it can be undertaken by applying sediment source fingerprinting methods. Due to the growing use of fingerprinting methods, several unmixing models such as IsoSource (Phillips and Gregg, 2003), MixSIR (Moore and Semmens, 2008), SIFT (Pulley and Collins, 2018) and FingerPro (Palazón et al., 2015a; Lizaga et al., 2018) have appeared over the last years for pollution and ecological purposes. To date, there are several studies on identifying source apportions by fingerprinting techniques (Klages and Hsieh, 1975; Walling et al., 1979; Yu and Oldfield, 1989; Collins et al., 1996; Evrard et al., 2013; Schuller et al., 2013; Palazón et al., 2015b; Meusburger et al., 2018; Upadhyay et al., 2018), but only a few have quantified the sediment provenance after an exceptional rainstorm event (Martínez-Carreras et al., 2010; Zhang et al., 2017), and none of these studies have

125 compared whether there were changes in the provenance of sediment before and after an
126 exceptional storm event.

127 To evaluate the unstudied effect of this unstudied phenomenon, its source
128 apportions were calculated using the new R package FingerPro mixing model (Lizaga et
129 al., 2018b) that was tested with artificial samples by Gaspar et al. (2019a). For this
130 purpose, we implemented the unmixing model in two different datasets, before and after
131 a three-day exceptional rainstorm event in a representative catchment of the Prepyrenean
132 region. The 2012 event corresponded to a return period of 142 yr calculated at the outlet
133 of the Yesa reservoir located 30 km north from the catchment (Serrano-Muela et al.,
134 2015). Our objectives are (i) to analyse whether sediment properties vary along the main
135 streams before and after the exceptional storm event, (ii) to quantify and trace the
136 sediment provenance before the 2012 exceptional rainstorm event in different parts of the
137 study catchment and (iii) to examine whether sediment source apportionments after the
138 exceptional storm event differed from the ones during normal discharge.

139 Therefore, our multi-approach combining spatiotemporal analysis of soil
140 properties and fingerprinting modelling is aimed to determine how an exceptional storm
141 event modifies the sediment properties of the streambed sediments and how contributions
142 from sediment sources might change. To this aim, our work represents a unique
143 opportunity to track the changes in sediment contribution associated with exceptional
144 storm events due to the availability of pre-event sediment and floodplain mixtures that
145 were resampled after the storm event. This paper sheds new light on the effect of heavy
146 storms in agriculture catchments and points out the most sensitive areas to these highly
147 erosive processes.

148 149 **2. Material and methods**

2.1. The study area

The study catchment (23 km²) is drained by an ephemeral stream tributary of the Arba River located in Barué in the middle part of the Ebro Basin (Fig. 1). From the geomorphological perspective, the catchment structure is dominated by the low angle dip of the bedding and the presence of a Quaternary glacis located at the lower eastern part of the catchment. The climate is characterised by cold winters and hot and dry summers. The rainfall periods are concentrated in the spring and autumn seasons while the droughts take place between these two humid periods. The area is subjected to very intense though sometimes localised storms. The maximum and minimum annual temperatures are 30°C and -6°C, respectively. The mean annual rainfall is about 500 mm.

At the start of the twentieth century, most of the catchment was agricultural land. In the 1960s, nearly 60% of the catchment was croplands. However, during the next 10 yr, 75% of the agricultural land was abandoned. Currently, ~16% of the catchment is still cultivated while open forest and pine occupy the remaining 83.5 % (Lizaga et al., 2017). The main land use/land covers are agricultural, open forest and pine afforestation, occupying 16%, 50% and 19% of the catchment area, respectively. In addition, most of the agricultural land is located on a Quaternary glacis and on fluvial terraces with gentle slopes occupying the valley floors. The upper part of the Quaternary glacis is dissected by the La Reina tributary stream, an ephemeral stream with documented exceptional discharges under heavy rainfalls. Rangelands occupy the highest altitudes and the revegetated abandoned crops are mostly located at intermediate altitudes where most of the abandoned crops were located in the past. Interspersed patches of highly disturbed areas, including bare soil (subsoil), are dispersed all over the catchment, although it is more abundant on the middle part on south-facing slopes. Valley floors are infilled by eroded sediment from the slopes and are deeply incised by streams, especially from the

middle part of the catchment. The stream channel banks composed of loess type material have steep talus that remains uncovered by vegetation. Thus, channel banks of these upland agroecosystem catchments are characterised by deep straight walls due to flow incision by high water energy released during heavy rainfalls.

2.2. Soil sampling and analysis

Potential sediment sources and sediment sampling locations were manually identified during fieldwork campaigns in a design sampling scheme. Special attention was paid to the connectivity index (Lizaga et al., 2017) and soil properties such as CaCO₃, pH, EC, SOC, grain size, land use, soil classification (Lizaga et al., 2019) and soil redistribution rates (Lizaga et al., 2018a).

A total of 161 source sediment samples were taken with a cylindrical core 5 cm long and 6 cm in diameter, with four replicates at each sampling point combined in the field to create a representative composite sample following the accepted methodology proposed in fingerprinting studies (Owens et al., 2016; Collins et al., 2017). Fingerprinting studies collect sediment source samples of variable depths, though 2 cm depth is frequently used. However, heavy rainfall events in upland Mediterranean agroecosystems produce deep rilling and can remove more than 2 cm of surface soil. Thus, a 5 cm sample depth was selected in this study for the appropriate characterisation of sediment eroded by exceptional rainfall events.

Samples were collected from cropland (AG), open forest (OF), pine afforestation (PI), eroded subsoil (SS) and channel bank (CB). Source samples were distributed over the land uses (AG, OF and PI) across the catchment using a 500 x 500 m grid to represent the areal percentage of each land use. The sample points retained their grid location as much as possible avoiding recent highly disturbed areas that could not be representative

of the sampling source. Furthermore, 14 subsoil samples were collected on eroded bare soil distributed over the catchment, and another 18 samples were collected along the main streams on the channel banks near the mixture samples (Fig. 1).

Two different types of sediment mixture samples were collected in the channel bed along the main streams from the headwaters to the outlet of the catchment, before and after the secondary tributary streams. Mixture sediment samples are: (i) 20 channel bed samples collected before and after the 2012 storm event (identified as SMP 1–20), and (ii) 8 floodplain sediment mixture collected at sampling points 2, 3, 6, 12, 14, 15, 17 and 20. Channel bed and floodplain sediment lie on top of sandstone outcrops and these surface sediments can be easily washed away during heavy autumn rainfall events. Thus, the aim of these different sampling methods was to provide a close replication of sediments deposited before and after the exceptional discharge event and the sediment in floodplains that corresponds to regular high discharge events (named as SFMP). Channel bed sediments were taken with a cylindrical core 5 cm long and 6 cm in diameter with three replicates at each sampling point. The same methodology was used for collecting the sediment in floodplains.

The samples were air-dried, grinded, homogenised and sieved to ≤ 0.063 mm following the most widespread methodology (Owens et al., 2016; Collins et al., 2017). In addition, the selection of the ≤ 0.063 mm particle size for sources and mixtures was related to the predominant silt texture of soils in the catchment (Table 1) and also because the content of sand, silt and clay fractions were similar between source and mixture samples (Table 1 and Fig. 2). Furthermore, the relationships between tracers and the size fractions support that ≤ 0.063 mm fraction compiles the existing range of variation for most of the study tracers. Particle size, stable elements, magnetic susceptibility and radionuclides were analysed in the ≤ 0.063 mm fraction for all 161 sediment samples.

Grain size and magnetic susceptibility were analysed following the same methodology as in Lizaga et al. (2019). The analyses of the stable elements were performed at the Consolidated Radio-isotope Facility (CORIF, University of Plymouth) by X-Ray Fluorescence (XRF) using a Niton XL3T 950 He GOLDD+ XRF Analyser. Samples were analysed for major and minor elements (Ba, Nb, Zr, Sr, Rb, Pb, Zn, Fe, Mn, Cr, V, Ti, Ca, K, Al, Si, and Mg). Concentrations, obtained after three measurements per element, are expressed in mg/kg.

Gamma emissions of ^{137}Cs , ^{226}Ra , ^{238}U , ^{232}Th and ^{40}K were analysed at the gamma lab of the Experimental station of Aula-Dei (EEAD-CSIC) following the methodology used in Lizaga et al. (2017) and Navas et al. (2018). The radionuclide activities are expressed as massic activity in Bq kg^{-1} dry soil and counted for 43,200 s.

2.3. Statistical analysis and sources selection

The laboratory results were statistically analysed using R. A non-parametric Kruskal Wallis test was used to evaluate whether sediment mixture properties varied between the pre- and post-storm event (Fig. 2). Correlation plots (Fig. 3) were used to evaluate the relationships and the differences between pre- and post-event soil properties. Furthermore, to identify the relationships of the different sources in the selected sediment mixtures, a Euclidian distance matrix with the normalised values and a cluster analysis using the ward.D2 method was used with all the study properties (Fig. 4). As each mixture point has different source samples, the subsequent clusters may vary from one point to another and from headwater to lowlands.

2.4. FingerPro mixing model and tracer selection

The estimation of the relative contribution of each potential sediment source to the pre- and post-event sediment mixtures and the statistical tests were done with the FingerPro unmixing model and package.

Source apportionment solutions were defined by the mean and standard deviation (SD) calculated from the results selected by the model. The SD of the selected solutions and the density graph of the model helps to compare and evaluate the solution scattering as large values indicate poor source contribution ascription.

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; Collins et al., 1997; Palazón et al., 2015a; Collins et al., 2017). Several studies following the methodology implemented by Collins and Walling (2002) compare the range in the sources to the range in the sediment mixture or target for each fingerprint property (Smith and Blake, 2014; Koiter et al., 2018). The two-step statistical procedure proposed by Collins et al. (1997) and Walling (2005) is included as an optional step in the FingerPro R package and was used in this study. In addition, because of the type of sediment mixtures and its temporal storage in the channel bed, P, SOC and grain size properties were considered non-conservative, and they were excluded from the analysis following Koiter et al. (2013).

As the first step in tracer selection, the range test cannot definitively identify all tracers that are behaving non-conservatively but it removes the tracers with the largest differences with the mixture sample that could also reveal the existence of a non-sampled source. As an intermediate step we used biplot charts as proposed by Pulley et al. (2015) using the correlationPlot () function included in the FingerPro package to further check the conservative behaviour of each pair of tracers. The second step suggested using the

KW test to remove those tracers that do not show significant differences between the selected sources. The tracer selection should not be only based on statistical tests but also in expert knowledge of the hydrological and geomorphological processes in the study area. However, the use of many tests could remove a considerable number of tracers that might restrict the discrimination between sediment sources (Blake et al., 2018). For this reason, boxplot charts, LDA (Linear Discriminant Analysis) plots and correlation plots are included in the FingerPro package to help in the decision. Three-step tracer selection was implemented in this study: the range test and Kruskal-Wallis followed by the inclusion or exclusion of some tracers based on ‘expert judgement’ informed by visualising the tools included in the FingerPro package. None of the functions included in the package are mandatory, and the tracer exclusions can be based on the charts and results from the statistical tests.

To check the quality of FingerPro model, a set of virtual mixtures based on the unmixing results and using the selected tracers at each sediment mixture point were created. By unmixing the virtual mixtures versus the mean values of the sources for the selected tracers it is possible to obtain for each mixture the RMSE values of the model. Thus, by using virtual mixtures the results allow us to validate the model performance.

3. Results

3.1. Temporal variation of soil properties along the streams

The measured properties of the sediment mixtures collected in the pre- and post-event campaigns are shown in Fig. 2. Mean clay content decreased from 12.7% to 7.6% for pre- and post-event sediments, respectively. In pre-event sediment, SOC contents were significantly higher (range: 0.46–3.31%) than in post-event sediment (range: 0.24–1.8 %). Mean radionuclide activities decreased from pre- to post-event sediments for

^{137}Cs ($1.1\text{--}0.9\text{ Bq kg}^{-1}$), ^{40}K ($467.3\text{--}367.6\text{ Bq kg}^{-1}$) and ^{232}Th ($31.5\text{--}29.9\text{ Bq kg}^{-1}$) but increased for ^{226}Ra ($26.0\text{--}30.3\text{ Bq kg}^{-1}$), and ^{238}U ($43.5\text{--}46.8\text{ Bq kg}^{-1}$). Major element contents varied in pre- and post-event sediment. Mean values were: Si ($165,996\text{--}182,772\text{ mg/kg}$), Al ($35,231\text{--}32,370\text{ mg/kg}$), Ca ($174,207\text{--}171,118\text{ mg/kg}$), Mg ($3320\text{--}3185\text{ mg/kg}$), K ($13,208\text{--}10,862\text{ mg/kg}$), Ti ($3036\text{--}3226\text{ mg/kg}$), Fe ($19,805\text{--}17,214\text{ mg/kg}$), Mn ($286\text{--}311\text{ mg/kg}$) and P ($987\text{--}1120\text{ mg/kg}$).

A decrease of about 38% in fine fraction content in the post-event sediment was coincidental with a decrease of stable elements and properties that were positively correlated with clay fraction such as SOC, ^{137}Cs , ^{40}K , ^{232}Th , Ba, Sr, Rb, Pb, Zn, Fe, K, Al and V (Figs. 2 and 3). On the contrary, the study properties with negative correlation with clay but positively correlated with the coarse fraction, such as the magnetic properties ^{226}Ra , Nb, Zr, Ti, P and Si, were enriched in the sediment after the storm event. ^{238}U , Mn, Ca and carbonates were not correlated with any grain size fraction and did not show any clear trend between pre- and post-event sediment. In general, there was an increase in the intercorrelation between the study elements and properties that were correlated with grain size fractions in post-event sediment (Fig. 3).

There were important variations when comparing the pre- and post-event study properties between at the headwaters, the middle and lower part of the catchment. A higher decrease in clay content (70%) was recorded in the middle part than in the headwaters and lower part of the catchment, but the opposite was observed for sand, which reached higher contents (59%) in the middle part of the catchment. Thus, most properties positively correlated with clay showed similar decreasing trends in the headwaters, middle and lower parts of the catchment.

The floodplain sediment as an intermediate stage between pre- and post- event sediments showed a transitional variation in elements and properties. Thus, the clay

fraction in pre-event sediment decreased significantly ($p < 0.05$) in floodplains (17%), but the decrease reached as much as 42% in post-event sediment accompanied by a subsequent increase in sand fraction of 10% and 100% in floodplain and post-event sediment, respectively. Most of the properties such as ^{137}Cs , ^{40}K , ^{226}Ra , ^{232}Th , Nb, Sr, Zr, Rb, Zn, Fe, K, Al, Ti, P, Si and V differed significantly between these stages and showed similar increasing or decreasing trends (Fig. 5). Furthermore, Ba, Cr, Ca, SOC and SOC fractions had similar values in pre-event and floodplain sediment with a sharp decrease in post-event sediment. However, ^{238}U , χ_{LF} , Pb, Mn and Ca did not show a clear trend between stages (Table 3).

3.2. Sources and tracers selection

The statistics of grain size, SOC and trace element properties for the potential sediment sources are presented in Table 1. The SOC contents were low, with a mean value of 2% and the SOC fractions ACF and SCF ranged from 0.3% to 5.9% and from 0.036% to 1.38%, respectively. The low frequency (χ_{LF}) and frequency dependent (χ_{FD}) mass magnetic susceptibility had a mean value of $46.64 \times 10^8 \text{ m}^3 \text{ kg}^{-1}$ and 7.31%, respectively. In AG, CB and SS sources, SOC contents were lower and significantly different from the other sources, with the highest values found in OF and PI. Furthermore, the means of ^{137}Cs , Ba, Sr and P in AG were significantly lower than those in the other land uses (OF, PI) ($p \leq 0.05$). Most properties in CB and SS significantly differed from the other sources except for radionuclides. Major elements such as Si, Al, Ca, Mg, K, Ti, Fe, Mn and P only had significant differences in SS compared to the other sources except for Fe and K, which had the lowest mean values in CB.

The LDA plot created with all the source samples showed overlapping between land use sources and illustrated low discrimination capacity for AG, OF and PI (Fig. 4).

The discrimination of sources that are not well characterised might reduce discrimination or lead to erroneous model results. Thus, land uses were grouped in two different combinations based on their spatial distribution in the catchment along with results from a cluster analysis pursued with tracer data. In the lower part of the catchment, cluster analysis showed the highest similarities between land uses with arboreal vegetation (OF and PI) (Fig. 4). Furthermore, AG predominated in the lower part of the catchment and had different mean values of ^{137}Cs , χLF , Ba, Zr, Fe, Mn, Ca, P and Sr than in OF and PI. Thus, it was decided to merge both arboreal land uses in one source (OF+PI). On the other hand, at the headwaters where PI dominates, AG and OF showed the highest similarities in the analysed tracers (Fig. 4). In addition, the tracers selected by the statistical test in each mixture point before and after grouping sources mostly coincide, supporting the adopted merging. This methodology was implemented to homogenise the results and to avoid including non-contributing or very low-contributing sources into our unmixing model.

Following this approach and the different source points selected for each sediment mixture, it was decided to create a set of optimum tracers for each mixture point. Table 2 shows the optimum set of tracers selected for unmixing sediment mixtures along the stream for the pre- and post- event sediment mixtures and floodplain sediment. In addition, the low RMSE values calculated when comparing the unmixing results for the virtual mixtures with that of the channel bed and floodplain sediment mixtures validate the results and the performance of the FingerPro model (Table 3).

3.3. Sediment source contributions pre- and post- 2012 rainstorm event

The average mean relative contributions of each potential source to the sediment mixtures indicates that overall, CB was the predominant source both before and after the

event ranging between 35 ± 7 to $87\pm13\%$, followed by SS with a mean contribution of $24\pm9\%$. On the other hand, AG contributed around $21\pm9\%$ at the lower part of the catchment but much less in the headwaters. In contrast, PI contributed around $10\pm9\%$ at the headwaters, but it was almost insignificant at the lower part of the catchment. The sediment contribution supplied by OF+PI was only noticeable in the middle part of the catchment at point 17 with a mean apportionment of $16\pm6\%$ in the pre-event sediment.

Large variations in source contributions were recorded for each sediment mixture, especially between sediment mixtures located at the headwaters and in the middle and lower parts of the catchment (Fig. 1). Furthermore, sediment mixtures varied greatly between the pre- and post- exceptional event.

In the headwaters, SS and CB were the main contributing sources. However, following the cluster group and the significant apportionment (16% and 17%) of the forests (OF+PI), it was decided to merge AG and OF (AG+OF) and separate the PI source. The results for sediment mixture points (SMP) 13 and 15 showed a mean sediment supply of 16% and 10% from the pine afforestation. The contribution from forests (OF+PI) was not observed downstream from SMP 17. For the downstream sediment mixture points, there were also significant differences between SMP 17 located in the central part of the catchment and both SMP 18 and SMP 20 located downstream from the La Reina tributary stream. The agricultural source contribution reached a maximum close to the outlet of the catchment (SMP 18 and SMP 20) and decreased marginally in upstream sediment. On the contrary, at SMP 17 the contribution of AG was negligible. However, the presence of sediment from forests was detected with a mean contribution of up to 14%, being less than 2% in SMP located downstream of SMP 17.

In the headwaters (SMP 13 and SMP 15) PI sediment was mostly washed out from the streams in post-event sediment mixtures. SMP 13 showed a similar decrease in SS, thus

increasing CB contribution up to 80%. However, SS in SMP15 increased slightly with the subsequent decrease in CB proportion. The middle part of the catchment also experienced a sharp decrease in contributions from the different land uses. Moreover, the SS apportionment in the middle part increased from 18% in the pre-event sediment to up to 27% in the post-event sediment. A different history occurs downstream the La Reina tributary stream at SMP 18 where agricultural apportionments increased largely while SS and CB decreased. At the catchment outlet, a large increment in CB apportionment was recorded along with a sharp decrease in SS and a small decrease of AG in the post-event sediment. Furthermore, a slight increase from the forest source (OF+PI) was recorded. The SS decrease recorded at the outlet of the catchment was supported by the results extracted from the SFMP where 90% of the sediment contribution was supplied by CB and AG. In addition, the unmixing results of the SFMP indicated an increase of PI and SS sediment in regular high discharge events but the disappearance of PI sediment during exceptional events. SFMP 17 revealed an increase in AG and a slight decrease in SS sediment in the floodplain while it showed a sharp increase in SS with a total wash out of AG sediment during the exceptional event. Besides that, at the catchment outlet SFMP 20 showed a decrease in AG and SS sediment but a progressive CB increase as seen in Table 3.

4. Discussion

4.1. Variation in soil properties due to the exceptional event

Compared with the other sources, the significant differences in most properties found in SS (except for the radionuclides) are because SS is composed of very degraded soils that expose the substrate. In addition, SS is mostly located in areas with high hydrological connectivity, likely increasing its delivery to streams during storm events.

In the talus of the streams, CB sediment consisting of loess type materials infilling the valley floor is the nearest available source to be deposited in the channel. As such, SS and CB are the most distinctive sources from the others. However, Fig. 4 shows some similarities between CB and AG sources likely because the agricultural land is mostly located on the valley floor on alluvial materials infilling the valleys that comprise the CB source.

The significant differences in mean contents of SOC, ^{137}Cs , Ba, Sr and P in agricultural land compared with PI and OF suggest that land use is one of the principal factors affecting the variation in soil properties after five decades of land abandonment as found by [Lizaga et al. \(2019\)](#). In addition, the scarce vegetation cover and the presence of more degraded soils with specific locations in the catchment point to AG, CB and SS sources as the most erodible areas. Thus, due to soil redistribution processes, these sources show significant differences in the study properties. However, in the headwaters the croplands recently abandoned due to more difficult access, which support less intensive farming, show more similarities with OF. Furthermore, the higher connectivity between OF that surrounds the AG areas in the headwaters further contributes to similarities found in their soil properties. All these factors operating together in the headwaters likely increase similarities between AG and OF as seen in the results of the cluster analysis.

Exceptional rainfall events produce increases in connectivity and suspended sediment loads and modify the channel bed sediments by decreasing or increasing the concentration of different size particles during floods. The significant differences for most study properties between pre- and post-event sediment point to exceptional storm events as the main factors in causing sediment mobilisation from different sources, resulting in subsequent variation of geochemistry and sediment properties as was also reported by

[Martins et al. \(1995\)](#). The sharp decrease experienced by the fine fraction and the increase in the coarse fraction suggests that exceptional storm events export high quantities of sediment composed mostly of fine sediment as was also found by [Bortoluzzi et al. \(2013\)](#) in a Brazilian catchment. This hypothesis is supported by the decrease in most sediment properties positively correlated with the clay fraction. However, the non-significant differences in ^{137}Cs and magnetic properties could be explained by the large variability of these properties across the catchment.

During heavy storm events, the sediment begins to be exported and reach a maximum, beyond which the sediment exported begins to decline leading to an ordered sedimentation and the increase of the mobilised element correlation ([Quesada et al., 2014](#); [Gaspar et al., 2019b](#)) (Fig. 3). In our catchment, high sediment mobilisation is supported by the increase in overall intercorrelation of the study elements that are correlated with the grain size.

4.2. Temporal and spatial variation of sediment mixture properties

The variation of sediment properties in the stream channel before and after the exceptional event as well as in the floodplains at an intermediate stage of sediment deposited by regular high floods is related to the export of the fine grain size fractions. Thus, the loss of fine material produces the subsequent enrichment in the content of coarse fractions after rainfall events as was also found by [Smith and Olyphant \(1994\)](#) resulting in the highest sand content in channel bed sediment after the exceptional rainfall event.

The elements positively correlated with argillaceous materials (i.e., aluminosilicates contained in the fine fraction such as ^{137}Cs , Rb, Sr, Fe, Zn, Al, Cr, Pb) show a clear decreasing trend from pre-event, floodplain and post-event sediment due to the reduction of fine materials that are exported during high floods. [Mitchell et al. \(1997\)](#) and [Quiquerez et al. \(2008\)](#) also reported high export rates of fine sediment material and

associated nutrients. Thus, vanadium, which is finely incorporated into clay minerals during weathering, is also exported. There are some elements such as Ba and Mn that have limited mobility because they are easily precipitated as sulphates and carbonates. Furthermore, Ba and Mn can also be strongly absorbed by clay minerals, which also explains the slight decrease of Ba and Mn in floodplain and post-event sediment and supports the hypothesis of high fine sediment export during storm events. On the other hand, Si is directly correlated with the coarse fraction due to the high content of silicon grains in the sandstone strata. Many Ti-containing minerals are resistant to weathering (also Zr) and increase with the coarse fraction. Additionally, Nb exhibits a strong affinity with Ti and Zr. All these mineral-element associations lead to increases of Ti, Zr, Nb and Si after the storm event in parallel with the increase in the coarse fraction. Therefore, the chemical changes observed are due to the mixing of soil sediment mobilised during the exceptional event with pre-existing soil sediments mobilised during regular rainfalls.

4.3. Sediment source contributions variation

The contribution of channel bed changes before and after the event (but also from headwaters to the lower part of the catchment) is due to the great modification power of these exceptional storm events. In SMP 13 located in the headwaters, 30% of apportions come from PI and SS sources, but during floods most of these sediments are exported, and thus CB becomes the predominant source. Our results suggest that during the exceptional event, most of the channel bed sediment is efficiently exported. PI sediment was also exported in SMP 15 during the storm event; however, due to the proximity of steep slopes (19 to 25°) with highly disturbed areas and the predominance of bare soils in the contributing area, SS appears as the dominant source after the storm event.

Results obtained from both the floodplain sediment and the channel bed sediment mixtures at SMP 15 where subsoil apportions are predominant suggest that during storm events, sediment from surrounding slopes with highly degraded soils directly reaches the stream. This interpretation is also supported by results at SMP 17 located in the middle part of the catchment downstream from SMP 15 with a similarly high subsoil contribution. The subsoil contribution then gradually decreases in the lower part of the catchment (SMP 18 and 20) after the storm event. Such exceptional rainfalls produce large variations on the sediment mobilised from different sources thus changing sediment source contributions to the streams as can be seen in [Fig. 6](#).

A different behaviour is observed in sediment mixtures located upstream from the La Reina ephemeral stream and those located in the lower part of the catchment at SMP 18 and 20. At these points, the fingerprinting analysis shows a high increase of AG provenance that is likely related to the incision of the main stream over the agricultural land located on the glacia and the sediment apportion from the La Reina ephemeral stream.

The deep incision of the streams and the almost vertical slopes of the channel banks along with the nature of non-cohesive infilling material are the reason that CB is the source that produces the highest sediment supply. The incision of the streams is highly variable across the catchment, but overall, it increases downstream from the La Reina ephemeral stream where the glacia starts. In addition, during heavy storms, geomorphological processes such as piping, topples and landslides are likely to increase apportionment from CB sources ([Gaspar et al., 2019](#)).

During heavy rainfalls, sediment resuspension due to energy expenditure in the channel is higher in the headwaters and the middle part of the catchment (i.e., SMP 13, SMP 15 and SMP 17) than in the lower part of the catchment. Sediment resuspension

could produce deposition downstream due to the loss of energy thus increasing the sediment storage in the lower part of the catchment. This is similar, though on a different scale, to what has been observed in the lower part of the Ebro River by [Quesada et al. \(2014\)](#). The cluster analysis results also support the different functioning of the headwaters and the lower part of the catchment. Furthermore, the results of the relative source contribution (RSC) (Table 3) highlight the high sediment export from subsoil and emphasise the low apportionments from natural covers such as OF. These results are in good agreement with studies by [López-Tarazón et al. \(2009\)](#) and [Palazón et al. \(2016\)](#) and further support the idea of bare soil as one of the main environmental problems for river ecosystems.

5. Conclusions

Large changes in the characteristics of sediment were produced by an exceptional storm event, modifying element concentrations and sediment provenance. The significant differences between pre- and post-storm sediment mixtures highlight the great impact of such storm events on channel bed sediment. Bearing in mind the observed spatial variations in sediment properties and grain-size distributions, one may conclude that the sediment mobilisation and transfer produced in the catchment was highly dynamic.

Placing the channel bed sediment apportionments in a geomorphological context, our model results indicate an important input from SS despite its spatial coverage in the catchment in amounts less than 2%. Therefore, the subsoil is suggested to be an important environmental problem with hot spots that are worth controlling. In contrast, the insignificant sediment apportionment from forests underlines the benefits of natural covers to prevent soil loss.

Composite fingerprints provide the opportunity to efficiently trace sediment sources before and after exceptional rainstorm events. Overall, our results provide evidence of the severe erosion produced by this exceptional rainstorm event and reveal important variations in sediment source patterns. Stream bank failure induced by natural tunnelling or piping and landslides significantly contributed to sediment delivery. The magnitude of agricultural and bare soil mobilisation during the course of this exceptional rainstorm was much greater than under normal discharge regimes. Similar conclusions are derived from the analysis of variations in sediment properties between pre-event SMP, SMFP and post-event SMP. The geomorphological analysis, the fingerprinting procedure, and the low RMSE obtained with virtual mixtures support the good performance of the new FingerPro unmixing model to quantify the different sediment source apportionments.

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FIGURE CAPTIONS

Fig. 1. Location of the study catchment in the central part of the Ebro Basin (NE Spain). 3D map of the different land uses in the catchment with the sources and mixture sampling point distribution through the catchment. (a) Pine afforestation, (b) subsoil, (c) open forest and (d) agricultural.

Fig. 2. Boxplots of pre- and post-storm sediment properties. Asterisks represent the elements that are significantly different between stages.

Fig. 3. Correlation coefficients of the different sediment properties before and after the exceptional storm event.

Fig. 4. Linear discrimination analysis (LDA) plot of the different sources in the Barué catchment. (13–20) Cluster analysis of the different sources presented in the mixture points. The darker colours show a stronger correlation while the brighter colours show a lower correlation.

Fig. 5. Bar plot of sediment properties for the three different flood stages: pre-event, regular flood and post-event.

Fig. 6. Results of the unmixing procedure before and after the exceptional storm event in each mixture point. An ANOVA test was performed to assess whether source contribution differed between pre- and post-event mixtures. Different letters indicate significant differences at the 95% level.