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# In-channel alterations of soil properties used as tracers in sediment fingerprinting studies

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ABSTRACT

Soil properties used as tracers in sediment fingerprinting studies are assumed to remain stable or vary in a predictable way in their transfer from sources to sinks, allowing a comparison with suspended sediment properties. Attention to the conservative behaviour of soil properties has largely focused on the differences in the particle size and organic matter content between sources and target sediments. However, in-channel biochemical alterations are also known to occur, and their magnitude is still poorly understood. An experiment to investigate the in-channel variations of soil properties during transport and storage was carried out with the most common soil properties used as tracers in sediment fingerprinting studies (i.e. colour, fallout radionuclides and geochemical elements). Twenty-eight soil samples collected from different land uses were introduced into an intermittent stream channel of a small Mediterranean catchment. Samples were recovered at different time intervals over one year. The changes in soil properties (average coefficient of variation 8.1 ± 8.8 %) were generally lower than the spatial variability of each source within the catchment (average coefficient of variation 16.3 ± 18.5 %). No significant differences were observed between samples from different land use types or when recovered at different time intervals. Soil properties that showed higher in-channel coefficients of variation were S, $^{137}$Cs, $^{210}Pb_{ex}$, As, Mo and Na, with annual coefficients of variation > 19 %. Conversely, carbon (C) and colour properties were the most stable in time (average coefficient of variation 2.1 ± 0.4 % and 2.6 ± 2.2 %, respectively). The results presented will be informative with regard to performing future suspended sediment fingerprinting studies in Mediterranean catchments, providing a better understanding of which soil properties are more sensitive to in-channel biochemical alterations.

## 1. Introduction

Sediment fingerprinting is a standard methodology for tracing the origin of suspended sediment (cf. Collins et al., 2020). The basis of its application is the comparison of different physical, geochemical and/or biochemical properties between soil samples collected in potential sediment source areas and sediment samples collected within the fluvial network (Collins et al., 1997; Klages and Hsieh, 1975; Wall and Wilding, 1976; Walling et al., 1979). However, the fingerprinting technique does not provide unequivocal source discrimination and the results exhibit uncertainties. These uncertainties can be associated with source and sediment sampling methods (e.g. Manjoro et al., 2017), the spatial

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variability of source soil properties (e.g. Du and Walling, 2016), statistical tests and models (e.g. Haddadchi et al., 2014; Nosrati et al., 2014; Palazón and Navas, 2017) or with the particle selectivity of soil erosion processes and the possible alteration of sediment properties during conveyance or deposition within the river network (e.g. Koiter et al., 2013).

To compare soil properties measured on potential sediment sources and suspended sediment collected within the fluvial network, it is necessary that the soil properties exhibit a conservative behaviour. However, some alteration processes are known to occur during mobilization and mixing along hydrologic pathways (Koiter et al., 2013), producing largely unknown effects on sediment tracing studies and possibly leading to inaccurate results. Therefore, the optimal tracers will always be those that remain stable or vary to a lesser extent regardless of the environment and the time elapsed.

Particle size and organic matter are known to influence the concentrations of certain soil properties. Many studies investigating the conservative behaviour of soil properties have thus focused on evaluating the impact of particle size distribution and organic matter content differences between sources and sediment collected downstream (Crockford and Olley, 1998; Hill et al., 1998; Horowitz and Elrick, 1987; Koiter et al., 2018; Laceby et al., 2017). The specific surface area of sediment (SSA) increases as the particle size decreases and affects the concentrations of some tracers (Horowitz, 1991). This is because many of the reactions that regulate these concentrations are related to surface chemistry or surface area reactions (Horowitz and Elrick, 1987; Laceby et al., 2017). A clear example of this is fallout radionuclide activity (e.g. $^{210}Pb_{ex}$, $^{137}Cs$). Values are normally higher in samples with a larger fraction of fine particles, and they usually show a non-linear relationship with SSA in samples presenting an SSA $> 1$ $m^2$ $g^{-1}$ (Fan et al., 2014; He and Walling, 1996). Organic matter is also absorbed more readily on clay-sized particles (Horowitz, 1991), and concentrations are susceptible to variations and transformations as a result of biological activity if sediment is stored within the channel, such as microbial decomposition or the transformation of inorganic forms into organic forms (e.g. mercury biomethylation) (Koiter et al., 2013; Thayer, 2002). The intensity of these processes will depend on the environmental conditions and storage time of the sediment. This could result in altered organic properties and, consequently, tracer properties, compared to the source material (e.g. colour properties; Ben-Dor and Banin, 1995; Pulley and Rowntree, 2016).

In addition, other sediment properties might change due to chemical precipitation, diagenesis, or the addition of new atmospheric elements such as N, S and $^{210}Pb$ (Koiter et al., 2013; Owens et al., 2012; Wilkinson et al., 2009). Remarkable transformations can take place during transport and in temporary sediment accumulation deposits (Koiter et al., 2013), influencing mineral magnetic properties (Crockford and Olley, 1998), Fe and Mn oxyhydroxides (Dabrin et al., 2021) and geochemical elements like K (Withers and Jarvie, 2008), among others.

Limitations associated with tracer conservatism are normally addressed by sieving samples to a specific particle size (e.g. He and Walling, 1996), removing the organic matter (e.g. Pulley and Rowntree, 2016) using correction factors (Collins et al., 1997; Russell et al., 2001) and trying to statistically define the optimal set of tracers with conservative behaviour (Collins and Walling, 2002; Collins et al., 1997; Lizaga et al., 2020; Smith et al., 2018; Walden et al., 1997; Wilkinson et al., 2013). However, some recent works have argued that most of these procedures might still result in the inclusion of non-conservative tracers in the unmixing models commonly used in sediment fingerprinting (Latorre et al., 2021).

Despite the recent developments in statistical tests and models, it is therefore necessary to continue investigating the spatiotemporal conservativism of sediment properties in order to determine the most stable tracers. Regarding this, few studies have been specifically designed to investigate the conservative behaviour of sediment tracers. These studies can be classified in two categories: (i) hillslope processes studies, focused on the enrichment or depletion of some properties linked to differential mobilization of particles with diverse sizes or different physical properties; and (ii) submersion experiments, which analyse the possible biochemical changes occurring within channels during sediment transport and storage. The hillslope process studies include the work of Motha et al. (2002) and Koiter et al. (2018). Those authors simulated different rainfall conditions at the plot scale to compare source soil and mobilized sediment properties (i.e. fallout radionuclides, major elemental geochemistry and mineral magnetism). Despite them finding a fine-grain and organic material enrichment in the eroded samples, only a small number of properties showed non-conservative behaviour (e.g. $Fe_2O_3$, $Al_2O_3$). On the other hand, the submersion experiments include work by Poulenard et al. (2012), Legout et al. (2013) and Uber et al. (2019). Those authors introduced the $< 63$ μm fraction of sieved source samples within a stream for 1 to 63 days to assess the potential effect of biogeochemical alterations on soil spectrometric signatures. Results showed low tracer variations (differences regarding the original data lower than 15 %) and indicated that spectral signatures were sufficiently conservative to be used as tracers.

Ascertaining the most conservative soil properties continues to be a key challenge in the optimization of sediment tracing techniques. This is especially true for understudied environments, such as catchments with intermittent hydrological regimes. Here, we present a 1-year submersion experiment performed in a Mediterranean catchment under an intermittent hydrological regime with large inter- and intra-annual contrasts. The objective was to discern which soil properties are more prone to biochemical in-channel alteration. The temporal variability of the tracers during in-channel storage was compared with the sources' spatial variability within the catchment, and variations were correlated with SSA and carbon (C) content to evaluate the influence of particle size and organic matter.

## 2. Study area

The Es Fangar Creek catchment (3.4 $km^2$; Fig. 1A and B) is located in the northern part of the island of Mallorca (Western Mediterranean Sea, Spain), in the mountainous area of the Serra de Tramuntana. The lithology is mainly composed of lower Jurassic calcareous and dolomite materials. Altitudes range between 72 and 404 m.a.s.l., with an average slope of 26 %. The climate regime is classified as Mediterranean temperate sub-humid (Guijarro, 1986) with an average annual temperature of 15.7 °C and mean annual rainfall of 926 mm $yr^{-1}$ (1964–2017; Biniatró AEMET station, located 1.1 km west from the study area) with a coefficient of variation of ca. 23 %. The hydrological regime, based on a 5 year length record (2012–2017), is intermittent flashy (49 % of zero-flow days; Fortesa et al., 2020b). Annual runoff coefficients ranged from 2.9 % to 14.2 % (average of 10.4 %) and quickflow from 9.9 % to 45 % (average of 33 %). 80 % of the suspended sediment load is exported during autumn and winter, with an annual average sediment yield of 5.38 t $km^2$ $y^{-1}$ (Fortesa et al., 2020a). Land use is forestland (47 %), rainfed herbaceous crops (36 %) and scrubland (17 %). In addition, 16 % of the catchment is covered by dry-stone agricultural terraces (Fig. 1C).

## 3. Material and methods

### 3.1. Hydrological monitoring

A gauging station was installed in the Es Fangar Creek (i.e. Fig. 1C) in 2012 to continuously monitor water and suspended sediment fluxes. The station was equipped with a Campbell CS451 pressure probe and an OBS-3 + turbidimeter with a double measurement range (0–1,000 / 1,000–4,000 NTU) and a wiper cleaning system. A Campbell CR200X logger recorded water stage and turbidity average values every 15 min based on 1-minute readings. Finally, a tipping bucket pluviometer was installed in 2014, located at 500 m.a.s.l. and ca. 2.5 km away from the Es

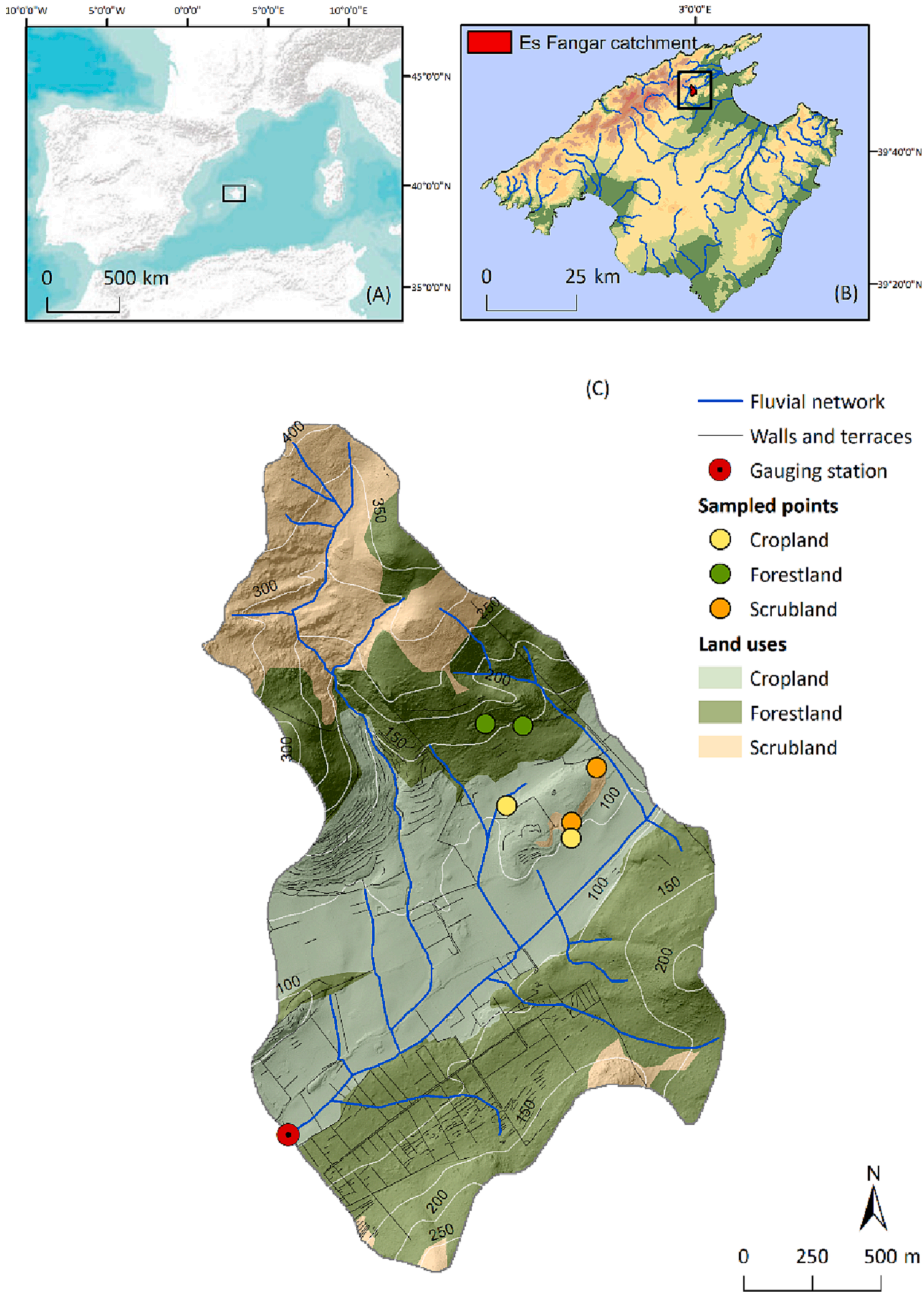


**Fig. 1.** (A) Location of Mallorca in the Western Mediterranean. (B) Location of the Es Fangar Creek catchment on the island of Mallorca. (C) Sampled points, gauging station, drainage network and terraced areas superimposed on the land use map.

Fangar gauging station (Fig. 1B). It was positioned 1 m above the ground to record rainfall data at 0.4 mm resolution.

### 3.2. Soil sampling, pre-treatment, and field experiment

The sampling strategy was designed in order to consider the three main catchment land use types (i.e. forest, crop and scrubland; Fig. 1C) as potential surface sediment sources. Vegetation cover and land use are the most important drivers of hillslope erosion processes (García-Ruiz, 2010; Kosmas et al., 1997; Thornes, 1990), and they are an optimal grouping for catchment management. Soil bulk samples were collected using a steel hand trowel in March 2018 from the upper 2 cm in six different plots (3 $m^2$ each) encompassing every land use category (2 plots per land use). Sampled plots (Fig. 1C) were selected according to accessibility and soil availability on hillslopes with high slope-to-channel connectivity. The catchment connectivity index was estimated from a high resolution (1 m $px^{-1}$) DEM (supplementary Fig. 1). The upper parts of the catchment, covered by scrubland, were not sampled because soil availability is low due to lithology, topography and climate, which favour karstic features instead of soil formation and hillslope-channel connectivity. In addition, previous studies (García-Comendador et al., 2021) indicated that most of the sediment was generated in the lower parts close to the main channel because of the combination of high connectivity between hillslopes and stream channels developed over soft lithologies and mainly occupied by rainfed herbaceous crops.

An initial attempt was made to collect overland flow by performing rainfall simulation experiments in each plot (García-Comendador et al., 2018). However, despite simulating > 50 mm $h^{-1}$ rainfall intensities, the amount of mobilised soil provided insufficient material to meet analytical requirements. Therefore, surface soil samples were collected manually from each plot.

Bulk samples were oven dried at < 40 °C and disaggregated using a pestle and a mortar. Samples were then mixed well and homogenised according to land use type and sieved to recover the < 63 µm fraction (ca. 1 kg for every type of land use). This particle size fraction was selected because i) it is the most commonly traced particle size fraction in sediment fingerprinting studies (Laceby et al., 2017) and ii) it allows relating the results to those obtained by García-Comendador et al. (2021) in the same catchment (used in the present study to define the spatial variability of soil properties; see sub-Section 3.4). Thirty-one samples, hereafter referred to as 'in-channel samples', were generated in total: nine for each land use (60 g each), which were placed in the stream channel, and four extra samples (referred to as 'TIS samples' and listed in Table 1) from the cropland plots, which were inserted inside a time-integrated sediment sampler (Phillips et al., 2000). Time-integrated sediment samplers were made using a PVC pipe with the cylinder ends sealed. An inlet tube and an outlet tube made from semi-rigid nylon pneumatic tubing (4 mm) were inserted into two holes drilled in the centre of each end cap to allow the water to flow. The tubes were fixed to the channel bed using steel pegs and cable ties.

With the exception of those samples used to establish the initial measurements, the rest were in direct contact with water inside a resistant material. To place the samples within the channel, including the TIS samples, they were split into three 20 g subsamples. Subsamples were then placed inside 5x7 cm polyamide bags with a25 µm Ø mesh. Sub-samples were sealed using cable ties (Fig. 2A). The arrangement of the samples was designed to minimise sediment losses Finally, the three subsamples were introduced inside another sealed larger bag (Fig. 2B) made of the same material and with the same mesh size.

Samples were then placed into the stream channel ca. 2 m downstream from the Es Fangar gauging station (Fig. 1D), where a cross-section with a rectangular broad-crested concrete weir was built for measuring low water stages (see dimensions in Fig. 2E, F). Samples were located 70 cm downstream from the weir. Eight 70 cm steel corrugated bars were inserted into the channel bed and sample bags were fixed to the metal bars using cable ties. The water had to reach a height of 17 cm

**Table 1**
List of samples used in the experiment. The samples extracted during the wet period are highlighted in green, and those extracted during the dry period are highlighted in yellow. TIS refers to samples introduced inside a time-integrated sediment sampler. 'Days submersed' and 'Days dry' refer to the total number of days that the samples were submersed and out of the water, respectively.

| Sample type | ID | Days in channel | Days submersed | Days dry | Baseflow index (%) | Initial mass (g) | Mass at collection (g) |
|---|---|---|---|---|---|---|---|
| Forestland | Forestland 0 | 0 | 0 | 0 | 0 | 60.00 | – |
| | Forestland 1 | 7 | 7 | 0 | 89 | 60.00 | 58.14 |
| | Forestland 2 | 30 | 22 | 8 | 24 | 60.00 | 57.75 |
| | Forestland 3 | 60 | 29 | 31 | 12 | 60.00 | 57.54 |
| | Forestland 4 | 90 | 35 | 55 | 9 | 60.00 | 57.93 |
| | Forestland 5 | 150 | 35 | 115 | 8 | 60.00 | 58.30 |
| | Forestland 6 | 210 | 35 | 175 | 8 | 60.00 | 58.22 |
| | Forestland 7 | 270 | 35 | 235 | 8 | 60.00 | 59.01 |
| | Forestland 8 | 365 | 37 | 328 | 8 | 60.00 | 57.05 |
| Cropland | Cropland 0 | 0 | 0 | 0 | 0 | 60.00 | – |
| | Cropland 1 | 7 | 7 | 0 | 89 | 60.00 | 57.18 |
| | Cropland 2 | 30 | 22 | 8 | 24 | 60.00 | 57.79 |
| | Cropland 3 | 60 | 29 | 31 | 12 | 60.00 | 57.17 |
| | Cropland 4 | 90 | 35 | 55 | 9 | 60.00 | 58.00 |
| | Cropland 5 | 150 | 35 | 115 | 8 | 60.00 | 57.55 |
| | Cropland 6 | 210 | 35 | 175 | 8 | 60.00 | 58.10 |
| | Cropland 7 | 270 | 35 | 235 | 8 | 60.00 | 57.23 |
| | Cropland 8 | 365 | 37 | 328 | 8 | 60.00 | 57.69 |
| Scrubland | Scrubland 0 | 0 | 0 | 0 | 0 | 60.00 | – |
| | Scrubland 1 | 7 | 7 | 0 | 89 | 60.00 | 58.17 |
| | Scrubland 2 | 30 | 22 | 8 | 24 | 60.00 | 58.24 |
| | Scrubland 3 | 60 | 29 | 31 | 12 | 60.00 | 57.76 |
| | Scrubland 4 | 90 | 35 | 55 | 9 | 60.00 | 57.85 |
| | Scrubland 5 | 150 | 35 | 115 | 8 | 60.00 | 58.14 |
| | Scrubland 6 | 210 | 35 | 175 | 8 | 60.00 | 57.05 |
| | Scrubland 7 | 270 | 35 | 235 | 8 | 60.00 | 57.87 |
| | Scrubland 8 | 365 | 37 | 328 | 8 | 60.00 | 57.22 |
| TIS samples | TIS 1 | 60 | 60 | 0 | 58 | 18.86 | 16.76 |
| | TIS 2 | 210 | 108 | 102 | 60 | 31.73 | 29.83 |
| | TIS 3 | 270 | 108 | 162 | 60 | 47.49 | 45.29 |
| | TIS 4 | 365 | 111 | 254 | 58 | 59.48 | 57.48 |

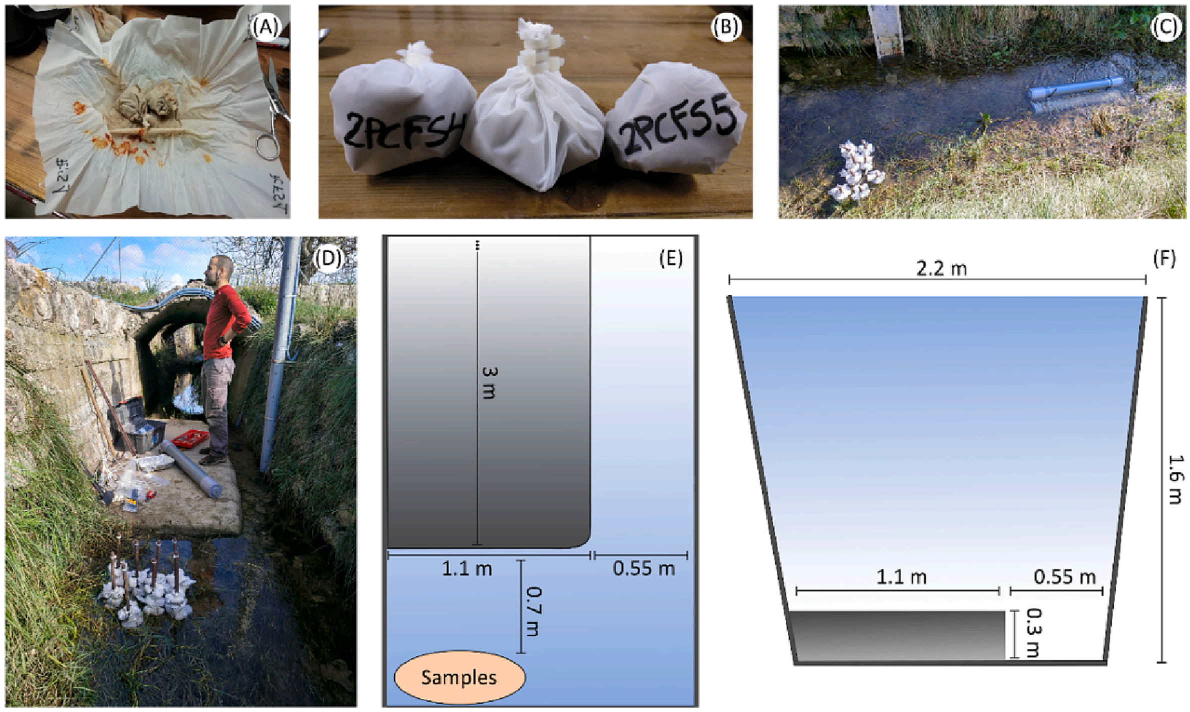


**Fig. 2.** Pictures showing (A) 20 g subsample bags on the larger piece of mesh, (B) sealed samples with the three subsample bags inside, (C) the location inside the channel and distance between samples and time-integrated sediment samplers, (D) upstream view of the Es Fangar stream with the samples fixed to the bed channel. Diagram of the plan (E) and transverse (F) proportions of the cross-section of the Es Fangar station.

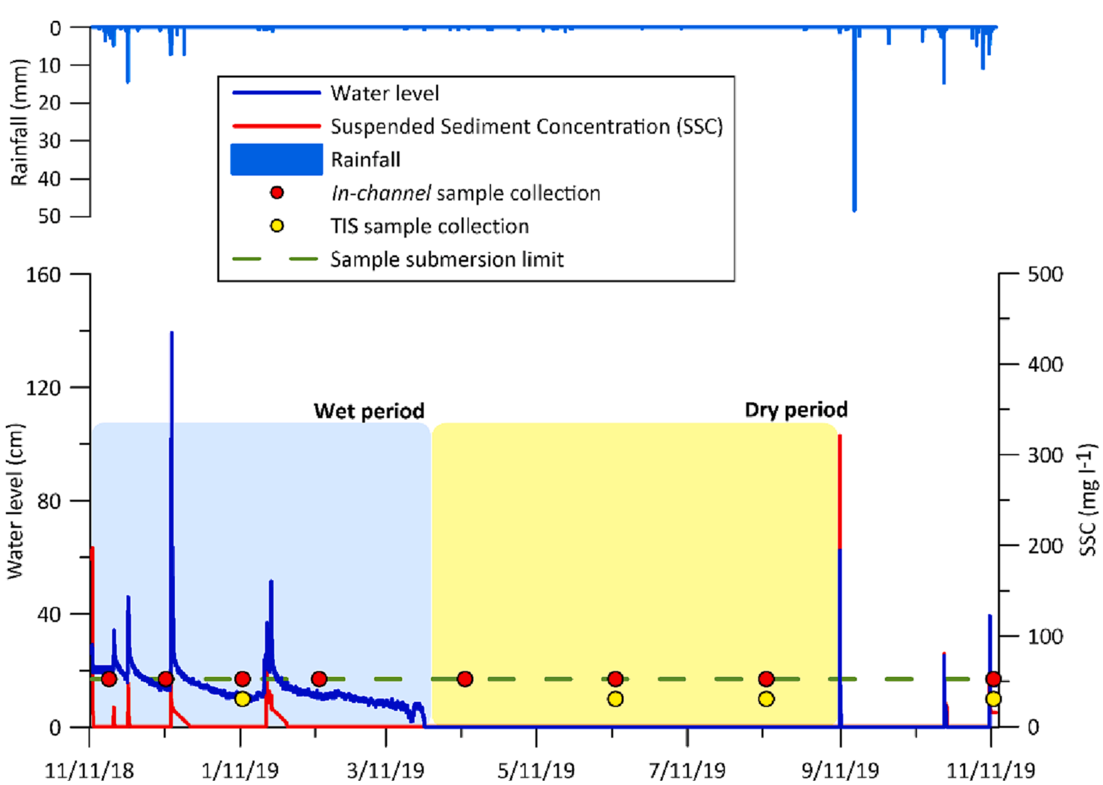


**Fig. 3.** Water level, hyetograph and sedigraph at the Es Fangar station during the study period, November 2018-November 2019. Points indicate sample collection dates (in-channel samples in red, TIS samples in yellow [samples introduced inside a Time Integrated Sediment sampler]) and the green dashed line indicates the submersion limit of the in-channel samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

at the pressure probe location in order to completely cover the samples. The time-integrated sediment sampler was fixed 5 cm from the channel bed (Fig. 2C). The water flow reached the inlet hole at a height of ca. 10 cm. Therefore, TIS samples were free to flow inside the sampler. For this reason, TIS samples were placed in an environment with different moisture, temperature and insulation conditions, and were also affected by the partial mobility derived from the water flow inside the sampler.

Eight-time intervals were selected to recover the samples after starting the experiment at t = 0 (i.e. 7, 30, 60, 90, 150, 210, 270 and 365 days). The number of days within the channel and the number of submersion days for each sample are listed in Table 1.

The total rainfall during the study period (November 2018-November 2019) was 663.6 mm, 28 % below the average rainfall (i.e. 926 mm $yr^{-1}$). The annual runoff and the runoff coefficient were 52 mm and 8 %, respectively. The mean discharge was 0.01 $m^3$ $s^{-1}$ with a maximum peak of 1.31 $m^3$ $s^{-1}$ (Fig. 3). For the whole study period, the total sediment load was 2.06 t, with a mean suspended sediment concentration of 1.19 mg $l^{-1}$ and a maximum peak of 321 mg $l^{-1}$, resulting in a sediment yield of 0.6 t $km^{-1}$ $y^{-1}$. Runoff was present 38 % of the time. Soil samples were completely submersed for between 7 and 37 days during the entire study period whilst TIS samples were submersed for between 60 and 111 days (Table 1).

### 3.3. Laboratory analysis

Both particle size distribution and the SSA for all samples were measured using a Malvern Mastersizer 3000 laser diffraction particle size analyser (Malvern instruments) after applying ultrasound at the Luxembourg Institute of Science and Technology (LIST, Luxembourg). The total Carbon (C), Nitrogen (N) and Sulphur (S) were measured by high-temperature combustion using a vario MACRO cube (Elementar, ltd.) at LIST. Using gamma spectrometry, excess lead-210 ($^{210}Pb_{ex}$) and caesium-137 ($^{137}Cs$) activities (Bq $kg^{-1}$) were measured using a high-purity coaxial intrinsic germanium (HPGe) detector (Canberra, ltd.) at the Environmental Radioactivity Laboratory of the University of the Balearic Islands (Spain).

Diffuse reflectance was measured with an ASD FieldSpect-II spectroradiometer in a dark room at 1 nm steps over the 400–2500 nm range following the same methodology used by García-Comendador et al. (2020). CIE xyY colour coefficients and RGB colour values were calculated according to the International Commission on Illumination (CIE, 1931). The ColoSol software (Viscarra Rossel et al., 2006) was used to estimate the CIE LAB, CIELUB, CIELHC, Munsell HVC, CIE XYZ, the decorrelated RGB, the redness index (hereinafter RI) and the Helmoltz chromaticity coordinates (i.e. dominant wavelength (DW) and purity of excitation (Pe %)).

Samples were digested using the USEPA 3051A microwave digestion method, as detailed below. Initially, 0.5 g of sieved soil and sediment samples were placed into polytetrafluoroethylene tubes, to which 9 ml of $HNO_3$ (strength 69 %)and 3 ml of HCl (strength 37 %) were added. Samples were placed on a temperature ramp in a microwave oven (Multiwave GO, Anton Paar, Austria) for 5 min until they reached 175 °C and were kept at this temperature for 10 min. After digestion, samples were transferred to 100 ml flasks, filled with ultrapure water (Millipore Direct-Q System) and filtered through 0.45 μm nylon filters (Labbox Labware, S.l). High-purity acids were used in the analyses (PamReac ApplyChem, SLU). Calibration curves to determine metals were prepared from a calibration standard 1,000 mg $l^{-1}$ (Sharlau, Spain). The concentrations of metals in the extracts were determined by ICP-AES (DV Optima5300, Perkin Elmer®, Inc.) equipped with a GemCone pneumatic nebulizer for viscous solutions and solutions with a high content of dissolved solids (Waltham, MA, USA). Following the recommendations of the United States Environmental Protection Agency (2000), detection limit values were assigned to below-par measures.

### 3.4. Evaluation of changes in soil properties

The Shapiro-Wilk ($p < 0.05$) normality test was performed on the particle size distribution data. The Wilcoxon signed-rank test was used to check whether particle size distributions changed during the experiment, by comparing original samples (t = 0) and the samples deployed in the channel, for every source category. Coefficients of variation (CV; expressed in %) were calculated for all soil properties. For data treatment, data were grouped into four periods: initial submersion (i.e. 0–7 days), constant flow (wet period, 7–90 days), period without flow (dry period, 150–270 days) and the whole year (Fig. 3 and Table 1). Spearman's correlation coefficient was computed to identify possible monotonic correlations between the different soil properties and (i) grain size (expressed as SSA; $m^2$ $kg^{-1}$), and (ii) C content as an approximation to organic matter content.

### 3.5. Spatial variability of soil properties within the catchment

Results of in-channel temporal variations for each soil property (expressed as coefficient of variation; CV) were compared with their spatial variability within the catchment (also expressed as CV) presented in García-Comendador et al. (2021) (hereafter referred as '*catchment source samples*'). The authors collected *catchment source* tracer data from forestland (n = 6), cropland (n = 5) and scrubland (n = 5) (García-Comendador et al., 2021). The comparison is meant to assess if the eventually variability in the soil properties due to transport and storage within the channel is higher or lower than the natural spatial variability of soil properties. When applying the sediment fingerprinting technique, a large part of the output uncertainty can be associated to source tracer variability (Pulley et al., 2017).

The same laboratory protocol was used for both types of samples (Section 3.4) but the samples from García-Comendador et al. (2021) were not used to investigate the in-channel soil properties variation. This was because a large amount of material was required for the experiment, which was unfortunately not available. It is however assumed that little differences would be observed (expressed as variations from immersion time) when using these samples instead of the samples collected within the erosion plots.

## 4. Results

### 4.1. Variability of soil properties in submerged samples

A mass loss was detected in all in-channel samples during the experiment (average of 2 ± 0.4 g; Table 1). However, no significant differences in particle size distribution were observed between the original samples (i.e. not exposed) and the rest (i.e. in-channel and TIS samples; Fig. 4). CVs of SSA in different land uses were < 10 % for all in-channel samples and TIS samples (Fig. 4E and Fig. 5D) during the entire study period. On the other hand, the average spatial variability observed in the *catchment source samples* was 19.8 ± 11.7 % for the three source types (Fig. 6A).

Nitrogen (N) and Carbon (C) CVs for all in-channel samples and TIS samples were < 20 % (Fig. 5D and Fig. 7). Sulphur (S) experienced a higher alteration, especially in cropland samples (Fig. 5D). Changes principally occurred in the first 7 days, with a cropland CV of 76.1 % between the original material and the first sample collection (Fig. 5A and Fig. 7). In addition, the crop CV of S for the whole study period (i.e. 43 %) was higher in comparison with the CV observed in the TIS samples (18 %, Fig. 6B). The S variability of in-channel crop samples was comparable to the spatial variability measured in the catchment source samples from crop lands (CV of 45.5 %, Fig. 6A).

$^{137}Cs$ and $^{210}Pb_{ex}$ CVs measured on the in-channel samples for the whole study period ranged between 10.4 and 31.4 % (Fig. 5D and Fig. 7), with them being slightly higher for $^{210}Pb_{ex}$. The variability was lower in comparison with the spatial variability measured in the

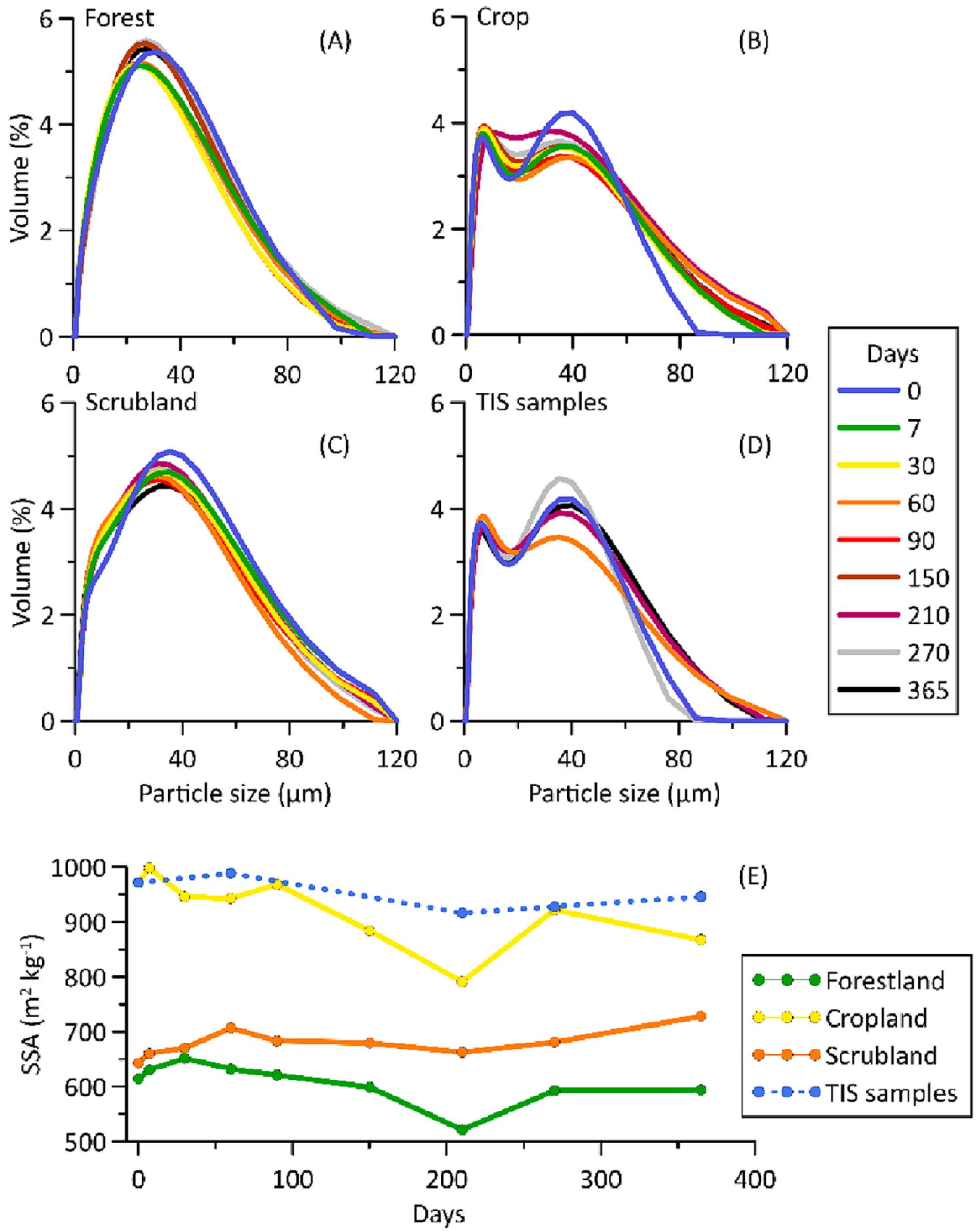


**Fig. 4.** Particle size distribution of in-channel (A) forestland, (B) cropland, (C) scrubland, and (D) TIS source samples. Specific surface area (SSA) per source type at the different sampling times (E).

*catchment source samples* for the three source types, with CVs ranging from 40.1 to 86.5 % for $^{137}$Cs, and from 33.9 to 73.4 % for $^{210}$Pb$_{ex}$ (Fig. 6A).

All colour properties presented CVs of < 10 % during the whole study period, but the Redness Index (RI) CVs were higher in the forestland (11.8 %) and cropland samples (10.2 %; Fig. 5, Fig. 7 and supplementary Fig. 2). Colour spatial variability within the catchment was also low (average CV of 10.3 ± 11.5 %; Fig. 6A), and only reached a CV of > 40 % in the RI measurements for the forestland and cropland samples.

Geochemical properties showed more temporal variability than colour properties. For the entire study period, CVs of the in-channel samples were < 25 % (Fig. 5D and Fig. 8), except for As, Mo, Pb and Na, which had CVs ranging between 25 and 40 % in at least one of the in-channel source categories or TIS samples (Fig. 5D and 8).

No significant changes were observed in the variability of most of the soil properties depending on the channel conditions (i.e. wet and dry periods; Fig. 5). During the initial submersion (i.e. 0–7 days), S showed the highest CV (76 % for cropland samples), followed by Cd, Cr, Mo, Pb, Na and K with CVs between 25 and 40 % in different in-channel source categories (Fig. 5A). Regarding the wet period, CVs between 25 and 40 % were only detected in Na for the forestland samples, $^{210}$Pb$_{ex}$, Mo and Pb for the cropland samples and Co and Ni for the scrubland samples (Fig. 5B). During the dry period (Fig. 5C), the highest CVs were observed in the forestland samples for As (45 %) and the cropland samples for Pb (51 %). Finally, during the whole study period (i.e. 365 days; Fig. 5D), the highest average CVs –considering all in-channel source types (i.e. forestland, cropland and scrubland)– were measured in S (27 ± 15 %), $^{210}$Pb$_{ex}$ (26 ± 7 %), As (32 ± 4 %) and Mo (23 ± 7 %).

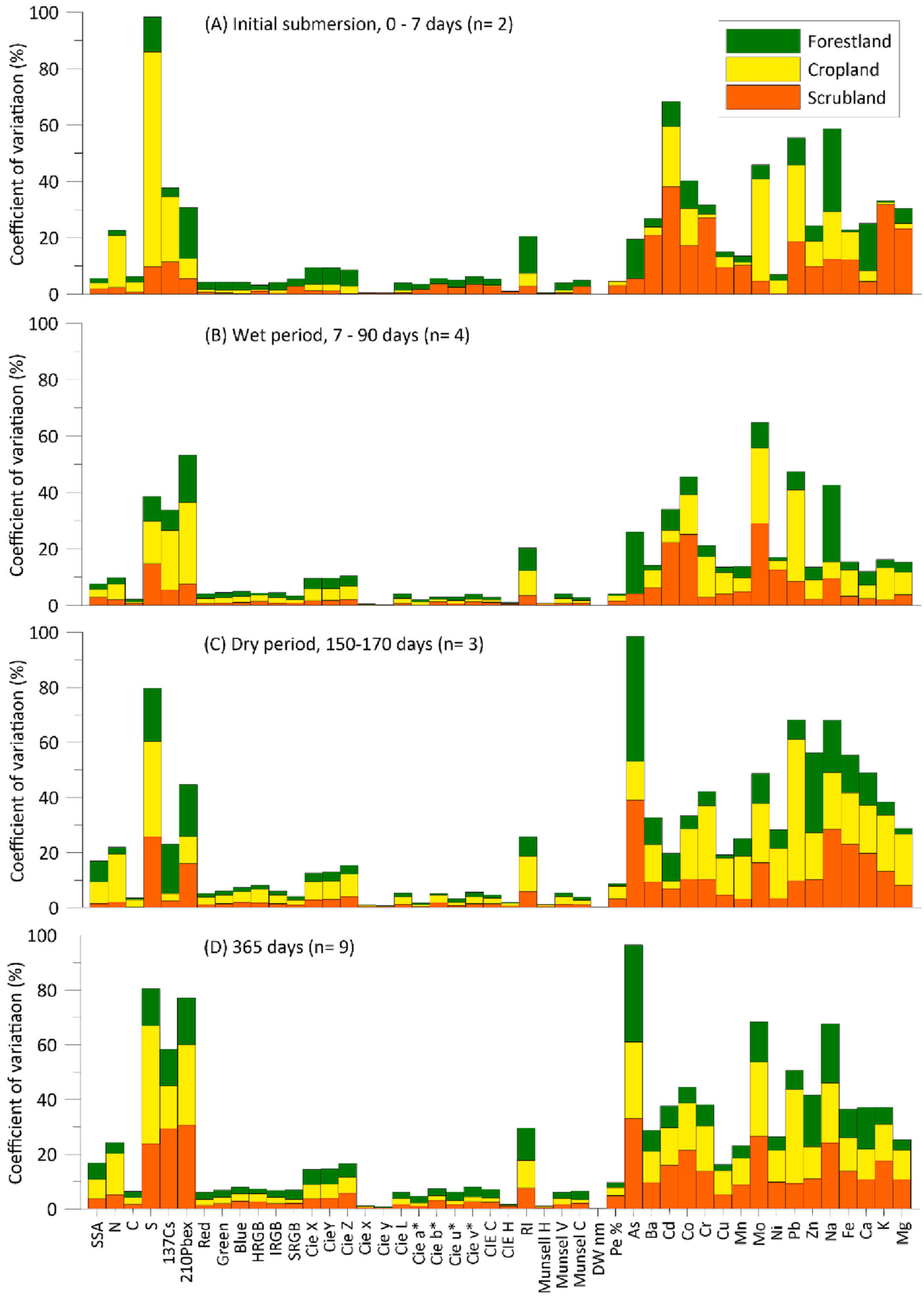


**Fig. 5.** Coefficient of variation in the stacked columns of the soil properties measured in the in-channel samples during four different periods: (A) the initial submersion period, (B) the wet period, (C) the dry period and (D) the whole year.

### *4.2. Correlation of soil properties with grain size and carbon content*

Spearman's correlation coefficient shows both positive and negative correlations between SSA and soil properties ($p < 0.05$). 16 properties showed positive correlations (9 with $R \geq 0.8$), whereas there were negative correlations for 26 soil properties (16 with $R \geq -0.8$; Fig. 9). Regarding C, 12 positive correlations with soil properties were obtained and negative with 23 ($p < 0.05$; Fig. 9). No positive correlations with coefficients>0.8 were elucidated, and only cie V presented a correlation coefficient larger than −0.8 with C.

## 5. Discussion

### *5.1. In-channel alteration of soil properties*

Particle size distributions and C content did not significantly change

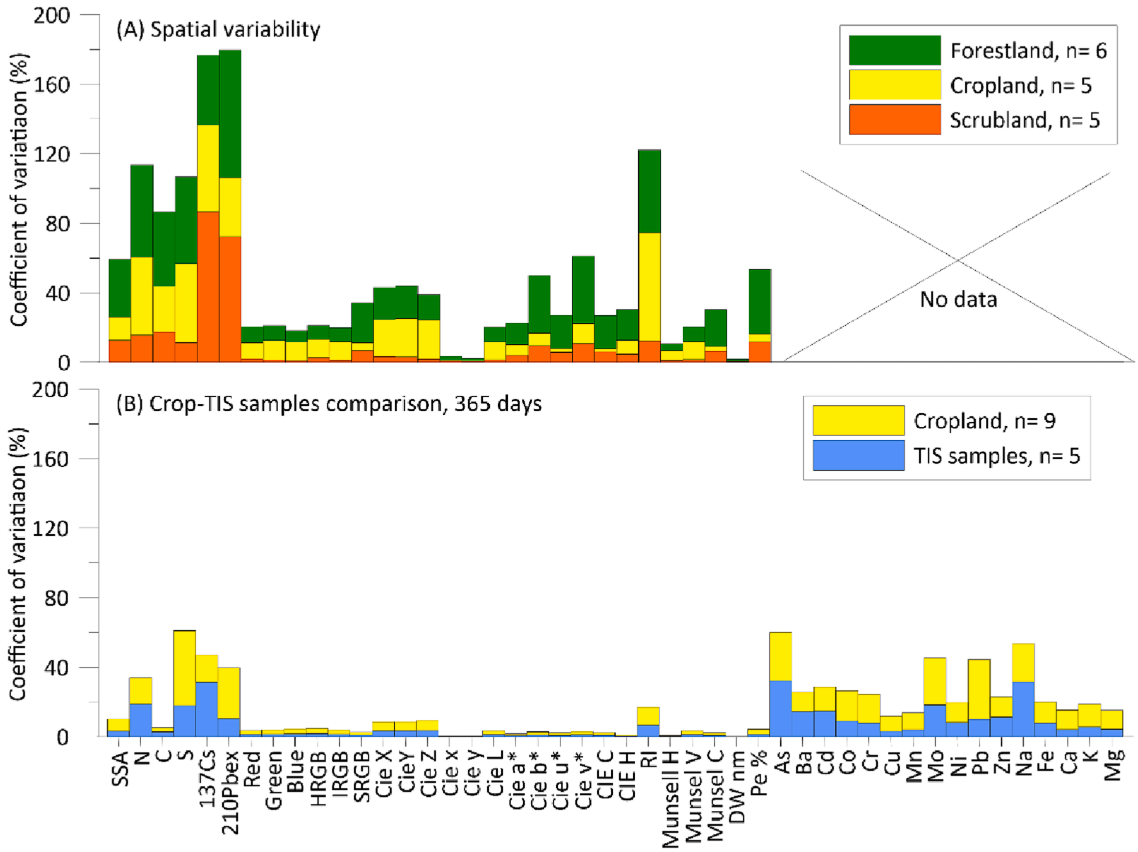


**Fig. 6.** (A) Coefficients of variation of FRNs activity, SSA, N, C, S and colour properties measured in the *catchment source samples* (García-Comendador et al., 2021), and (B) coefficients of variation of soil properties measured in the in-channel samples collected in cropland fields and TIS samples. It should be noted that in this case the y-axis has a larger scale (200%) than in Fig. 5 in order to accommodate the stacked columns of the (A) spatial variability data.

(average CV for all land uses and TIS samples of 2.1 ± 0.3 %), allowing a direct comparison of in-channel soil properties measured after different intervals of time. Note that a varying percentage of particles were>63 μm (Fig. 4). This was partially due to (i) the fact that some non-spherical particles with a diameter larger than this size could still have passed through the sieve, and (ii) the shortcomings of the laser diffraction instruments in estimating volume concentration for non-spherical particles. Their projected cross-sectional area averaged over all possible orientations of the particle orientations relative to the direction of the beam is larger than that of a sphere with an equal volume (Jonasz, 1991), which might lead to a measured particle being assigned a larger size fraction than it actually has (Eshel et al., 2014).

Most of the soil properties presented a low degree of alteration during the experiment, independent of the source type (i.e. forestland, cropland and scrubland; average CV = 8.1 ± 8.8 %). Variability values were lower than the average variability measured in the *catchment source* soil properties (Fig. 6A; average CV = 16.3 ± 18.5 %). Thus, the spatial variability of C, N and S content within the Es Fangar catchment was higher (average CV of 28.8 ± 12.8 %, 37.9 ± 19.7 % and 35.5 ± 21.1, respectively, for all land use types) than the in-channel variability (average in channel CVs for all land use types of 2.1 ± 0.4 %, 8.1 ± 6 % and 26.8 ± 14.9 % for C, N and S, respectively). C and N content in sediment can undergo transformations in streams or riparian areas, which are often considered hot spots of biochemical processes (Koiter et al., 2013). Thus, microbial transformations can cause denitrification, decomposition of organic matter or the release of organic C and N to stream waters (Vidon et al., 2010) or can even transform inorganic elements into organic forms (Thayer, 2002). Despite the lack of capacity to decipher the magnitude of these processes in the Es Fangar catchment, the observed temporal changes were slightly different to the variability measured in topsoil samples (0–2 cm) between June and July 2015 in a 1.8 ha pasture field in SW England (Collins et al., 2019). The authors of that study collected soil samples four times and observed average CVs of 14.9 and 4.5 % for C and N, respectively.

Fallout radionuclides in-channel average CVs for all land use types were 19.4 ± 8.7 for $^{137}$Cs and 25.7 ± 7.5 for $^{210}Pb_{ex}$. Here, a constant downward trend in $^{210}Pb_{ex}$ activity in the scrubland samples was observed, which was more evident during the dry period. This trend could possibly be explained by losses in the water column (Foster et al., 2006; Koiter et al., 2013). Radioactivity decay was discarded as a cause of reduction in soil $^{210}Pb_{ex}$ activity due to its long half-life (22.3 years). Another cause could be the measurement uncertainty of the $^{210}Pb_{ex}$ activity measurements, because they are technically complicated. Estimated uncertainties for $^{210}Pb_{ex}$ may be as high as ± 30–50 % (Mabit et al., 2008), leading to errors in the determination of $^{210}$Pb supported in equilibrium with $^{226}$Ra. Accordingly, these equilibrium differences will inevitably spread to the determination of $^{210}Pb_{ex}$ (Mabit et al., 2014). However, the high decrease in activity registered in the last scrubland sample (i.e. 365 days) is also reflected in other properties such as $^{137}$Cs, C or N (Fig. 7). In addition, despite SSA and $^{210}Pb_{ex}$ showing a negative correlation (-0.39; $p < 0.05$; Fig. 9), these abrupt changes were not documented in the other land use types despite their higher SSA variability. We therefore cannot definitely state the cause of the variability in scrubland samples.

Colour parameters were the most stable tracers with in-channel average CVs of 2.6 ± 2.2 %, with CVs > 10 % observed only in the forestland and cropland redness index (11.8 and 10.2 % respectively). This low variability in colour properties is in accordance with other similar studies. Legout et al. (2013), considering all submersion intervals from their experiment (i.e. 1, 7, 14, 35 and 63 days), described

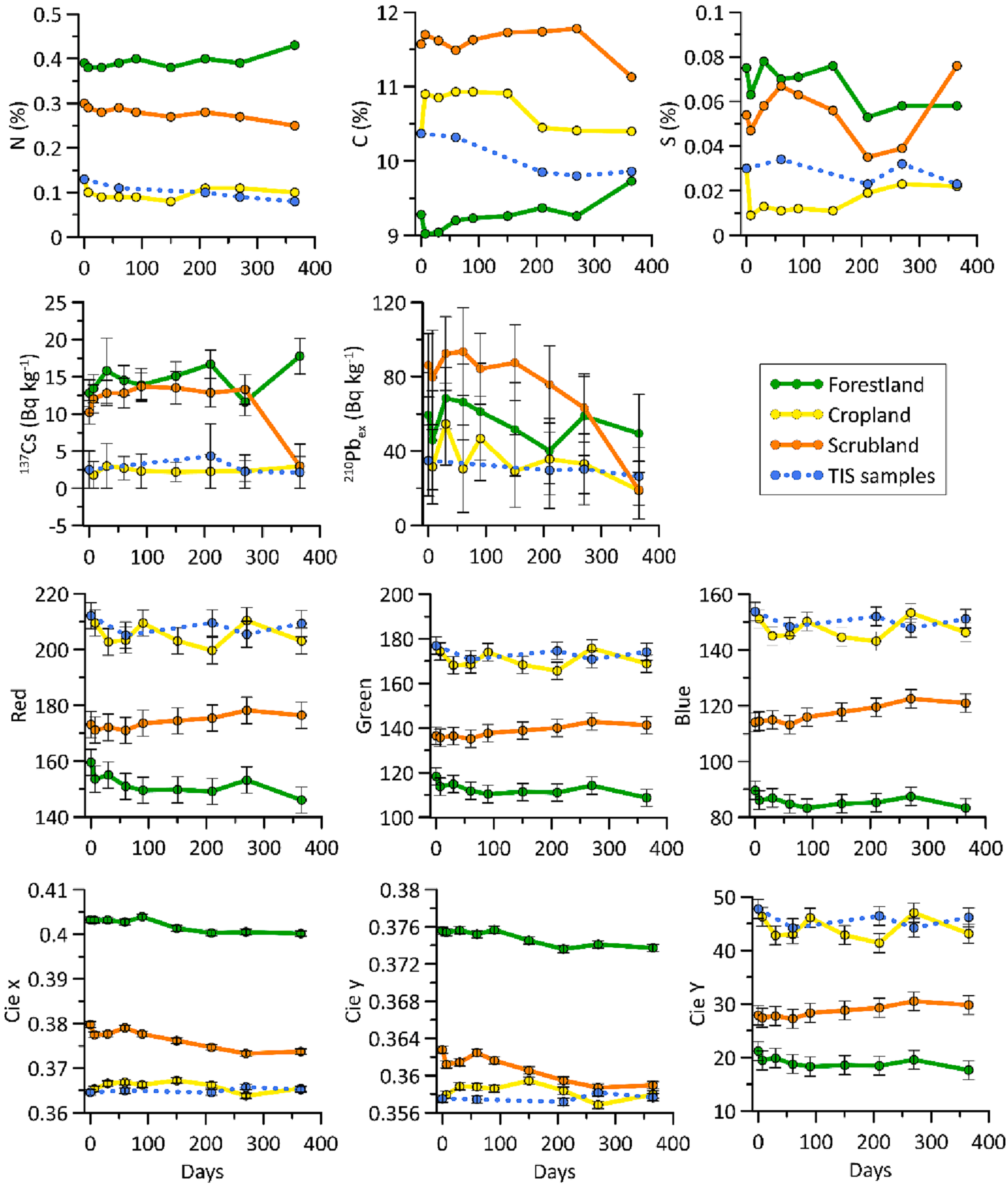


**Fig. 7.** Temporal variability of N, C, S (%), $^{137}$Cs, $^{210}$Pb$_{ex}$ (Bq kg$^{-1}$) red, green, blue, cie ×, cie y and cie Y tracer values measured in the in-channel samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

changes in colour properties of < 10 %, and Uber et al. (2019) recognized changes of < 10 % in all cases with average changes of < 4 % after 1, 3, 7, and 22 days. Finally, Poulenard et al. (2012), only identified errors ranging between 5 % and 15 % using submersed samples (1 day, 1 week and 2 weeks) to calculate the real proportions of the same samples before submersion using a Partial Least Square model, corroborating the low variability of colour properties.

In contrast, geochemical elements showed a more heterogeneous behaviour. The more stable elements during the study period were Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn, Fe, Ca, K and Mg with in-channel average CVs for all land uses ranging from 5.4 to 16.9 %. On the contrary, As, Mo and Na presented a higher variability (average CVs from 22.6 to 32.2 %). The results obtained were unexpected in some elements. For example, Ca, K and Mg are often considered non-conservative tracers because of

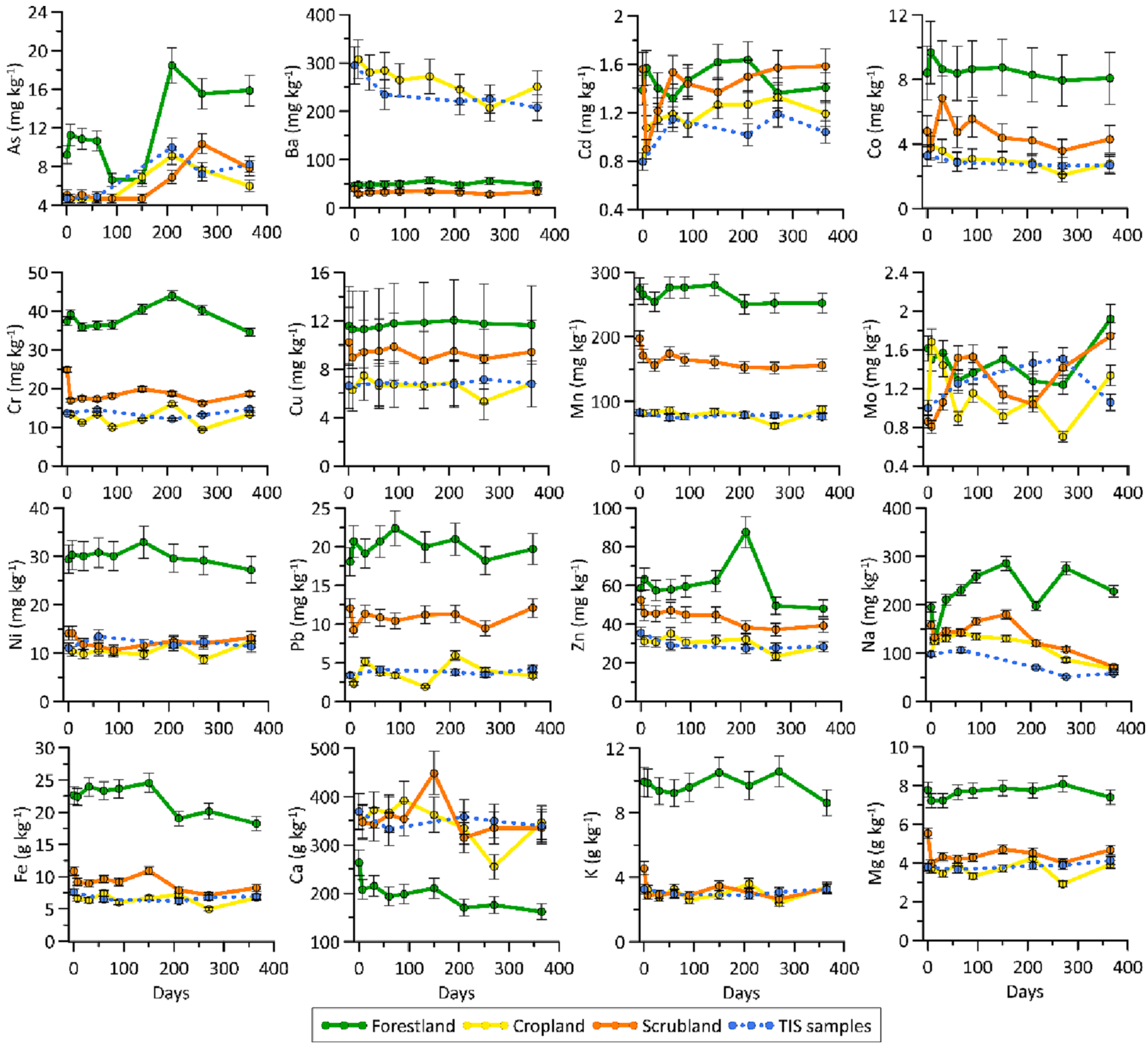


**Fig. 8.** In-channel temporal variability of As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Na Fe, Ca, K, Mg measured in the in-channel samples.

their water solubility potential (Kraushaar et al., 2015), but they showed low variability in the Es Fangar catchment, even during the wet period (Fig. 5). Na is also usually defined as a non-conservative tracer (Négrel et al., 2015). However, some studies defined it as conservative because of its low reactivity to hydrochloric acid extraction, as was also the case for Ti, Al, Li, V, Cr, Ba, and As (Dabrin et al., 2021). On the contrary, here As showed the highest variability.

In general, the three land use types showed a similar variability in soil properties, although it was slightly higher in cropland samples (Fig. 5). Comparing cropland and TIS samples (average in-channel CV for all properties of 9.3 ± 0.1 % and 8.6 ± 9.2 % respectively), direct insolation deprivation and presumable differentiated humidity and temperature conditions did not have significant effects on soil properties in this specific case.

The general low variability observed in soil properties, and its correlations with SSA and C (Fig. 9) seems to emphasize the role of particle size and organic matter in the conservative behaviour of soil properties rather than other in-channel alterations (Koiter et al., 2018).

### *5.2. Limitations of the experiment and implications for sediment fingerprinting*

It is difficult to replicate the natural sediment transport and deposition processes due its high variability in time and space. In this experiment, soil samples were exposed to the hydro-meteorological variability of a Mediterranean intermittent river as samples were on the channel bed for one year. Nonetheless, the results must be addressed with caution. In-channel samples were not affected by differential hillslope erosion, transport, and deposition processes, but remained within the channel in contrasted conditions (i.e. wet and dry periods) due to the fixed positioning of the sample bags fixed to the steel pegs. The samples were placed in nylon bags to reduce the loss of particles in order to assess variations mainly associated with biochemical changes.

The nylon bags and steel pegs fixed into the bed channel could also have influenced the soil properties. The extent of this impact has not been addressed. However, the stability of Fe and C concentrations suggests a low influence on the soil property values. Similarly, the effect of temporary compaction of the sieved soil in the nylon bags remains unknown. In addition, as in the case of $^{210}Pb_{ex}$, some of the variations may

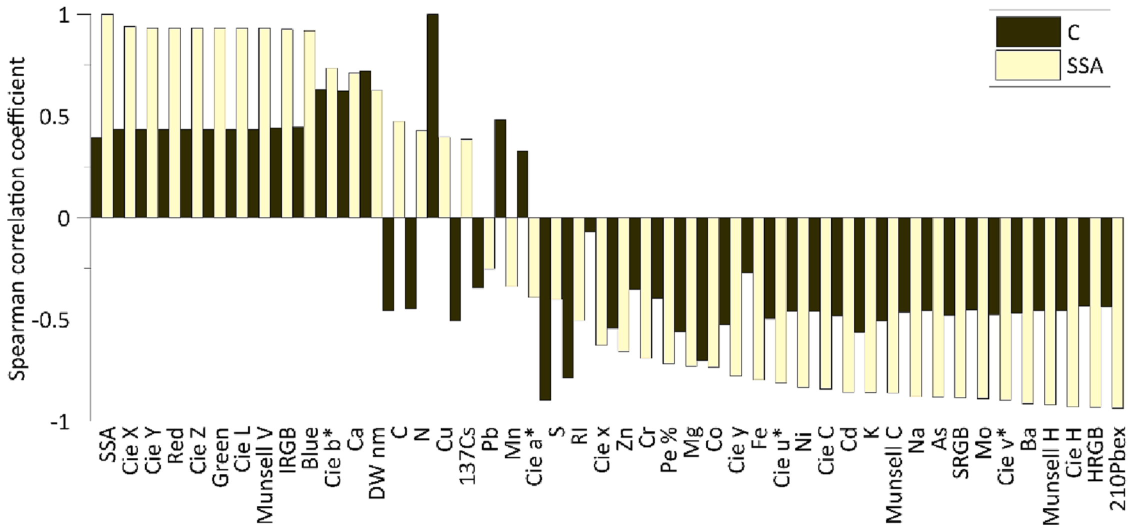


**Fig. 9.** Spearman correlation coefficient between the soil properties analysed on the in-channel samples and, carbon (C, black) and specific surface area (SSA, pale yellow). Values are ordered based on correlations with SSA from left to right (1 to −1). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

be related to measurement uncertainties associated with measuring devices.

Mediterranean fluvial systems have a singular complexity. Their heterogeneous hydrological regimes promote significant spatial and temporal differences in the hydrological response, accentuated by the relationships between natural and human-induced variables (Fortesa et al., 2020b). The conjunction of these features can promote unique abiotic and biotic conditions in their streams –even in different points of the same channel– which might lead to a distinctive alteration of sediment properties. In this study, samples were exposed to contrasting environmental conditions (i.e. dry and wet periods) where different processes (e.g. diagenesis, organic matter additions, loss of properties due to solubility; Koiter et al., 2013) and influencing of sediment properties could occur. Furthermore, sediment transport is highly influenced by high-intensity torrential floods which ensure that > 80 % of annual suspended sediment load is exported in < 10 % of the time (Estrany et al., 2009; Rovira and Batalla, 2006). In the Es Fangar catchment, previous research spanning five hydrological years, showed that 91 % of the suspended sediment load was exported in 5 % of the time (Fortesa et al., 2020a). Together with the small size of the catchment, this process suggests a rapid suspended sediment transit (and exhaustion) from sources to the catchment outlet, which could decrease the influence of biochemical changes on soil properties. However, in-channel discontinuities over prolonged time intervals can be produced in the sediment conveyor belt, generating temporary sediment deposition. In addition, some sediment may be stored within channel bed gravels in anoxic reducing conditions, which can cause alterations. Finally, in-channel transformations only represent a part of the potential changes in properties during erosion and sediment delivery processes and on-site processes (at hillslopes) should also be considered (Koiter et al., 2018; Motha et al., 2002).

Notwithstanding the aforementioned challenges, our results may be useful when assessing uncertainties associated with tracer selection and alteration in suspended sediment fingerprinting studies conducted in Mediterranean fluvial systems. In addition, the alteration of emerging tracers in sediment fingerprinting studies –as compound-specific stable isotope or biomarkers (Collins et al., 2020)– during transport in Mediterranean environments, should be further explored.

## 6. Conclusions

An experiment to investigate in-channel soil property variations was performed. Most soil properties investigated showed a low variability during the experiment. The catchment spatial source variability was higher than the in-channel variability. In addition, no significant differences were observed between the different land use samples or collection intervals. SSA and C content also presented low variability over time, allowing a direct comparison between the original and the submerged samples. No differences were found either with cropland or TIS samples, indicating low variability in soil properties even in different environmental conditions. Soil properties that showed higher in-channel CVs were S, $^{137}$Cs, $^{210}$Pb$_{ex}$, As, Mo and Na. Conversely, C and colour properties were the most stable in time. Despite their limitations, the results presented will be informative for performing future suspended sediment fingerprinting studies in Mediterranean catchments by providing a better understanding of which soil properties are more sensitive to in-channel biochemical transformation.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catena.2023.107036.

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