Title:

Variability in source sediment contributions by applying different statistic test for a Pyrenean catchment.

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Abstract

Information on sediment contribution and transport dynamics from the contributing catchments is needed to develop management plans to tackle environmental problems related with effects of fine sediment as reservoir siltation. In this respect, the fingerprinting technique is an indirect technique known to be valuable and effective for sediment source identification in river catchments. Large variability in sediment delivery was found in previous studies in the Barasona catchment (1509 km², Central Spanish Pyrenees). Simulation results with SWAT and fingerprinting approaches identified badlands and agricultural uses as the main contributors to sediment supply in the reservoir. In this study the < 63 µm sediment fraction from the surface reservoir sediments (2 cm) are investigated following the fingerprinting procedure to assess how the use of different statistical procedures affects the amounts of source contributions. Three optimum composite fingerprints were selected to discriminate between source contributions based in land uses/land covers from the same dataset by the application of (1) discriminant function analysis; and its combination (as second step) with (2) Kruskal–Wallis *H*-test and (3) principal components analysis. Source contribution results were different between assessed options with the greatest differences observed for option using #3, including the two step process: principal components analysis and discriminant function analysis. The characteristics of the solutions by the applied mixing model and the conceptual understanding of the catchment showed that the most reliable solution was achieved using #2, the two step process of Kruskal–Wallis *H*-test and discriminant function analysis. The assessment showed the importance of the statistical procedure used to define the optimum composite fingerprint for sediment fingerprinting applications.

Keywords: Sediment fingerprinting, Optimum composite fingerprint, Mixing model, Sediment source ascription, Mountain catchment, Spanish Pyrenees

1 Introduction

Sediment fingerprinting procedure is employed to identify the primary sediment sources within catchments, to quantify the relative contribution of these sources to the sediment flux and to document the temporal and spatial variability of these source contributions (Walling, 2005; Minella et al., 2008; Collins et al., 2010a, 2010b). Therefore, sediment fingerprinting applications have expanded greatly to support the development of sediment management strategies aimed at dealing with environmental problems associated with erosion and sediment related problems (e.g. Schuller et al., 2013; Tiecher et al., 2015). Together with the expansion in sediment fingerprinting applications it has been an increase in the choices of sediment fingerprinting procedures, often which are tailored to the wide range of potential controls on sediment properties, and the contributions from catchment sediment sources (Walling, 2013). Most sediment fingerprinting approaches involve comparing the properties of samples collected from different target sediments with the properties of potential source

areas, such as the surface of different land uses/land covers (e.g. Smith and Blake, 2014; Pulley et al., 2015; Palazón et al., 2016).

Sediment source apportionments are quantified based on the identification of differences in the tracer properties or ‘fingerprints’ of the potential sediment sources on the basis of statistical analysis and interpretation. Although a single sediment property cannot be used to source fingerprinting (Mukundan et al., 2012), it is widely recognized that the inclusion of a combination of several physical and chemical properties incorporated into a composite fingerprint increases the possible level of discrimination and thereby increases the reliability of the relative contribution of those sources (e.g. Walling et al. 1993; Collins and Walling 2002; Wasson et al. 2002; Walling, 2005; Collins et al., 2010a, 2010b). These tracer properties may include geochemical, radionuclide, mineral magnetic, organic constituent, stable isotope and colour properties (Foster and Lees, 2000). While a large number of potential fingerprint properties has been used in sediment fingerprint applications, the need to use statistical tests to confirm the ability of potential fingerprint properties to discriminate between sediment sources and to assist in the selection of the ‘best’ properties to include in a composite fingerprint became more important and therefore was increasingly recognized.

One of the methodological differences within the range of different applications of the sediment fingerprinting procedure in the literature is related to the statistical analysis used to identify the subset of the tracer properties which ‘best’ discriminate between sources (Palazón et al., 2015b). Although the two step process outlined by Collins et al. (1997) which combined Kruskal–Wallis H -test as first step and discriminant function analysis as second step has been extensively used in source fingerprinting studies (e.g., Russell et al., 2001; Minella et al., 2008; Hughes et al., 2009; Schuller et al., 2013; Stone et al., 2014), other procedures have been used to select the most effective optimum composite fingerprint, such as the use of principal component analysis (e.g. Tiecher et al., 2015). In many cases the use of each statistical process is due to the specific characteristics of the study areas or used fingerprints and, therefore, the selection of the most effective optimum composite fingerprint for each specific application can become time-consuming and complex. Furthermore, previous studies (e.g. Haddadchi et al., 2014; Palazón et al., 2015b) showed that results of the sediment fingerprinting procedure are sensible to different optimum composite fingerprints selected by different statistical procedures pointing to the need for a careful selection of the statistical procedures in each case study.

The importance of the Barasona reservoir, located in the Spanish Pyrenees, as a supplier of water for irrigation to the lowlands and its siltation management problems have been investigated since the 1990s (e.g. Fargas et al., 1997; Avendaño-Salas et al., 1997; Navas et al., 1998; Valero-Garcés et al., 1999). From these studies, those which identified sediment sources pointed to the badlands developed in Eocene marls as the main source of sediment (e.g. López-Tarazón et al., 2015) and some of them also identified agricultural lands as the secondary source of sediments (e.g. Alatorre et al., 2010; Palazón and Navas, 2014, 2016). The study catchment is representative of land

use changes that have occurred in the Mediterranean region and which often are cited as primary controls on sediment production (Navas et al., 2008). Our main objective is to assess the variability in source contributions derived by selecting the most reliable optimum composite fingerprints using different statistical procedures. Understanding how statistical operations influence the selection of tracers to discriminate sources is of interest especially for catchments where sediment sources based on land use might not be clearly discriminated because of recent changes in land uses.

2 Material and Methods

2.1 Study area

The drainage catchment of the Barasona reservoir is characterized by high relief with an altitude range from 424 to 3404 m a.s.l., a mean elevation of 1313 m and an average catchment slope of 39% (Fig. 1b). The drainage area of the basin studied here is 1509 km². The lithological competence of the five main Pyrenean structural units (WNW–ESE-trending geologic units), within the catchment controls the distribution of the geomorphological processes and slope ranges (Palazón and Navas, 2014). These structural units arrange from south to north as follows: the external ranges that delimit the catchment to the south, composed mainly of sandstones and limestones; the intermediate depression, a relative lowland area, composed of detrital sedimentary rocks; the internal ranges composed of large packages of limestones interbedded with marls and sandstones that have developed deep and narrow gorges; the internal depressions (located into the previous structural unit) comprise depressions formed on more erodible materials which develop badlands on marls and the axial Pyrenees composed of quartzites, limestone, shales, granites and granodiorites, with large mountain bodies and the highest Pyrenean peak (Aneto Peak 3404 m a.s.l.).

The catchment has a mountain climate, wet and cold, influenced by the Atlantic Ocean and the Mediterranean Sea (García-Ruiz et al., 2001). The combination of these influences together with the abrupt relief generates gradients in temperature and precipitation as recorded for both north–south and west–east regions. Annual precipitation and temperature range from 500 mm and 12 °C at the outlet (424 m a.s.l.) to more than 2500 mm and less than 4 °C on the highest divides (> 3000 m a.s.l.).

Fig 1.- a) Location of the Barasona catchment in the Iberian Peninsula, the location of the karst system at the headwater and the distribution of the source samples for the catchment and the mixture samples in the reservoir; b) distribution of the soil types, the DEM of the catchment, land uses and land covers and c) photos of the main land use/land cover sources.

The hydrologic regime is transitional nival–pluvial, characterised by two maxima (García-Ruiz et al., 2001): the first due to snowmelt during the spring period (April–June) and the second due to precipitation during late autumn (October–November). Main floods are related with these two maxima and also for localized summer thunderstorms. The Ésera River is regulated by small reservoirs, canals and dams, whereas, the Isábena River is non-regulated.

Forest and pastures occupy more than 50% of the catchment, followed by scrublands (> 20%) and cultivated land that occupies around 20% (Fig. 1b). Climatic and topographic gradients from south to north also influence the distribution of the predominating land uses which varied from cultivated lands in the lowland southern areas, to forest in the middle part, to alpine grassland in the highlands. Important changes in land use occurred during the last 60 years in the Spanish Pyrenean region, resulting in substantial agricultural land abandonment to natural reforestation that has affected most parts of the agricultural areas (Navas et al., 2008).

In general, the soils of the catchment are stony and mostly shallow overlying fractured bedrock with textures ranging from loam to sandy loam. Soils are alkaline and generally well-drained with limited average water content and moderate to low structural stability.

The Barasona reservoir, located in the central part of the Spanish Pyrenees, has suffered siltation problems since its construction in 1932 (Navas et al., 1998; Valero-Garcés et al., 1999). A bathymetric survey in 1995 indicated that it had lost one third of its capacity in the first 65 years of operation yielding a specific sediment yield of $3.50 \text{ t ha}^{-1} \text{ year}^{-1}$ (Avendaño-Salas et al., 1997). Siltation rates dated with ^{137}Cs in retrieved sediment cores were high varying between 2 and 18 cm yr^{-1} (Navas et al., 2004) with a general decreasing rate trend after ^{137}Cs maxima (1963) mostly due to stabilisation of land uses changes as recorded in nearby reservoirs (Navas et al., 2009). The majority of the discharge to the reservoir is from the Ésera River catchment and, its main tributary, the Isábena River catchment, which together drainage 1479 km^2 of the catchment. Part of its headwater (30 km^2) is an internal catchment as it drains a karst system (Fig 1; Palazón and Navas, 2013).

2.2 Sample collection

A total of 384 individual surface source samples, 4 samples per sampling point, were collected by using a cylindrical core 5 cm long and 6 cm of diameter and combined in the field to form 96 composite samples (83 surface soil and 13 subsoil). Representative sites to be sampled in the Barasona catchment were selected by a non-aligned random spatial sampling method as implemented in open-source R package (spsample function on the sp library). This method generates a random sample while preserving an even spatial distribution of points across the study area. Therefore the mountainous characteristics of the catchment, areas with slope and altitude above 30% and 2000 m a.s.l., respectively, were excluded because in general these areas consist of rock outcrops. In addition, the number of representative sites for each source category was

checked to ensure that they were balanced in relation to the percentage distribution of the main land uses/land covers in the Barasona catchment (Fig. 1a).

Of the soil samples, 35 were from forest, 25 from agricultural fields and 23 from scrubland (Fig. 1c). Forest sources included land uses within the forest land cover observed in the region, comprising pristine forest with patches of human reforested pine forest, alpine grassland and dense scrubland (from forest burned areas). The latter were included in the forest sources as they were thought to correspond with forest areas where burning practice to produce pastures for livestock had been common in the beginning of the past century. These land uses are referred to as 'forest' in the remainder of the paper. Scrubland sources included the rest of the scrublands and low-density rangelands. Agricultural sources are representative of the main cultivation practices in the catchment comprising annual production of rain-fed cereals (barley, wheat and sunflowers) with the combination of conservation and traditional tillage. Subsoil source samples comprised six composite samples from badlands in Eocene marls in the intermediate part of the catchment and another seven composite samples from bare soils and eroded areas. Subsoil sources are representative of eroded areas and badlands. As in general, the main rivers flow through blocky or rocky channels, erodible channel banks are either non-existent or poorly developed and are only found locally in some secondary streams, therefore, they were not sampled. Therefore, based in the main land uses and covers, agricultural, forest, scrubland and subsoil were selected as sediment sources to gain knowledge about their relative contribution to the reservoir filling and to assess its importance for land management strategies.

Barasona target sediment samples were collected across the bottom reservoir deposits in October of 2011, before the autumn rainfalls when the water level was near at its minimum value and most of the deposited sediments were exposed. Seven locations from the bottom of the reservoir were selected (Fig. 1a) to be representative of the most recent and accessible reservoir filling. Four reservoir surface sediment samples of 2 cm depth were sampled and composited in the field. The sample depth could be considered as representative of sediment deposition for around one hydrological year (Valero-Garcés et al., 1999; Navas et al., 2004).

2.3 Analysis

All samples were initially oven-dry at 35 °C, gently disaggregated and sieved to <63 µm to isolate a comparable grain size fraction between source and sediment materials (e.g. Walling 2005; Smith and Blake 2014). Source and sediment mixtures samples were analysed to obtain the potential tracer properties, or fingerprints (Table 1).

Table1.- Analysed tracer properties, or fingerprints.

Analyse	Potential fingerprints	n
Elemental composition	Li, K, Na, Be, Mg, Ca, Sr, Cr, Cu, Mn, Fe, Al, Zn, Ni, Co, Cd, Tl, Bi, V, Ti, Pb, B, Sb, As, P, S, Mo and Se	28
Mass activities of environmental radionuclides	²³⁸ U, ²²⁶ Ra, ²³² Th, ⁴⁰ K, ²¹⁰ Pb and ¹³⁷ Cs	6
Magnetic susceptibility	frequency dependence of susceptibility (χ_{FD}), mass susceptibility at low frequency (χ_{LF})	2

The analysis of the total elemental composition was carried out after total acid digestion with HF (48%) in a microwave oven (Navas and Machín, 2002). Analyses of the 28 elements were performed in triplicate by inductively coupled plasma atomic emission spectrometry with a Perkin Elmer OPTIMA 3200 DV ICP-AES and resulting concentrations expressed in milligrams per kilogram. Those elements returning measurements below the detection limit in most of the study samples (Co, Cd and Se) were excluded.

Radionuclide activity concentrations in the samples were measured using a Canberra high-resolution, low background, hyperpure germanium coaxial gamma detector model XtRa GX3019. The detector had a relative efficiency of 50% and a resolution of 1.9 keV (shielded to reduce background) and was calibrated using standard samples that had the same geometry as the measured samples. Subsamples of 50 g were loaded into plastic containers (Navas et al., 2005a, b, 2014). Count times over 24 h provided an analytical precision of $\sim\pm 3$ –10% at the 95% level of confidence. Gamma emissions of the environmental radionuclides (expressed in Bq kg⁻¹ air-dry soil) were measured in the bulk soil samples considering the appropriate corrections for laboratory background (Palazón et al., 2015a). Moreover, the fallout radionuclide termed unsupported or excess ²¹⁰Pb (²¹⁰Pb_{ex}) was estimated to distinguish it from the ²¹⁰Pb fallout component (Gaspar et al., 2013; Mabit et al., 2014).

Mass-specific magnetic susceptibility (χ) was measured using a Bartington Instruments dual-frequency MS2B sensor (Bartington Instruments Ltd. 2000) at low and high frequency to determine frequency dependence of susceptibility (χ_{FD}). Mass-specific magnetic susceptibility at low (χ_{LF}) frequency was expressed as 10⁻⁸ m³ kg⁻¹.

2.4 Sediment fingerprinting approach

The first step of the standard fingerprinting procedure involved the exclusion of non-conservative fingerprint properties for the analysis. P was excluded on the basis of the risk of non-conservative behaviour during downstream transport (Granger et al., 2007). While the conservative behaviour of the tracer properties were not clear for all river systems, a range test was initially applied to ensure that target fingerprint values lay

within the range of the fingerprint property values of the sources (Martínez-Carreras et al., 2010; Wilkinson et al. 2013; Schuller et al. 2013; Smith and Blake 2014). The tracer property values from target samples falling outside the range in source values could be considered non-conservatives and, therefore, removed for subsequent analysis. In this case study the range test assessment excluded χ_{FD} .

Some studies have included tracer dataset pre-treatments to account for differences in particle size, organic matter and conservativeness correction factors (e.g. Collins et al. 1997, Gruszowski et al. 2003, Motha et al. 2003) that could affect the comparison of tracer concentrations between sources and sediments. Recent works (e.g. Haddadchi et al., 2013; Smith and Blake 2014), however, have shown that the relationships between fingerprint concentrations and correction factors may produce unquantified errors because of their own inherent complexity which makes it difficult to generalise their use. Therefore, it was decided not to incorporate them in this fingerprinting procedure.

The second step of the fingerprinting procedure includes the use of statistical analysis of difference to identify a subset of tracer properties, or optimum composite fingerprint, that discriminate the sediment sources. As potential source material were characterised by measurements of a large number of fingerprint properties ($n = 34$), the ability of the remaining potential fingerprinting properties to discriminate between the sediment sources and to provide an optimum composite fingerprint was investigated using the Kruskal–Wallis H-test (KW), the stepwise discriminant function analysis (DFA) and the principal components analysis (PCA). The non-parametric KW identified those properties which offered contrasts between the potential sources at the 5% confidence level pinpointing the existence of any interclass contrast (Collins and Walling, 2002). Therefore, KW helps to remove any tracers which did not show a significant difference in concentration between at least two of the sediment sources (Pulley et al., 2015). The DFA identifies an optimum composite fingerprint that maximise the discrimination between the sources whilst minimizing the number of tracer properties based on the minimisation of Wilks' lambda. The lambda value approaches zero as the variability within source categories is reduced relative to the variability between categories. PCA provides a useful means to analyse variance in tracer datasets and reduce dimensionality (D'Haen et al., 2012). The application of the PCA was based in the identification of tracer properties with the highest component loadings following a Varimax rotation of the principal components with eigenvalues in excess of 1. In this study the optimum composite fingerprint was investigated by conducting the DFA and combining this statistical test, in a second step, with KW and PCA. Therefore, three composite fingerprints with the minimum numbers of tracer properties that provide the greatest discrimination between the analysed sources were investigated by the following statistical test options: 1) DFA alone; 2) the commonly used two step process KW+DFA (Collins et al. 1997); and 3) the two step process PCA+DFA.

The final step of the fingerprinting procedure involved the estimation of source contributions for target samples with mixing models assuming a conservative mass balance. Within this, the sources, characterised by the tracers from the optimum

composite fingerprint, were multiplied by its unknown source sediment apportionments and summed have to be equal to the same equivalent tracers from the mixture sediment samples. The system has to satisfy two constraints: that the apportionments must lie between 0 - 100 % and sum to 100 %. As in general this system of equations is over-determined and as such it does not have a closed solution, an optimization procedure is needed to obtain the source apportionments. Mass balance equations were solved to provide source apportionments minimising an objective function, or goodness of fit (GOF), based on the sum of squares of the relative errors between the measured property values associated with the sample mixture and those predicted by the mixing model for a given set of relative source apportionments (based on Collins et al. 1997)

$$GOF = 1 - \frac{1}{n} \times \sum_{i=1}^n \left\{ \left(\frac{|b_i - \sum_{j=1}^m x_j a_{i,j}|}{\Delta_i} \right)^2 \right\}$$

where b_i is the value of tracer property i ($i = 1$ to n) in the sediment sample, $a_{i,j}$ is the mean concentration of tracer property i in source type j ($j = 1$ to m), x_j is the unknown relative weighting contribution of source type j to the sediment sample, m is the number of potential source types, n is the number of tracer properties selected as optimum composite fingerprint, and Δ_i is used as correction factor to normalize the tracer properties ranges.

A simple and flexible Monte Carlo global sampling routine was adopted as optimization method. This was configured to provide the optimal solution after exploration of the entire parameter space by the generation of uniformly distributed values and define the solution from the same and comparable number of solutions (see more methodological details in Palazón et al., 2015b). A large number of possible solutions (10^6) were generated, tested and ranked by their GOF value to extract the 100 solutions which most minimise the objective function (GOF closer to 100%) and provide the optimal solution. Therefore, the optimal solution was characterised by the mean and the standard deviation of the extracted source apportionments, providing the quality of the solution by its dispersion, and the lowest GOF value achieved by the optimization procedure for the selected solutions. Moreover, the 100 solutions used to characterise the optimal solution enabled the examination of frequency distributions of the extracted apportionments to assess the distributions of the solutions. Within this Monte Carlo, source variability was simulated with an iterative sampling routine according to their Student's t distribution defined by the mean and standard deviation values of each source group.

3 Results

3.1 Optimum composite fingerprints

Different tracer properties, in number and type, were selected as optimum composite fingerprints by the used statistical tests options (Table 2). The DFA alone selected 7 tracer properties. The KW identified 19 tracer properties which offered contrasts

between the four potential sources at the 5% confidence level. The two step process KW+DFA finally selected 5 tracer properties. PCA solution identified 8 components with eigenvalues in excess of 1 explaining 84% of the total variance in the tracer dataset (Table 3). The Varimax rotation allowed identification of 22 tracer properties with components loadings greater than 0.65 to include a large number of tracers. The 2 step process PCA+DFA finally provided 10 tracer properties.

Table 2: Optimum composite fingerprints obtained with the assessed statistical test.

Option	Statistic analysis	Selected fingerprints and optimum composite fingerprint	Wilks' lambda	Samples correctly classified
DFA	DFA	- ^{40}K , ^{137}Cs , Al, Bi, B, Fe, Sr	0.11	86.5
KW+DFA	KW	- ^{40}K , ^{137}Cs , $^{210}\text{Pb}_{\text{ex}}$, ^{232}Th , χ_{LF} , As, B, Ca, Cu, K, Li, Mg, Ni, Pb, Se, S, Sr, Ti, Zn	0.18	86.5
	DFA	- ^{40}K , ^{137}Cs , Li, Sr, Ti		
PCA+DFA	PCA	- ^{40}K , ^{137}Cs , ^{232}Th , ^{238}U , χ_{LF} , Al, As, B, Be, Bi, Cr, Cu, K, Li, Ni, Pb, Sb, Se, Ti, Tl, V, Zn	0.092	84.4
	DFA	- ^{40}K , ^{137}Cs , Al, Bi, Cr, K, Ni, Ti, V, Zn		

Table 3.- Principal components analyses results.

Principal component	Eigenvalue	Variance %	Accumulated %
1	10.305	33.242	33.242
2	5.124	16.532	49.774
3	2.783	8.978	58.752
4	2.292	7.395	66.147
5	1.824	5.885	72.033
6	1.382	4.461	76.493
7	1.214	3.917	80.41
8	1.013	3.268	83.678

The percentage of samples correctly classified by the four individual sediment sources and the Wilks' lambda value obtained by the applied DFAs differed between the assessed options (Table 2). Whereas the percentages of total samples correctly classified were similar between the options and greater than 84 %, the Wilks' lambda values achieved were similar for DFA and PCA+DFA and greater for KW+DFA. The PCA+DFA option achieved the best Wilks' lambda value but the worst classification of the samples. Although DFA results for all options suggested that source discrimination was fulfilled, the source samples from scrubland were found to overlap with the

agricultural and forest sources when the first two discriminant functions were plotted (Fig. 2).

Therefore, the PCA+DFA optimum composite fingerprint was composed by the largest number of tracer properties and the KW+DFA by the lowest number. All optimum composite fingerprints had the ^{40}K and ^{137}Cs radionuclides in addition to other chemical elements. None option included magnetic susceptibility properties as tracers. From the chemical elements, none of them was in the three options and some of them were in at least two optimum composite fingerprints: Al and Bi were selected by DFA and PCA+DFA, Sr was selected by DFA and KW+DFA and Ti by KW+DFA and PCA+DFA. The optimum composite fingerprints from the DFA and PCA+DFA shared most common tracers.

The selected tracers for each optimum composite fingerprint showed different patterns between sources from clearly different contents for ^{137}Cs to less differentiated contents with overlap between source as for Cr, Ni, and V (Fig. 3). The tracers variability from DFA (apart from Al and Bi) and KW+DFA showed higher or lower differences between the sources but there is overlap. Whereas from PCA+DFA with 10 selected tracers, four tracers (Al, Cr, Ni and V) only showed slight differences between sources and two (Bi and Zn) only showed differences for one source.

Fig 2.- Two-dimensional scatter plot of the first and second discriminant functions from the assessed stepwise discriminant function analysis: a) DFA; b) KW+DFA; and c) PCA+DFA.

Fig 3.- Box plots of the tracers selected as the optimum composite fingerprint for the agricultural, forest, scrubland and subsoil sources by: a) DFA; b) KW+DFA; and c) PCA+DFA.

3.2 Source apportionments

Different source apportionments were obtained for the reservoir sediment samples with the assessed options with different optimum composite fingerprints (Table 4). Similar source apportionments were obtained for DFA and KW+DFA in contrast to PCA+DFA (Fig. 4). Contributions from the forest and scrubland sources were low and similar for DFA and KW+DFA and greater for the PCA+DFA with the largest increment for scrubland source. The agricultural source had more different apportionments for each assessed option with, in general, greatest contributions for the DFA and lowest for the PCA+DFA. Subsoil source contributions were the highest for most of the options and assessed sediment samples. Within the reservoir sediments, the most different was sample G with the lowest subsoil apportionments for all assessed options and the highest apportionments from agricultural sources for the DFA and KW+DFA and the highest contribution from scrublands for the PCA+DFA.

Table 4.- Mean percentages of GOF, source contributions and their standard deviations (in parentheses) obtained as optimal solutions from the mixing model for forest, agricultural, scrubland and subsoil sources to the Barasona reservoir mixture samples (A, B, C, D, E, F and G) for the assessed options (DFA, KW+DFA, PCA+DFA).

Option		GOF	Forest	Agricultural	Scrubland	Subsoil
DFA	A	98.6	3.6 (3.2)	29.4 (15.6)	7.4 (6.6)	59.5 (13.1)
	B	99.1	2.8 (2.5)	31.2 (16.3)	6.1 (6.2)	59.9 (14.5)
	C	99.1	3.1 (2.6)	21.8 (12.9)	5.9 (5.1)	69.2 (12.0)
	D	99.4	2.4 (2.2)	41.1 (14.6)	7.1 (5.6)	49.4 (12.7)
	E	99.6	2.2 (1.9)	27.1 (13.2)	4.4 (4.1)	66.3 (12.9)
	F	99.5	2.4 (2.0)	46.4 (17.1)	5.8 (6.0)	45.5 (14.3)
	G	98.9	2.6 (2.1)	73.1 (19.4)	9.2 (7.9)	15.1 (17.1)
KW+DFA	A	98.9	5.2 (3.8)	15.7 (12.1)	6.4 (5.4)	72.7 (11.2)
	B	99.7	2.3 (1.9)	14.7 (9.7)	5.2 (4.0)	77.9 (9.0)
	C	99.5	3.0 (2.3)	16.1 (11.7)	5.2 (4.9)	75.7 (11.0)
	D	99.6	2.0 (1.9)	30.3 (15.8)	6.9 (6.0)	60.8 (13.0)
	E	99.7	2.4 (2.2)	14.1 (9.4)	5.3 (4.2)	78.3 (7.9)
	F	99.7	1.6 (1.5)	40.1 (19.7)	4.4 (4.0)	53.8 (18.2)
	G	99.2	1.9 (1.8)	84.0 (12.9)	5.9 (4.9)	8.2 (11.0)
PCA+DFA	A	90.5	6.4 (5.6)	7.4 (7.0)	9.2 (7.1)	77.0 (8.9)
	B	95.8	6.7 (5.7)	7.4 (6.6)	8.0 (7.3)	77.9 (8.7)
	C	93.0	8.6 (6.5)	9.3 (7.5)	11.6 (9.4)	70.4 (10.4)
	D	87.9	6.6 (5.5)	9.3 (9.0)	36.1 (24.1)	48.0 (20.6)
	E	95.5	6.0 (4.9)	8.9 (7.0)	11.2 (7.6)	73.9 (8.2)
	F	89.7	7.0 (6.0)	8.8 (7.4)	31.2 (21.9)	53.0 (18.9)
	G	77.6	6.6 (5.7)	9.0 (10.6)	56.0 (29.0)	28.4 (24.4)

Fig 4.- Source contribution for the reservoir sediment samples obtained by the assessed options: DFA; KW+DFA and PCA+DFA.

The dispersions of the solutions were variable from values of standard deviation from 1.5 to 30% (Table 4). Forest was the source which provided the lowest dispersion for all options. Scrubland also performed low dispersions, around 5 %, but only for the DFA

and KW+DFA with greater values for the sediment samples solved with the optimum composite fingerprint selected by the PCA+DFA. In contrast agricultural and subsoil sources yielded standard deviations greater than 9 % for DFA and KW+DFA with lower for the latter option and lower values for most of the sediment samples solved by the PCA+DFA. The latter option provided greater standard deviations ($> 18\%$) for the samples D, F and G for scrubland and subsoil sources. In general the option which provided lowest standard deviations for most of the solutions (samples and sources) was the PCA+DFA but its GOFs values indicated the lowest minimization of the objective function.

3.3 Frequency distribution of source apportionments

The configuration of the optimization procedure to solve the mixing model enabled assessing the frequency distributions of the selected solutions which defined the optimum solution. Moreover, the frequency distributions also assisted to limit the probable contribution ranges where there were more possibilities to be the solution and, inversely, to provide ranges where null contributions could be expected. As for the source apportionments, different frequency distributions for each assessed source contribution were obtained for the different optimum composite fingerprints and the sediment samples assessed (Fig. 5).

From the assessed source contributions, the frequency distributions of the solutions extracted to define the optimal solution showed narrow, symmetrical and unimodal distributions for forest sources. Similar to that occurred in most cases for scrubland sources which in the other were skewed (Fig. 5). Agricultural and subsoil sources showed more variable patterns with multimodal patterns and also patterns without a non-defined solution within the selected solution population.

From the assessed optimum composite fingerprints selected with the different statistical tests, for all sediment samples the distributions showed variable patterns with in general multimodal and dispersed patterns for agricultural and subsoil sources for DFA and less dispersed and more narrow patterns for these sources for KW+DFA and PCA+DFA. From the assessed targets, samples D, F and G provided more dispersed solutions. The greatest differences between options were for sample G that had non-defined solutions for DFA and PCA+DFA for most sources, except for scrubland. The optimum composite fingerprint which provided a better defined solution for sample G was the KW+DFA which in turn gave a more defined solution for most sources.

Fig.- 5 Frequency distributions of the 100 solutions obtained with the mixing model by the assessed options (: DFA; KW+DFA and PCA+DFA) for the Barasona reservoir mixture samples (A, B, C, D, E, F and G).

4 Discussion

From the assessed statistical test options, the widely used two step statistical process KW+DFA proposed by Collins et al. (1997) was the most restrictive in the final number of the tracer properties selected due to the robust statistical filter of difference provided by KW in this case study. The two step process PCA+DFA had the largest number of properties and from them most of the tracers have fewer differences between sources. The applied PCA selected properties with fewer differences between sources and, therefore, the posterior DFA seemed to require more properties than the other statistic procedures to achieve a subset of fingerprints which best discriminate between sources. The selection of the minimum number of properties which best discriminate between sources were influenced by the different groups of fingerprints included in each DFA analysis affecting the final provided optimum composite fingerprints.

The fallout radionuclide ^{137}Cs was crucial and its inclusion in all optimum composite fingerprints point out to its effectiveness as sediment source tracer because its largest differences between activities in surface sources for the different land uses. Although ^{40}K was also included in all options, it showed lower differences between sources than ^{137}Cs with higher amounts in the subsoil source. This could be related with the range of contents of potassium in sedimentary rocks related with the argillaceous materials (Kabata-Pendias and Pendias, 2001) which are the dominant lithology of the substrate in the subsoil sources.

From the other tracers which were selected to take part in more than one optimum composite fingerprints, Sr and Ti also showed clear differences in their contents between sources. Large differences of Sr content in subsoil sources, which almost doubled those in the other land uses, are likely related to the carbonate sediment nature of the parent materials which concentrate Sr (Navas and Machín, 2002) and the high clay mineral capacity to absorb this element (Kabata-Pendias and Pendias, 2001). Lower Ti content in subsoil samples in comparison with the other sources might reflect the effects of weathering. As Ti minerals are very stable, the loss of some clay-size layered silicates might increase the amount of Ti in the upper horizons of soil (Kabata-Pendias and Pendias, 2001). Therefore, better developed and undisturbed soils as in the scrubland and forest sources could have their topsoils more enriched in Ti than eroded areas.

Lower differences between sources were found for Li and Bi with higher amounts in the subsoil source, whereas contents in the other land uses are similar. This could be related with the range of contents found for both elements in sedimentary rocks (Kabata-Pendias and Pendias, 2001) related with the argillaceous materials predominating in the subsoil sources. A similar behaviour and origin is found for K which appears highly related with the contents of the radioisotope ^{40}K . Differences in the content of Fe between sources are related with the contents of oxides and hydroxides that are more abundant in developed soils which predominate in forest and scrubland sources. The

greater content of B and Zn in agricultural sources is likely related to micronutrients added with fertilizers.

The magnetic properties were not found to discriminate the sediment sources in this study. In a previous fingerprinting study by Palazón et al. (2014) carried out in the headwater of the Barasona catchment, the low-frequency magnetic susceptibility (LF) was selected for the optimum composite fingerprint to discriminate between soil sources. However, as for the Isábena catchment (Palazón et al., 2015a), this was not the case in the Barasona catchment likely because its predominant lithology comprises sedimentary rocks with more homogeneous values of magnetic susceptibility, which differed from that of soils in the headwater of the Barasona catchment.

Although the four characterised sources reflected well the dominant land uses/land covers in the catchment and satisfactory source discriminations consistent with the conceptual understanding of the catchment were achieved, some overlapping existing between forest, scrubland and agricultural sources is likely related with rapid changes in land uses that occurred in the past century. This is meaningful in the context of known catchment history and reflects the succession states between former agricultural areas (Brosinsky et al., 2014) that are partly reverting to natural forests after land abandonment (e.g. Lasanta and Vicente-Serrano, 2012) which might influence the fingerprint content of the sources. Besides the similar lithological characteristics of the overlapping points might also account for the lack of clear discrimination between these two sources. In spite of this source characterization which aims to assess differences in sediment contributions to the reservoir filling between the main differentiated and problematic source contributors (subsoil and agricultural land) and the secondary sources (scrubland and forest), a sediment source discrimination based in an objective statistical procedure as recently proposed Pulley et al. (2016) will be investigated in future research for increasing the robustness of the source characterisation to derive relative source contributions.

Similar to findings reported in a previous study (Palazón et al., 2015b), differences in source contributions obtained for the same sediment sample when using different optimum composite fingerprints were observed. This fact strengthens the need to be careful when selecting statistical tests to investigate the optimum composite fingerprint for catchment applications.

Source apportionments were more similar for DFA and KW+DFA options, in spite of DFA and PCA+DFA were the options which shared more properties in their optimum composite fingerprints. The mixing model configuration provided a statistical comparable optimal solution, based in a defined number of solutions, that enabled the comparison between the options and solutions. Although standard deviations of PCA+DFA were the lowest for most of the solutions (samples and sources), GOFs achieved by this statistic procedure were the smallest and KW+DFA showed a more defined solution for most sediment samples (including G). The large number of properties selected by PCA+DFA, with most of them showing less differentiated

fingerprint contents for the sources, could introduce covariance and noise favouring the source overlapping effect in the mixing model affecting its performance and forcing it to provide a solution. Moreover, this could be also related with lowest GOFs values achieved by the mixing model with this optimum composite fingerprint.

The reliable interpretation of sediment provenance requires knowledge of different potential source areas and sediment mixtures or targets. Mixing model solutions for DFA and KW+DFA are more consistent with the results of other studies undertaken in the Barasona catchment for modelling sediment source productions which identified badland and agricultural sources as major and secondary contributors (Alatorre et al., 2010; Palazón and Navas, 2014). Furthermore, forest and scrubland sources are also expected to contribute less to the reservoir than agricultural and badland sources, since the soil is predominantly better protected by the vegetation cover (Palazón and Navas, 2016) limiting both sediment detachment and subsequent transport. Contribution results for the sample G could be used to assess the ability of the fingerprinting procedure to discriminate between the assessed sediment sources. As this sample is located in a branch located at the lower eastern part of the reservoir that receives the discharge of the Sarrón stream, therefore, its source contributions are likely to be different to the other reservoir samples as sediments in this part of the reservoir should be closely related to the characteristics of its contributing subcatchment. The stream drains a small area of the catchment mostly covered with agricultural lands with high connectivity to the stream by small gullies. Other distinctive feature is the absence of badlands. Moreover, the subcatchment is isolated connecting to the rest of the Barasona catchment only through the reservoir. Therefore, sediment contributions of sample G are expected to have predominant contributions of agricultural sources and null contributions from badlands despite other subsoil sources could be represented. As the PCA+DFA optimal solution for sample G unfitted this conceptual understanding, the reliability of its solutions for the reservoir sediments should be questioned and therefore PCA+DFA results are not considered to provide meaningful apportionments in this case study.

Although recent work using unmixing models has shown that the inclusion of larger numbers of tracer properties in optimum sediment fingerprints can actually decrease uncertainty ranges in source apportionments (Pulley et al., 2015) and also provide better results in the region (Palazón et al., 2015b), for the Barasona catchment the optimum composite fingerprint selected by the two step process KW+DFA with the least number of properties appeared to provide the best and most reliable option for the discrimination of contributing sources.

It should be taken into account when interpreting the findings of this study that sampling in the reservoir was undertaken for a single campaign due to available funding limiting the observation to the most recent reservoir filling. Even so, the fingerprinting results were in accordance with previous studies in the catchment about sediment production of the catchment. More sampling campaigns (yearly or seasonally) could show temporal changes in catchment source apportionments as recorded from suspended sediment samples in the Isábena catchment (Brosinsky et al., 2014).

5 Conclusions

In this study three statistically selected optimum composite fingerprints were used to assess sediment source contribution solutions based in land uses/land covers for reservoir sediment samples. Different source contribution estimates between the composite fingerprints indicated that the statistical procedure for property selection is fundamental to obtain reliable source contribution results for each specific application.

Configuration of the mixing model provided comparable solutions which facilitate the selection of the best option by direct comparison of the results. The standard deviation and the frequency distribution of the solutions obtained for the source contributions by the assessed sediments and the achieved GOFs were used to compare the options. The statistical discrimination based on the widely used KW+DFA tracer selection two step process was found to be the most effective option yielding the most reliable results for this case study. Furthermore, differences in source apportionments between PCA+DFA and the other two options could be related to inclusion in the composite fingerprint of properties which showed less differences between sources (Cr, Ni, V) which may cause the overlapping of sources affecting the mixing model results.

Although fingerprinting results for the reservoir could be considered representative for this large catchment, additional sediment samples along the rivers could enhance the knowledge about source apportionments delivered through the system to the Barasona reservoir. Further research is needed to understand the role of varying sediment source contributions and upstream erosion on sediment dynamics within the catchment.

The inherent complexity of a river system to produce and transport fine sediment indicates that care should be taken when sediment fingerprinting results are interpreted. Previous conceptual understanding of the erosion processes taking place in the study catchments are found to be important in evaluating the reliability of the apportionments provided by the unmixing models.

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References

- Alatorre, L.C., Beguería, S., García-Ruiz, J.M., 2010. Regional scale modeling of hillslope sediment delivery: a case study in the Barasona Reservoir watershed (Spain) using WATEM/SEDEM. *J. Hydrol.* 391, 109–123.
- Avendaño-Salas, C., Sanz-Montero, E., Cobo-Rayán, R., Gómez-Montaña, J.L., 1997. Sediment yield at Spanish reservoirs and its relationship with the drainage basin area. In: *Proceedings of the 19th Symposium of Large Dams. ICOLD (International Committee on Large Dams), Florence, Italy*, pp 863–874.

- Brosinsky, A., Foerster, S., Segl, K., López-Tarazón, J.A., Piqué, G., Bronstert, A., 2014. Spectral fingerprinting: characterizing suspended sediment sources by the use of VNIR-SWIR spectral information. *Journal of Soils and Sediments*, 14:1965–1981.
- Collins A.L., Walling D.E., Leeks G.J., 1997. Source type ascription for fluvial suspended sediment based on a quantitative composite fingerprinting technique, *Catena* 29, 1–27.
- Collins A.L., Walling D.E., 2002. Selecting fingerprint properties for discriminating potential suspended sediment sources in river basins. *J Hydrol* 261:218–244.
- Collins, A.L., Walling, D.E., Stroud, R.W., Robson, M., Peet, L.M., 2010a. Assessing damaged road verges as a suspended sediment source in the Hampshire Avon catchment, southern United Kingdom. *Hydrol. Process* 24, 1106–1122.
- Collins, A.L., Walling, D.E., Webb, L., King, P., 2010b. Apportioning catchment scale sediment sources using a modified composite fingerprinting technique incorporating property weightings and prior information. *Geoderma* 155, 249–261.
- D'Haen K., Verstraeten G., Degryse P., 2012. Fingerprinting historical fluvial sediment fluxes, *Prog. Phys. Geogr.* 36, 154–186.
- Fargas, D., Martínez Casasnovas, J.A., Poch, R., 1997. Identification of critical sediment source areas at regional level. *Phys. Chem. Earth.* 22, 355–359.
- Foster I.D.L., Lees J.A., 2000. Tracers in geomorphology: theory and applications in tracing fine particulate sediments, In: Foster I.D.L., (Ed), *Tracers in Geomorphology*, John Wiley and Sons Ltd.; Chichester, pp 3–20.
- García-Ruiz, J.M., Beguería, S., López-Moreno, J.I., Lorente, A., Seeger, M., 2001. Los recursos hídricos superficiales del Pirineo aragonés y su evolución reciente. *Geoforma Ediciones*, Logroño, Spain.
- Gaspar, L., Navas, A., Walling, D.E., Machín, J., Gómez Arozamena, J., 2013. Using ^{137}Cs and ^{210}Pb to assess soil redistribution on slopes at different temporal scales. *Catena* 102, 46–54.
- Granger, S.J., Bol, R., Butler, P.J., Haygarth, P.M., Naden, P., Old, G., Owens, P.N., Smith, B.P.G., 2007. Processes affecting transfer of sediment and colloids, with associated phosphorus, from intensively farmed grasslands: tracing sediment and organic matter. *Hydrol. Process.* 21, 417–422.
- Gruszowski, K.E., Foster, I.D.L., Lees, A., Sediment sources and transport pathways in a rural catchment, Herefordshire, UK. *Hydrol. Process.* 17, 2003, 2664–2681.
- Haddadchi A., Ryder D.S., Evrard O., Olley J., 2013. Sediment fingerprinting in fluvial systems: review of tracers, sediment sources and mixing models, *Int. J. Sediment Res.* 28, 560–578.

- Haddadchi A., Olley J., Laceby P., 2014. Accuracy of mixing models in predicting sediment source contributions, *Sci. Total Environ.* 497, 139–152.
- Hughes, A.O., Olley, J.M., Croke, J.C., McKergow, L.A., 2009. Sediment source changes over the last 250 years in a dry-tropical catchment, central Queensland, Australia. *Geophys J Roy Astron Soc*, 104, 262–75.
- Kabata-Pendias, A., Pendias, H., 2001. Trace elements in soils and plants. CRC, Boca Raton, pp 315.
- Lasanta, T., Vicente-Serrano, S.M., 2012. Complex land cover change processes in semiarid Mediterranean regions: an approach using Landsat images in northeast Spain. *Remote Sens Environ* 124, 1–14.
- López-Tarazón, J.A., López, P., Gemma Lobera, G., Ramon J. Batalla, R.J., 2015. Suspended sediment, carbon and nitrogen transport in a regulated Pyrenean river. *Sci. Total Environ.* 540, 133-143.
- Mabit, L., Benmansour, M., Abril, J.M., Walling, D.E., Meusburger, K., Iurian, A.R., Bernard, C., Tarján, S., Owens, P.N., Blake, W.H., Alewell, C., 2014. Fallout ^{210}Pb as a soil and sediment tracer in catchment sediment budget investigations: a review. *Earth-Sci. Rev.* 138, 335–351.
- Martínez-Carreras, N., Udelhoven, T., Krein, A., Gallart, F., Iffly, J.F., Ziebel, J., Hoffmann, L., Pfister, L., Walling, D.E., 2010. The use of sediment colour measured by diffuse reflectance spectrometry to determine sediment sources: application to the Attert River catchment (Luxembourg). *J. Hydrol.* 382, 49–63.
- Minella, J.P.G., Walling, D.E., Merten, G.H., 2008. Combining sediment source tracing techniques with traditional monitoring to assess the impact of improved land management on catchment sediment yields. *J. Hydrol* 348, 546-563.
- Motha, J.A., Wallbrink, P.J., Hairsine, P.B., Grayson, R.B., Determining the sources of suspended sediment in a forested catchment in southeastern Australia. *Water Resour. Res.* **39**, 2003,1056.
- Mukundan, R., Walling, D.E., Gellis, A.C., Slattery, M.C., Radcliffe, D.E., 2012. Sediment source fingerprinting: transforming from a research tool to a management tool. *American Water Resources Association (JAWRA)*. 48(6), 1241-1257.
- Navas, A., Valero, B., Machín, J., Walling, D., 1998. Los sedimentos del embalse de Joaquín Costa y la historia de su depósito. *Limnetica* 14, 93–112.
- Navas, A., Machín, J., 2002. Spatial distribution of heavy metals and arsenic in soils of Aragón (northeast Spain): controlling factors and environmental implications. *Appl. Geochem.* 17, 961–973.

- Navas, A., Valero-Garcés, B.L., Machín, J., 2004. An approach to integrated assessment of reservoir siltation: the Joaquín Costa reservoir as a case study. *Hydrol. Earth Syst. Sci.* 8, 1193–1199.
- Navas, A., Soto, J., López-Martínez, J., 2005a. Radionuclides in soils of Byers Peninsula, South Shetland Islands, Western Antarctica. *Appl. Radiat. Isot.* 62 (5), 809–816.
- Navas, A., Soto, J., Machín, J., 2005b. Mobility of natural radionuclides and selected major and trace elements along a soil toposequence in the central Spanish Pyrenees. *Soil Sci.* 170 (9), 743–757.
- Navas, A., Machín, J., Beguería, S., López-Vicente, M., Gaspar, L., 2008. Soil properties and physiographic factors controlling the natural vegetation re-growth in a disturbed catchment of the Central Spanish Pyrenees. *Agrofor. Syst.* 72 (3), 173–185.
- Navas, A., Valero-Garcés, B., Gaspar, L., Machín, J., 2009. Reconstructing the history of sediment accumulation in the Yesa reservoir: An approach for management of mountain reservoirs. *Lake Reserv. Manage.* 25 (1), 15–27.
- Navas, A., López-Vicente, M., Gaspar, L., Palazón, L., Quijano, L., 2014. Establishing a tracer based sediment budget to preserve wetlands in Mediterranean mountain agroecosystems (NE Spain). *Sci. Total Environ.* 496, 132–143.
- Palazón, L., Navas, A., 2013. Sediment production of an alpine catchment with SWAT. *Z. Geomorphol.* 57, 69–85.
- Palazón, L., Gaspar, L., Latorre, B., Blake, W.H., Navas, A., Evaluating the importance of surface soil contributions to reservoir sediment in alpine environments: a combined modelling and fingerprinting approach in the Posets-Maladeta Natural Park, *Solid Earth* 5, 2014, 963–978.
- Palazón, L., Navas, A., 2014. Modeling sediment sources and yields in a Pyrenean catchment draining to a large reservoir (Ésera River, Ebro Basin). *J. Soil Sediment.* 14, 1612–1625.
- Palazón, L., Gaspar, L., Latorre, B., Blake, W.H., Navas, A., 2015a. Identifying sediment sources by applying a fingerprinting mixing model in a Pyrenean drainage catchment. *J. Soils Sediments* 15, 2067–2085.
- Palazón, L., Latorre, B., Gaspar, L., Blake, W.H., Smith, H.G., Navas, A., 2015b. Comparing catchment sediment fingerprinting procedures using an auto-evaluation approach with virtual sample mixtures. *Sci. Total Environ.* 532, 456–466.
- Palazón, L., Navas, A., 2016. Land use sediment production response under different climatic conditions in an alpine-prealpine catchment. *Catena* 137:244–255.

- Palazón, L., Latorre, B., Gaspar, L., Blake, W.H., Smith, H.G., Navas, A., 2016. Combining catchment modelling and sediment fingerprinting to assess sediment dynamics in a Spanish Pyrenean river system. *Sci. Total Environ.* DOI: 10.1016/j.scitotenv.2016.06.189
- Pulley, S., Foster, I., Antunes, P., 2015. The uncertainties associated with sediment fingerprinting suspended and recently deposited fluvial sediment in the Nene river basin. *Geomorphology*, 228, 303-319.
- Pulley, S., Foster, I., Collins, A.L., 2016. The impact of catchment source group classification on the accuracy of sediment fingerprinting outputs, *Journal of Environmental Management*, DOI: 10.1016/j.jenvman.2016.04.048.
- Russell, M.A., Walling, D.E., Hodgkinson, R.A., 2001. Suspended sediment sources in two small lowland agricultural catchments in the UK. *J Hydrol* 252:1–24.
- Schuller, P., Walling, D.E., Iroumé, A., Quilodrán, C., Castillo, A., Navas, A., 2013. Using ^{137}Cs and ^{210}Pb and other sediment source fingerprints to document suspended sediment sources in small forested catchments in south-central Chile. *J. Environ. Radioact.* 124, 147–159.
- Smith, H.G., Blake, W.H., 2014. Sediment fingerprinting in agricultural catchments: a critical re-examination of source discrimination and data corrections. *Geomorphology* 204, 177–191.
- Stone, M., Collins, A.L., Silins, U., Emelko, M.B., Zhang, Y.S., 2014. The use of composite fingerprints to quantify sediment sources in a wildfire impacted landscape, Alberta, Canada. *Sci. Total Environ.*, 473-474, 642-650.
- Tiecher, T., Caner, L., Minella, J.P.G., Santos, D.R.D., 2015. Combining visible-based-color parameters and geochemical tracers to improve sediment source discrimination and apportionment. *Sci. Total Environ.*, 527-528, 135-149.
- Valero-Garcés, B.L., Navas, A., Machín, J., Walling, D., 1999. Sediment sources and siltation in mountain reservoirs: a case study from the Central Spanish Pyrenees. *Geomorphology* 28, 23–41.
- Walling, D.E., Woodward, J.C., Nicholas, A.P., 1993. A multi-parameter approach to fingerprinting suspended sediment sources. In: Peters NE, Hoehn E, Leibundgut Ch, Tase N, Walling DE (eds) *Tracers in hydrology*. IAHS Publication no. 215. IAHS, Wallingford, pp 329–338
- Walling, D.E., 2005. Tracing suspended sediment sources in catchments and river systems. *Sci. Total Environ.* 344, 150-184.
- Walling, D.E., 2013. The evolution of sediment source fingerprinting investigations in fluvial systems. *J. Soils Sediments* 13, 1658–1675.

Wasson, R.J., Caitcheon, G., Murray, A.S., McCulloch, M., Quade, J., 2002. Sourcing sediment using multiple tracers in the catchment of Lake Argyle, Northwestern Australia. *Environ Manage* 29:634–646

Wilkinson, S.N., Hancock, G.J., Bartley, R., Hawdon, A.A., Keen, R.J., 2013. Using sediment tracing to assess processes and spatial patterns of erosion in grazed rangelands, Burdekin River basin, Australia. *Agr. Ecosyst. Environ.* 180, 90–102.