• **Title**

Comparing catchment sediment fingerprinting procedures using an auto-evaluation approach with virtual sample mixtures

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Highlights:

• Virtual sample mixtures were generated from possible sediment sources.

• 24 fingerprinting procedures were tested.

• Goodness of fit should not be used as an accuracy index of contribution estimates.

• More tracers in a composite fingerprint would improve source apportionment results.

• Different contributions can be obtained with different fingerprinting procedures.

Abstract

Information on sediment sources in river catchments is required for effective sediment control strategies, to understand sediment, nutrient and pollutant transport, and for developing soil erosion management plans. Sediment fingerprinting procedures are employed to quantify sediment source contributions and have become a widely used tool. As fingerprinting procedures are naturally variable and locally dependant, there are different applications of the procedure. Here, the auto-evaluation of different fingerprinting procedures using virtual sample mixtures is proposed to support the selection of the fingerprinting procedure with the best capacity for source discrimination and apportionment. Surface samples from four land uses from a Central Spanish Pyrenean catchment were used i) as sources to generate the virtual sample mixtures and ii) to characterise the sources for the fingerprinting procedures. The auto-evaluation approach involved comparing fingerprinting procedures based on four optimum composite fingerprints selected by three statistical tests, three source characterisations (mean, median and corrected mean) and two types of objective functions for the mixing model. A total of 24 fingerprinting procedures were assessed by this new approach which were solved by Monte Carlo simulations and compared using the root mean squared error (RMSE) between known and assessed source ascriptions for the virtual sample mixtures. It was found that the source ascriptions with the highest accuracy were

achieved using the corrected mean source characterisations for the composite fingerprints selected by the Kruskal Wallis H-test and principal components analysis. Based on the RMSE results, high goodness of fit (GOF) values were not always indicative of accurate source apportionment results, and care should be taken when using GOF to assess mixing model performance. The proposed approach to test different fingerprinting procedures using virtual sample mixtures provides an enhanced basis for selecting procedures that can deliver optimum source discrimination and apportionment.
Keywords: sediment fingerprinting, mixing model, sediment source ascription, sediment contribution, river catchments

Abbreviations: GOF: goodness of fit; RMSE: root mean squared error; KW: Kruskal–Wallis *H*-test; DFA: discriminant function analysis; PCA: principal components analysis.

1. Introduction

Research on source fingerprinting procedures and their development to provide information on the sources of sediment transported through a river catchment can be traced back to the 1970s including works of Klages and Hsieh (1975), Wall and Wilding (1976) and Walling et al. (1979). Since these early works, sediment source fingerprinting applications have expanded greatly. Walling (2013) identified a key driver behind the expansion of such work as the need to support the development of sediment management strategies aimed at dealing with environmental problems associated with fine sediment. This expansion in sediment fingerprinting procedure led to the use of variable sediment fingerprinting applications tailored to the wide range of potential controls on sediment properties and the contributions from catchment sediment sources. Sediment fingerprinting procedures offer potential to quantify the contribution of different catchment sediment sources, evaluate erosion dynamics and serve as a basis to develop management plans to tackle erosion and sediment related problems, especially in catchments with land use conflicts (Pacheco et al., 2014; Valle Junior et al., 2014).

Based on differences in source material properties, fine sediment fingerprinting allows the discrimination and apportionment of sediment derived from sampled catchment sources (Walling et al., 1999). The use of statistical tests to confirm the ability of the properties to discriminate between the sources and to select the best subset of properties for the composite fingerprint in most early fingerprinting studies were unnecessary as they were based in a limited number of sources (e.g. two) and tracer properties (perhaps only one). Along with the development of the fingerprinting procedure, the number of potential sources and fingerprint properties increased and, therefore, the need to use statistical tests to select the optimum composite fingerprints became more important and therefore was increasingly recognized. As a minimum, n - 1 properties are necessary to discriminate rigorously between n sources. Additional properties are frequently necessary to increase the reliability of the results (Walling, 2013). These tracer properties may include geochemical, radionuclide, mineral magnetic, organic constituent, stable isotope and colour properties (Foster and Lees, 2000). Therefore, the sediment fingerprinting procedure typically first identifies a subset of tracer properties that discriminate the sampled sources by different statistical tests (Collins and Walling, 2002) and then estimates the proportional contributions from each source using mixing models to solve the set of linear equations characterised by the selected tracer properties (e.g. Yu and Oldfield, 1989; Motha et al., 2003; Martinez-Carreras et al., 2010; Blake et al., 2012; Owens et al., 2012; Schuller et al., 2013; Smith and Blake, 2014). Source apportionments are obtained by the solution of a set of linear equations characterised by an objective function, which represents the relation between a tracer property value in sediment with the sum of multiplications between that tracer value and the unknown apportionment for each source by optimization approaches. Several variants of the objective function have been used by different authors by incorporating correction factors for differences in particle size and organic matter content between target and source material samples (Collins et al., 1997) and the use of weightings and elemental correlations for the individual tracer properties, in order to vary the emphasis placed on individual properties when fitting the model (e.g. Collins et al., 2010, 2012; Laceby and Olley, 2014). Although most fingerprinting studies employed local optimization routines to obtain the source contributions, these routines can fail to find the best optimum solution (Collins el at, 2012). Genetic algorithm optimization and the use of stratified random sampling of the property probability distributions using Latin Hypercube Sampling have been proposed to overcome this problem (e.g. Collins et al., 2012; Haddadchi et al., 2013). Other tools such as Bayesian approaches in mixing model applications have also been successfully applied in fingerprinting procedures (e.g. Fox and Papanicolaou, 2008; Massoudieh et al., 2012; D'Haen et al., 2013).

There is a range of different applications of the sediment fingerprinting procedure in the literature and, in general, the greatest methodological differences are related to: i) the statistical analysis used to identify the subset of the tracer properties which discriminate between sources; ii) the way in which the sources were characterised for the mixing model (i.e. mean, median or corrected mean); iii) the use of correction factors (including weighting and elemental correlations) in the objective function; iv) the type of the objective function and v) the optimisation procedure used to solve the mixing model. These differences between applications were in many cases due to the specific characteristics of the study areas and, therefore, the selection of the most effective fingerprinting procedure for each specific application can become time-consuming and complex.

The accuracy and sensitivity of the tracer selection and source un-mixing procedures associated with sediment fingerprinting have received limited attention. Haddadchi et al., (2013) compared mixing models applying local and global optimization methods to datasets from two different catchments and indicated that the mixing model outputs could change remarkably depending on which mixing model was used. More recently, Haddadchi et al. (2014) compared the accuracy of four defined mixing models to solve artificial mixture samples from three well-differentiated sources concluding that there is a need to test mixing models using known source and mixture samples prior to applying them to field samples. Laceby and Olley (2014) compared different mixing models used in the literature to analyse artificial mixture samples based on catchment sources and concluded that the most accurate procedures incorporated correlations between elements and did not use tracer discriminatory weightings. These few studies highlight the methodological uncertainty hampering the wider adoption of the fingerprinting approach for identifying sediment sources. There remains a need for further methodological guidance to aid the assessment of accuracy and to support pre-selection of the most effective fingerprinting procedures for catchment applications.

Whereas the accuracy of the fingerprinting procedures has started to be evaluated with well-differentiated sources (Haddadchi et al., 2014), this study aims to evaluate the accuracy of a set of fingerprinting procedures for a river catchment in which sources are less well differentiated. The selected catchment is representative of the Mediterranean environment that was subject to intense land use changes that drive sediment production and where sediment sources based on land use might not be clearly discriminated. As an approach for pre-selecting the most effective fingerprinting procedure, we propose to test the discriminatory accuracy of different fingerprinting procedures by generating virtual sample mixtures using known and natural source samples. These virtual sample mixtures were used to assess the capacity of various fingerprinting procedures to reproduce the known source apportionments. The auto-evaluation of the procedure could guide the fingerprinting procedure design and be used to assess the robustness of the results.

2. Material and methods

2.1 Study area

The samples used to characterise potential sources and create the virtual sample mixtures were collected in the Isábena River catchment (445 km^2) of the Central Spanish Pyrenees (Fig.1). Climatically, the catchment falls in the Mediterranean domain. Mean annual precipitation in the catchment is around 767 mm and ranges from

450 mm at the outlet to 1600 mm at the headwater (Verdú et al., 2006). The mean annual temperature ranges from 12.5 °C at the outlet to 10°C in the headwater. The headwater of the catchment is partially karstified with predominance of Cretaceous limestones. In the intermediate part of the catchment the presence of Eocene marls comprises depressions in which badlands are developed. In the southern lowland area, Tertiary sedimentary rocks (clays, sandstones and conglomerates) are predominant. The climatic and topographic characteristics of the catchment influenced the distribution of land uses in the Isábena catchment. Therefore, the agricultural lands predominate in the lowland areas, whereas forests and interspersed grasslands and scrubland dominate the highlands (Fig 1). Forests and grassland are the main land uses occupying more than 50 % of the catchment, followed by cultivated land that occupies less than 20 % and scrublands which cover 10% of the catchment surface area. Important changes in land use occurred during the last 60 years in the Spanish Pyrenean region, resulting in substantial land abandonment that has affected most parts of the agricultural areas triggering the subsequent process of natural reforestation (Navas et al., 2008).

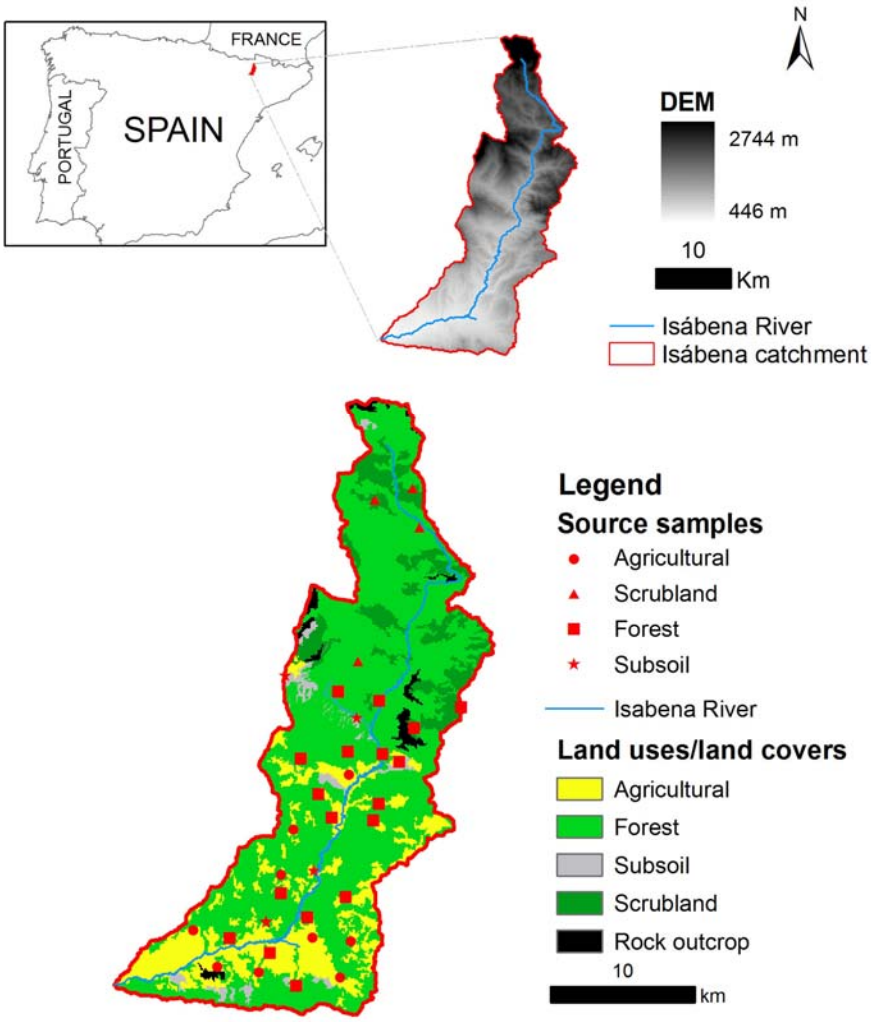


Fig. 1 Location and DEM of the Isábena River catchment with the sites and types of surficial source samples and the distribution of land uses/land covers in the catchment.

The sediment production in the Isábena catchment of around 400 t km^{-2} $year^{-1}$, contributes to the siltation of the downstream Barasona reservoir (e.g. Palazón and Navas, 2014). Previous studies point out that although badlands occupy less than 1% of the catchment they constitute the main source of sediment (Alatorre et al., 2010; López-Tarazón et al., 2012; Palazón and Navas, 2014). Most studies indicated that the secondary source of sediment is the cultivated lands (Alatorre et al., 2010, Palazón and Navas, 2014). The above-mentioned studies showed that erosion processes in the catchment are greatly affected by the vegetation cover which in turn is related to differentiated soils developed on heterogeneous lithologies. Therefore because of the importance of land uses and land covers in the production of sediment this study is based in source categories that are classified by land use/land covers. Thus, source samples are classified as agricultural, forest, scrubland and subsoil sources. 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. Forest sources are composed of oaks and pines with interspersed grasslands. Scrubland sources and forest sources are separated because the scrubland sources might represent areas which were burned at the beginning of the previous century to produce pastures for grazing, and at present, have dense vegetation. Subsoil sources are representative of eroded areas and badlands.

2.2 Sample selection and analysis

Source samples were collected by using a cylindrical core 5 cm long and 6 cm of diameter. In each sampling point four samples were taken and combined in the field to form a representative composite source samples. Eighteen composite samples were collected from cultivated fields, 9 from forest, 4 from scrubland and 5 from subsoil sources (See figure 1). Surface sources were sampled in representative sites 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 areas of the catchment, areas with slope above 30% and altitude above 2000 m a.s.l. were excluded from the sampling, besides in general these areas consist of rock outcrops. In addition, the number of representative sites to be sampled 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 Isábena River catchment (Fig. 1). 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 material (e.g. Walling, 2005).

Sample grain size was determined using a laser diffraction particle size analyser. Prior to analysis, organic matter was eliminated with an H_2O_2 (10%) digest heated to 80 °C. Samples were disaggregated with sodium hexametaphosphate (40%), stirred for 2 hours and dispersed with ultrasound for one minute. Soil organic carbon content was analysed using finely ground subsamples with a dry combustion method using LECO *RC-612* multiphase carbon analyser designed to differentiate forms of carbon by oxidation temperature.

Mass specific magnetic susceptibility (χ) (10^{-8} m^3 kg^{-1}) 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}).

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). Samples were analysed for the following 28 elements: Li, K, Na (alkaline), Be, Mg, Ca, Sr (light metals), Cr, Cu, Mn, Fe, Al, Zn, Ni, Co, Cd, Tl, Bi, V, Ti and Pb (heavy metals), B, Sb, As (metalloids), and P, S, Mo and Se. Analyses were performed in triplicate by inductively coupled plasma atomic emission spectrometry (ICP-AES) and resulting concentrations expressed in mg/kg. Those elements returning measurements below the detection limit (Co, Cd and Se) were excluded from the study. P was also excluded on the basis of the risk of non-conservative behaviour during downstream transport (Granger et al., 2007).

The methods used in the analysis of radionuclides are described in detail elsewhere (Navas et al., 2005a, b, 2014). Radionuclide activity concentrations of ^{238}U, ^{226}Ra, ^{232}Th,

^{40}K, ^{210}Pb, and ^{137}Cs (expressed in Bq kg^{-1} air-dry soil) in the samples were measured using a Canberra high resolution, low background, hyperpure germanium coaxial gamma detector. The detector had a relative efficiency of 50% and a resolution of 1.9 keV (shielded to reduce background), and was calibrated using standard soil samples that had the same geometry as the measured samples. Plastic containers were filled with 50 g subsamples.

Considering the appropriate corrections for laboratory background, ^{238}U was determined from the 63-keV line of ^{234}Th, the activity of ^{226}Ra was determined from the 352-keV line of ^{214}Pb (Van Cleef, 1994); ^{210}Pb activity was determined from the 47 keV photopeak, ^{40}K from the 1461 keV photopeak; ^{232}Th was estimated using the 911-keV photopeak of ^{228}Ac, and ^{137}Cs activity was determined from the 661.6 keV photopeak.

2.3 Virtual sample mixtures and fingerprinting procedure auto-evaluations

Virtual sample mixtures were generated using tracer data from the four selected representative catchment sources for testing of the various sediment fingerprinting procedures. A total of 333 virtual sample mixtures for each combination of 2, 3 and 4 sources were generated assuming zero contributions from the remaining sources when only 2 or 3 sources were used. The various combinations of sources in the virtual sample mixtures aimed to be representative of all possible source apportionment mixtures. Combinations of source samples and their apportionments were selected randomly with the only assumption that apportionments have to sum 1. Each virtual sample was derived as a simple proportional mixture using the tracer property data for the source categories. Since source samples are used to generate the virtual sediment sample mixtures, the tracer concentrations of the virtual sediments lie within the range of the sources. The source categories were represented by one of their individual samples which were randomly selected for generating each virtual sample mixture. Mean or median values of the sources were not used to generate the virtual samples.

From the different applications of the fingerprinting procedure, we tested combinations of four optimum composite fingerprints derived from three statistical tests, three source characterisations (mean, median and corrected mean) and two types of the objective function used in the minimization of the mixing model. All of these combinations resulted in a total of 24 procedures.

The accuracy of the fingerprinting procedures to solve the virtual sample mixtures was characterised by the averaged root mean squared error (RMSE) between the predicted and known apportionments used to generate the virtual sample mixtures for each un-mixing case.

The error rates obtained by a given fingerprinting procedure depend on several factors, such as the number of sources or the selected error norm, and therefore an error limit is required. For this purpose, a random guess method computed using a large number of random samples (n= 10^7) was used as a reference of the expected maximum error in discriminating source apportionments in which un-mixing apportionments were proposed randomly.

2.4 Statistical analysis for source discrimination

As potential source material were characterised by measurements of a large number of fingerprint properties (n=29), different statistical tests could be used to identify a subset of those properties capable of discriminating between the potential sources and to provide an optimum composite fingerprint. The Kruskal–Wallis *H*-test (KW), the stepwise discriminant function analysis (DFA) and two different applications of the principal components analysis (PCA1 and PCA2) were used in this study. The nonparametric 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). The DFA identifies an optimum source fingerprint that comprises the minimum number of tracer properties that provide the greatest discrimination between the analysed source materials 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. Principal components analysis (PCA) provides a useful means to analyse variance in tracer datasets and reduce dimensionality (D'Haen et al., 2012). Two applications of the PCA identified with eigenvalues in excess of 1 were used. One application was used to identify tracer properties with the highest component loadings following a Varimax rotation of the identified principal components (PCA1). The other PCA application was based in the transformation of the original dataset (source and virtual sample mixtures) projecting them into a new coordinate system defined by the identified principal components (PCA2). The PCA2 was used to assess natural clustering of samples and to evaluate overall sources variability.

2.5 Estimation of source contribution

The relative contribution of each potential sediment source for the virtual sample mixtures was assessed assuming that the tracer properties come exclusively from the possible sources by a conservative mass balance, where:

$$\sum_{j=1}^{m} a_{i,j} \cdot x_j = b_i$$

which satisfies the following constraints:

$$\sum_{j=1}^{m} x_j = 1$$

$$0 \leq x_j \leq 1$$

where, $a_{i,j}$ is the mean concentration of tracer property i in source type j ($j = 1$ to m), b_i is the value of tracer property i ($i = 1$ to n) in the sample mixture, x_j is the relative weighting contribution of source type j to the virtual sample mixture, m is the number of potential source types, and n is the number of tracer properties.

Because the model is overparameterised it does not have a closed solution and a numerical method is required to obtain the relative contributions of sources (e.g. Walling et al., 1993; Collins et al., 1997). Most procedures involve an optimisation procedure based on minimisation of an objective function reflecting the difference between the measured property values associated with the sample mixture and those predicted by the mixing model for a given set of relative source contributions. In other studies, the objective function is based on the sum of squares of the relative errors and several variants of this objective function have been proposed (e.g. Motha et al., 2003, 2004; Hughes et al., 2009; Evrard et al., 2011; Navratil et al., 2012). In this study the predicted relative apportionments from each mass balance equation were solved minimising two objective functions and a goodness of fit (GOF) was obtained for each option. GOF1 based on the sum of the relative errors and GOF2 based on the sum of squares of the relative errors

$$GOF1 = 1 - \frac{1}{n} \times \left(\sum_{i=1}^{n} \frac{\left| b_i - \sum_{j=1}^{m} x_j a_{i,j} \right|}{\Delta_i} \right)$$

$$GOF2 = 1 - \frac{1}{n} \times \sum_{i=1}^{n} \left\{ \left(\frac{\left| b_i - \sum_{j=1}^{m} x_j a_{i,j} \right|}{\Delta_i} \right)^2 \right\}$$

where Δ_i is used as correction factor to normalize the tracer properties ranges.

From the different optimization methods used in fingerprinting procedures, a Monte Carlo global sampling routine was adopted. The convergence of the solutions was evaluated prior to the mixing model analysis by testing different numbers of iterations to ensure the complete exploration of the parameter space and reducing the sampling error to negligible levels. Therefore the optimal number of iterations for the Monte Carlo was fixed to 10^6 iterations. Similar results, with enhanced efficiency, could be obtained using Latin Hypercube Sampling (Collins et al., 2012; Laceby and Olley, 2014). In this work, random sampling was selected because of simplicity and flexibility under required constraints.

Special attention has been given to the parameter space sampling stage, bounded by the required constraints. The random weights are generated in order to ensure uniform distributed values to equally test all the possible solutions[a]. The selected method generates $m - 1$ random values in the interval $[0,1]$, sort the values so that:

$$0 < x_1 < x_2 \ldots < x_{m-1}$$

and constructing the weight:

$$w = (x_1, x_2 - x_1, \ldots, x_{m-1} - x_{m-2}, 1 - x_{m-1})$$

The method ensures the uniform distribution of the relative weighting. As an example for three random weights in figure 2 it can be seen that the selected method produce

[a] This fact follows from Bill Huber explanations; the authors thank mathoverflow.net for providing a forum where we could ask and find about this and be provided with an authoritative reference.

uniformly distributed weights compared with the straight procedure of producing m random numbers and normalizing them to sum unity. The latter method was rejected as this approach produced non-uniform distributions of random values.

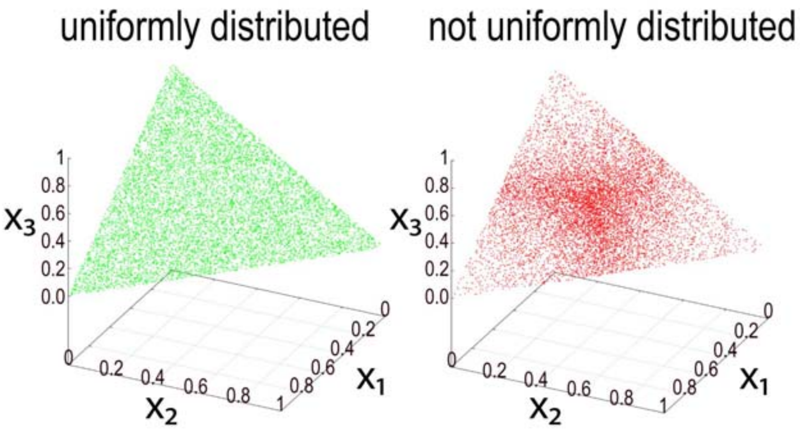
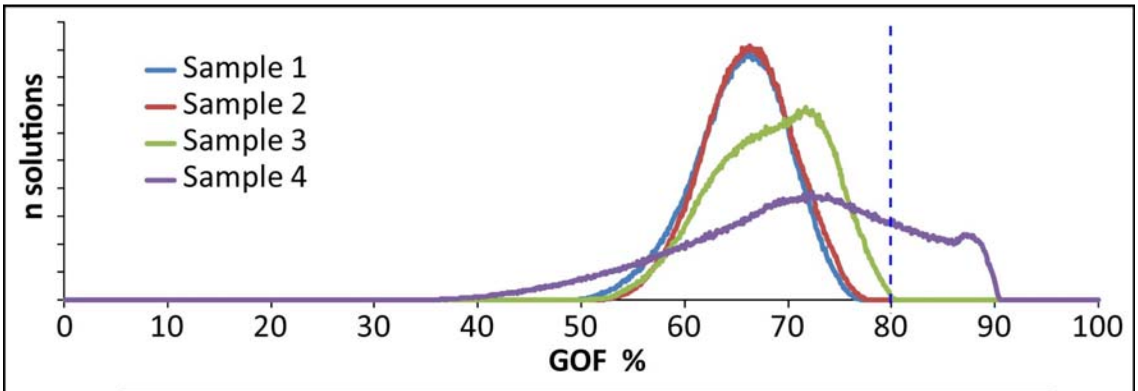


Fig. 2 Distribution of random values examples with 3 possible sources.

Unlike most fingerprinting studies, the optimized model solution was not selected by setting a fixed threshold of the GOF value (i.e. GOF > 80%). Examples of generated solutions were evaluated by plotting all the tested options ordered by the GOF value (Fig. 3). It was observed that i) there were mixture samples with no solutions that achieved the GOF threshold of 80% (e.g. Samples 1 and 2) and ii) there were mixture samples that generated increasing but different numbers of solutions that exceeded the 80% GOF threshold (e.g. Samples 3 and 4). Depending on the nature or variability characteristics of the sources and mixture samples, setting a threshold of the GOF value could result in estimates of source contributions based on different numbers of possible solutions (Fig. 3). Instead, the generated solutions were ranked by GOF and the optimal solution was computed from the 100 solutions that best fitted the source fingerprints as to correspond with the 0.01% of the generated iterations ($n = 10^6$). The optimal solution for each virtual sample mixture was characterised by the mean weighted source contribution, the standard deviation and the lowest GOF value.



GOF = 80%	Sample 1	Sample 2	Sample 3	Sample 4
n solutions	-	-	85	2728

Fig. 3 Distribution of solutions by GOF value for four example samples.

This new data processing procedure, written in C programming language, was designed to evaluate multiple sediment samples simultaneously and, for each sample, deliver the optimal solution and its dispersion.

The natural source variability, which is restricted by a unique value in the model, could be represented by different approximations. In this study, three characterisations of the sources were tested based on the source central values (mean and median) and an iterative procedure (corrected mean) which also represents the source dispersions. While the mean and median values remained unchanged during the Monte Carlo iterations, the corrected mean value of each fingerprint property was randomly modified according to their Student’s t distribution (similar to the work of Caitcheon et al., 2012 and Olley et al., 2013) constituting a multiple Monte Carlo analysis. Student’s t distributions were defined by the mean and standard deviation values of each source group. This distribution was selected and was postulated to be appropriate because the numbers of samples were small (Krause et al., 2003).

3. Results

3.1 Statistical discrimination of tracer properties

Different numbers of tracer properties were discriminated by the statistical tests used to select the properties included in the optimum composite fingerprints (Table 1). The KW differentiated 16 tracer properties which offered contrasts between the four potential sources at the 5 % confidence level. The DFA selected 7 tracer properties that provided the greatest discrimination between sources with 100 % of samples correctly classified in the four sources and a composite fingerprinting Wilks´ lambda of 0.012.

Table 1.- Optimum composite fingerprints obtained with the assessed statistical test.

Statistical test	Optimum composite fingerprint
Kruskal–Wallis *H*-test	^{137}Cs, ^{226}Ra, ^{232}Th, ^{238}U, LF, FD, Bi, B, Ca, Fe, Li, Mg, Ni, S, Sr, Ti
Discriminant Function Analysis	^{137}Cs, Al, Bi, Cr, Fe, Ni, V
Principal components analysis (PCA1)	^{40}K, As, Be, Bi, B, Cu, K, Mg, Ni, Sb, Tl

Although DFA results suggested that good source discrimination was achieved, source samples from forest were found to overlap with the agricultural source when the first two discriminant functions were plotted (Fig. 4).

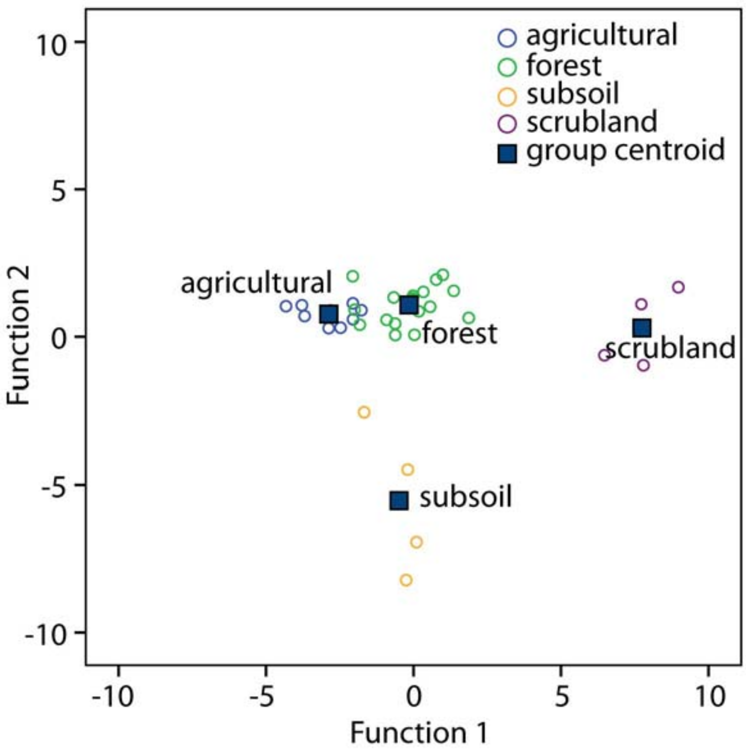


Fig. 4 Two-dimensional scatter plot of the first and second discriminant functions from stepwise discriminant function analysis (DFA).

PCA solution identified 7 components with eigenvalues in excess of 1 explaining 99.9 % of the total variance in the tracer dataset. These components were used for the two applications of this statistical test. The Varimax rotation allowed identification of 11 tracer properties for the PCA1 mixing model analysis with component loading greater than 0.8. The PCA2 resulted in a new dataset because the tracer concentrations (both sources and virtual sample mixtures) were transformed into the 7 principal components introducing the overall variability of the dataset in the mixing model.

All optimum composite fingerprints identified by the statistical test for source tracer properties selected a radionuclide as a minimum and different numbers of other chemical elements (Table 1). Only the Kruskal–Wallis *H*-test selected magnetic susceptibility properties. Bi and Ni were the unique common fingerprint tracers for all optimum composite fingerprints.

3.2 Estimation of source contribution

Source contributions were obtained for all virtual sample mixtures based on solutions to the system of linear equations with the two GOFs and source characterisations by the mean, median and corrected mean values of the different optimum composite fingerprints. Different contributions were obtained by the assessed fingerprinting procedures for the same mixture sample. As an example, figure 5 shows differences between estimated and known proportions for three of the virtual sample mixtures that were selected according to different percentage contributions. In general, a high variety of source ascriptions for the same mixture were obtained by the 24 fingerprinting procedures.

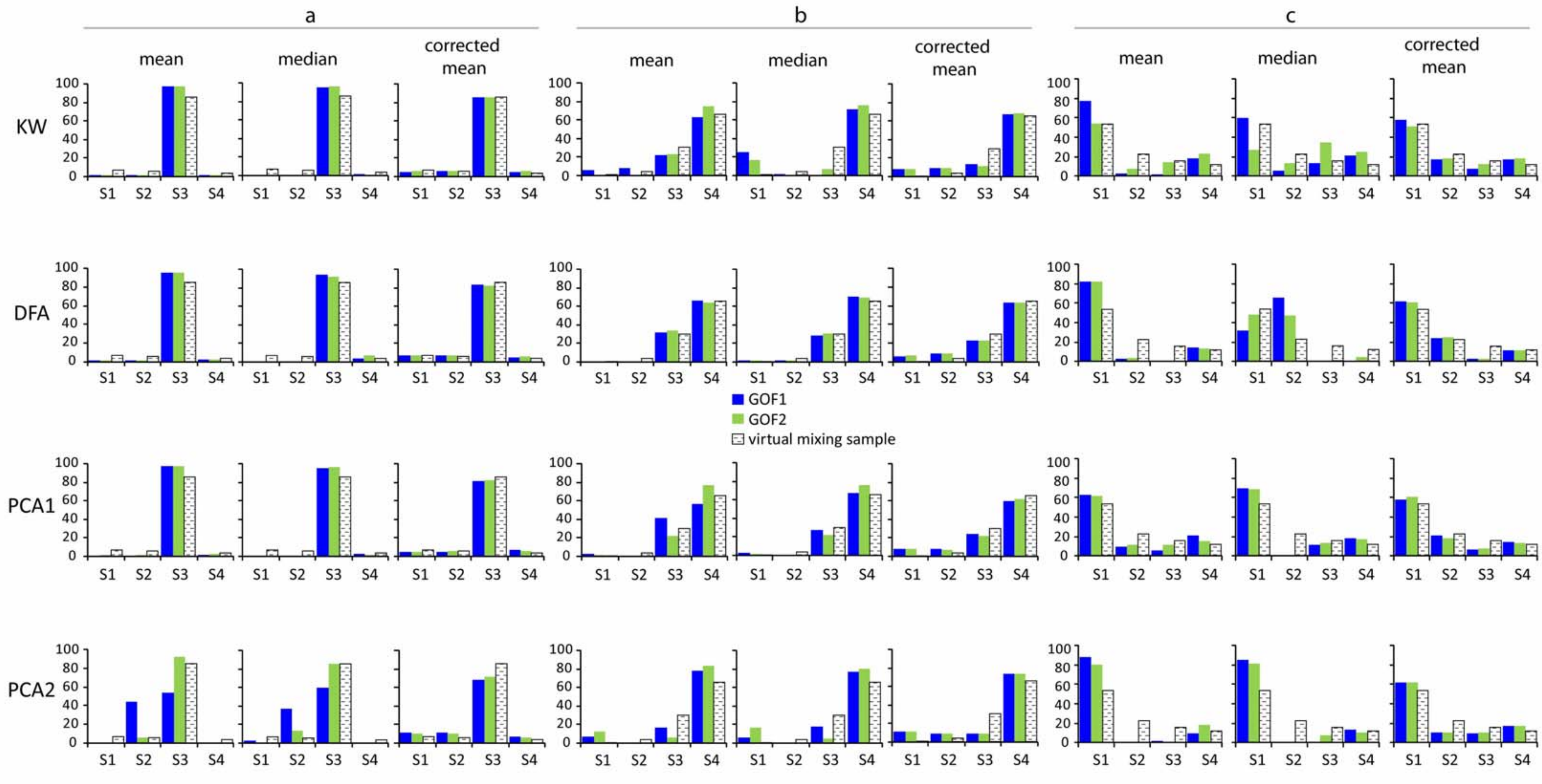


Fig. 5 Estimated source contributions based on mixing model solutions for three (a, b, c) virtual sample mixtures for the 24 fingerprinting approaches assessed.

The GOF values obtained from the 24 procedures ranged from 52 to 100 % (Table 2). The highest GOF values were obtained with the GOF2 for all options. In general, for the same fingerprinting procedure, the lowest GOFs were related to the virtual sample mixtures obtained from the combination of 2 source samples (with zero proportional contributions from the other sources), whereas the highest GOF values were related to combinations of 4 source samples (Fig. 5). From the assessed options, the greatest GOFs were obtained when using the corrected mean for source characterisation compared to the other procedures tested. Comparing results for the same GOF and source characterisation, the DFA optimum composite fingerprint yielded the most variable GOF values, whereas their mean GOF values were the highest of the assessed options. Model results for the virtual sample mixtures characterised by the PCA2 were less variable than the other statistical test.

Table 2.- GOF values from the assessed fingerprinting procedures.

	KWmG1	KWmG2	KWmdG1	KWmdG2	KWcorG1	KWcorG2
mean	93	99	92	99	94	99
maximum	97	100	98	100	97	100
minimum	77	92	73	87	81	94

	DFAmG1	DFAmG2	DFAmdG1	DFAmd G2	DFAcorG1	DFAcorG2
mean	94	99	93	99	96	100
maximum	99	100	100	100	99	100
minimum	64	82	54	71	74	90

	PCA1mG1	PCA1mG2	PCA1mdG1	PCA1mdG2	PCA1corG1	PCA1corG2
mean	92	99	92	98	95	99
maximum	98	100	99	100	98	100
minimum	70	89	65	83	77	92

	PCA2mG1	PCA2mG2	PCA2mdG1	PCA2mdG2	PCA2corG1	PCA2corG2
mean	90	98	90	98	95	99
maximum	99	100	99	100	99	100
minimum	77	92	77	92	85	97

DFA: Discriminant Function Analysis; KW: Kruskal–Wallis *H*-test; PCA1: Principal components analysis with selection of tracer properties; PCA2: Principal components analysis with projection of the dataset; m: mean; md: median; cor: corrected mean Student-t distribution; GX: goodness of fit type.

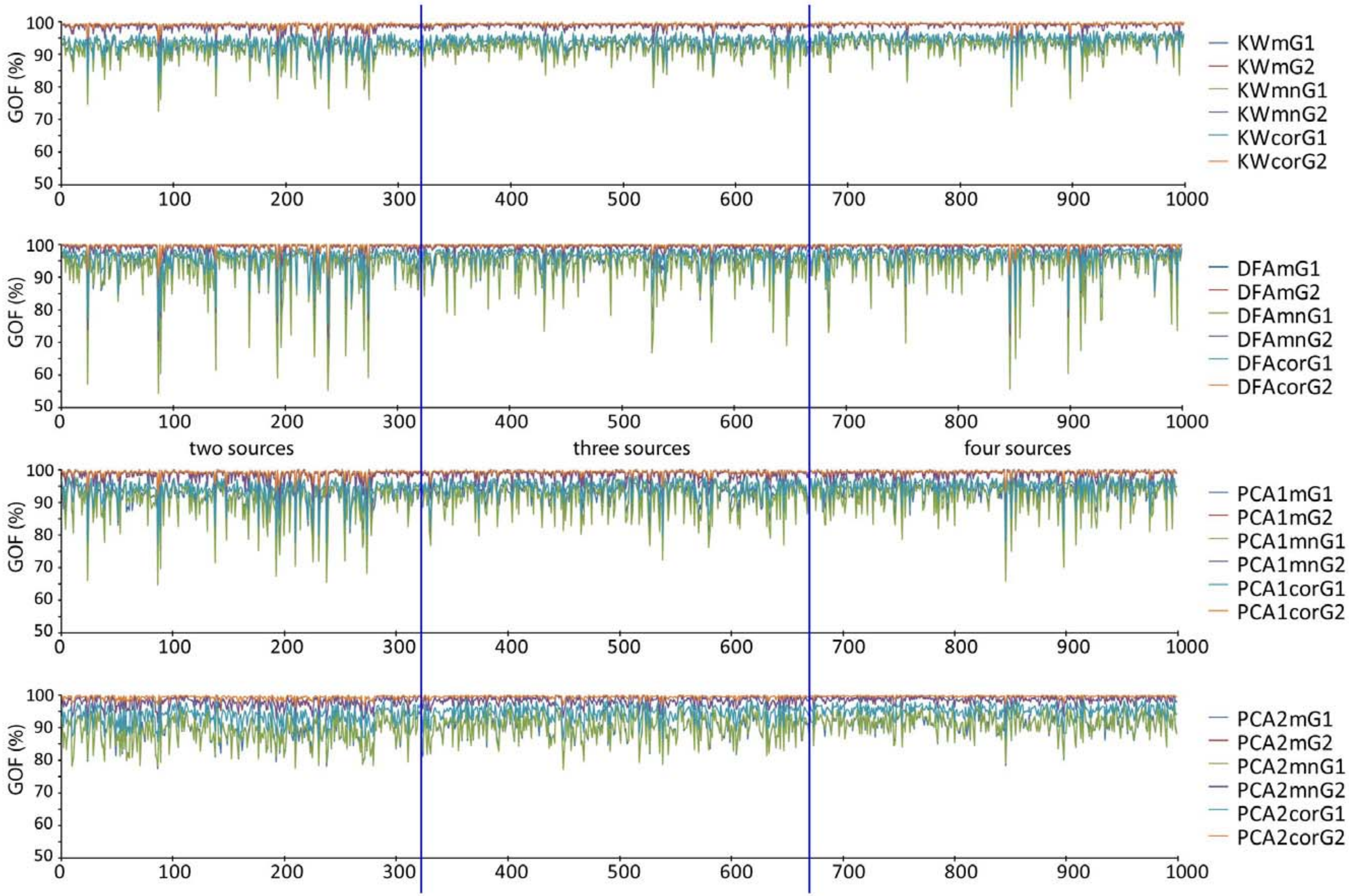


Fig. 6 Distribution of GOF values for the virtual sample mixtures.

3.3 Auto-evaluation of fingerprinting procedures

The accuracy of the procedures to solve the virtual mixtures and reproduce the known source apportionments was assessed by the RMSE between generated apportionments for the virtual sample mixtures and relative apportionments obtained by the 24 fingerprinting procedures. RMSE for the assessed options ranged from 1 to 69 % with mean values for each option of < 23 % (Table 3). In the same way as for GOF, results for RMSE were better for combinations of the virtual sample mixtures with contributions from the four sources than those with fewer sources (Fig. 7). The auto-evaluation assessment also showed virtual samples with GOF values > 90 % that exhibited RMSE > 50 %.

Table 3.- RMSE statistical values from de assessed fingerprinting procedures.

	KWmG1	KWmG2	KWmdG1	KWmdG2	KWcorG1	KWcorG2
median	16.6	15.4	15.5	15.9	13.7	13.3
mean	19.1	18.1	17.6	18.5	16.0	15.7
sd	12.2	11.6	11.3	11.6	9.6	9.4
max	63.5	64.0	62.3	58.1	58.1	57.8
min	0.7	1.0	0.3	1.2	1.1	1.1

	DFAmG1	DFAmG2	DFAmdG1	DFAmd G2	DFAcorG1	DFAcorG2
median	20.5	20.3	18.7	18.4	16.2	16.3
mean	23.2	23.2	21.2	20.9	18.9	18.9
sd	14.3	14.2	13.4	12.9	11.2	11.1
max	64.4	65.2	65.7	64.8	57.2	59.3
min	0.3	0.5	0.8	0.7	1.1	0.8

	PCA1mG1	PCA1mG2	PCA1mdG1	PCA1mdG2	PCA1corG1	PCA1corG2
median	21.6	20.5	19.5	19.1	16.7	16.5
mean	23.2	22.3	20.8	21.2	18.7	18.6
sd	12.7	12.3	11.8	12.0	10.2	10.3
max	66.7	61.9	62.2	64.7	53.5	53.8
min	1.2	0.7	0.8	0.9	2.1	1.7

	PCA2mG1	PCA2mG2	PCA2mdG1	PCA2mdG2	PCA2corG1	PCA2corG2
median	20.0	17.3	18.4	17.3	15.5	15.4
mean	22.5	19.9	20.5	19.3	17.3	17.4
sd	13.6	12.6	12.1	11.6	9.1	9.2
max	68.6	67.4	63.9	65.8	55.9	57.3
min	0.7	0.1	0.7	0.6	0.9	1.1

DFA: Discriminant Function Analysis; KW: Kruskal–Wallis *H*-test; PCA1: Principal components analysis with selection of tracer properties; PCA2: Principal components analysis with projection of the dataset; m: mean; md: median; cor: corrected mean Student-t distribution; GX: goodness of fit type.

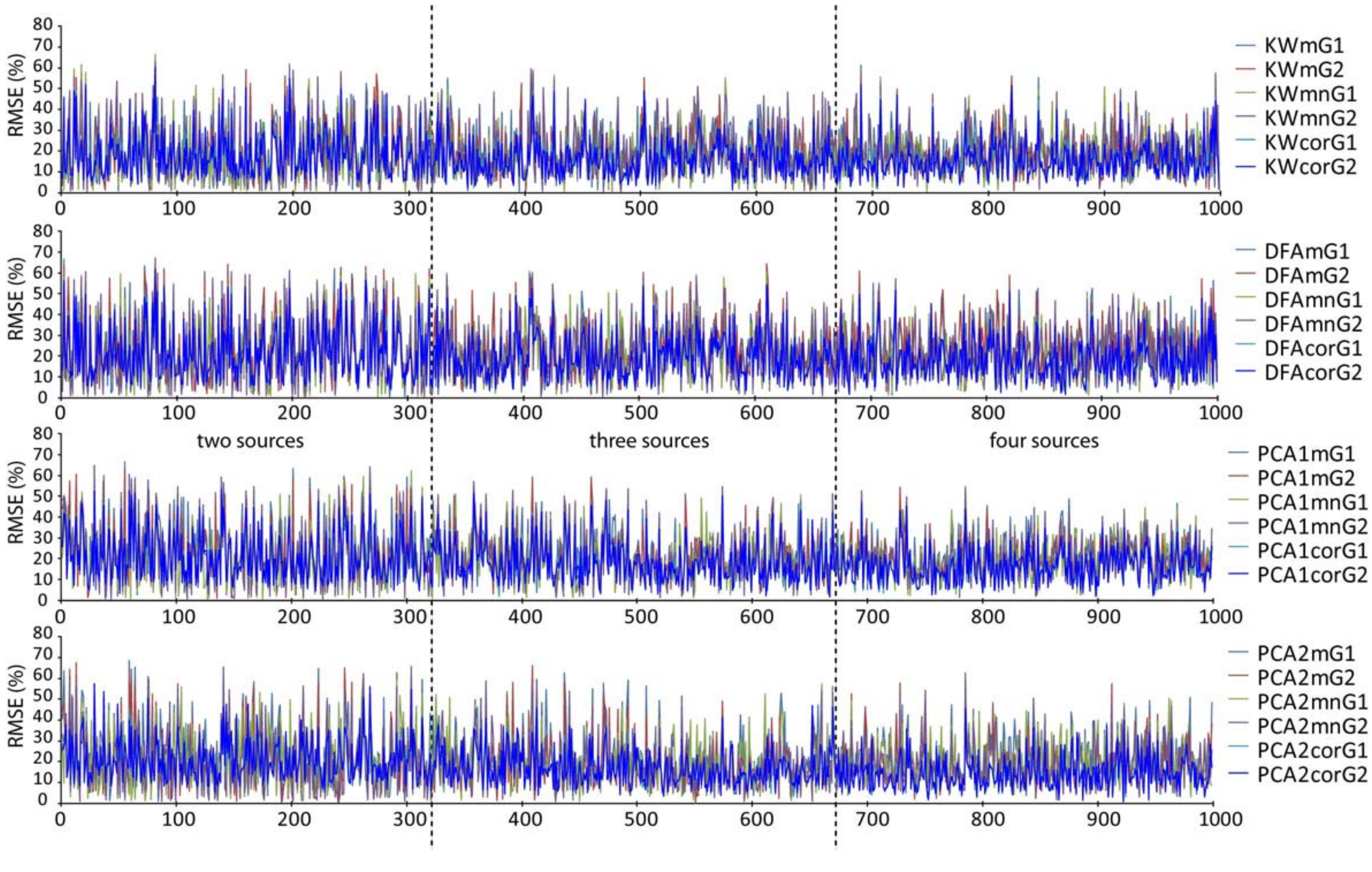


Fig. 7 Distribution of RMSE values for the virtual sample mixtures.

Plots of the RMSE achieved by the two GOF procedures for each statistical test and source characterisation showed that both GOF types had similar fits with highest correlations for the procedures with source characterisations by corrected mean in figure 8. Despite GOF2 reaching the highest values, both objective functions yielded similar un-mixing results although differences between RMSE were very low. In general, GOF2 yielded lower RMSE values than GOF1.

RMSE allowed us to assess the accuracy to reproduce the known source contributions of the different fingerprinting procedures and to select the procedure with the best discriminatory capacity for the study case. In general the RMSE values obtained were better for corrected mean than for median and mean (Table 3). Comparing the statistical tests used to select the optimum composite fingerprints for the models, RMSE were better for KW followed by the test with PCA2 (Table 3).

The results of the "random guess method" for the combination of four sources yielded an average RMSE of 25.3 % (Table 4) which allowed us to define an upper limit of the RMSE for the assessed procedures. The lowest discriminating capacity procedures were based on the mean for the optimum composite fingerprint selected by the DFA and PCA1 with GOF1 (Table 3).

Table 4.- Results of the random guess method. Average Mean Absolute Error (MAE) and Root Mean Squared Error (RMSE) for different numbers of source combinations for randomly generated mixture cases ($n=10^7$).

Number of sources	MAE	RMSE
2	33.3	33.3
3	26.7	29.8
4	21.4	**25.3**
5	17.8	21.7
6	15.2	18.9
7	13.2	16.7
8	11.7	15.0
9	10.5	13.6
10	9.5	12.4

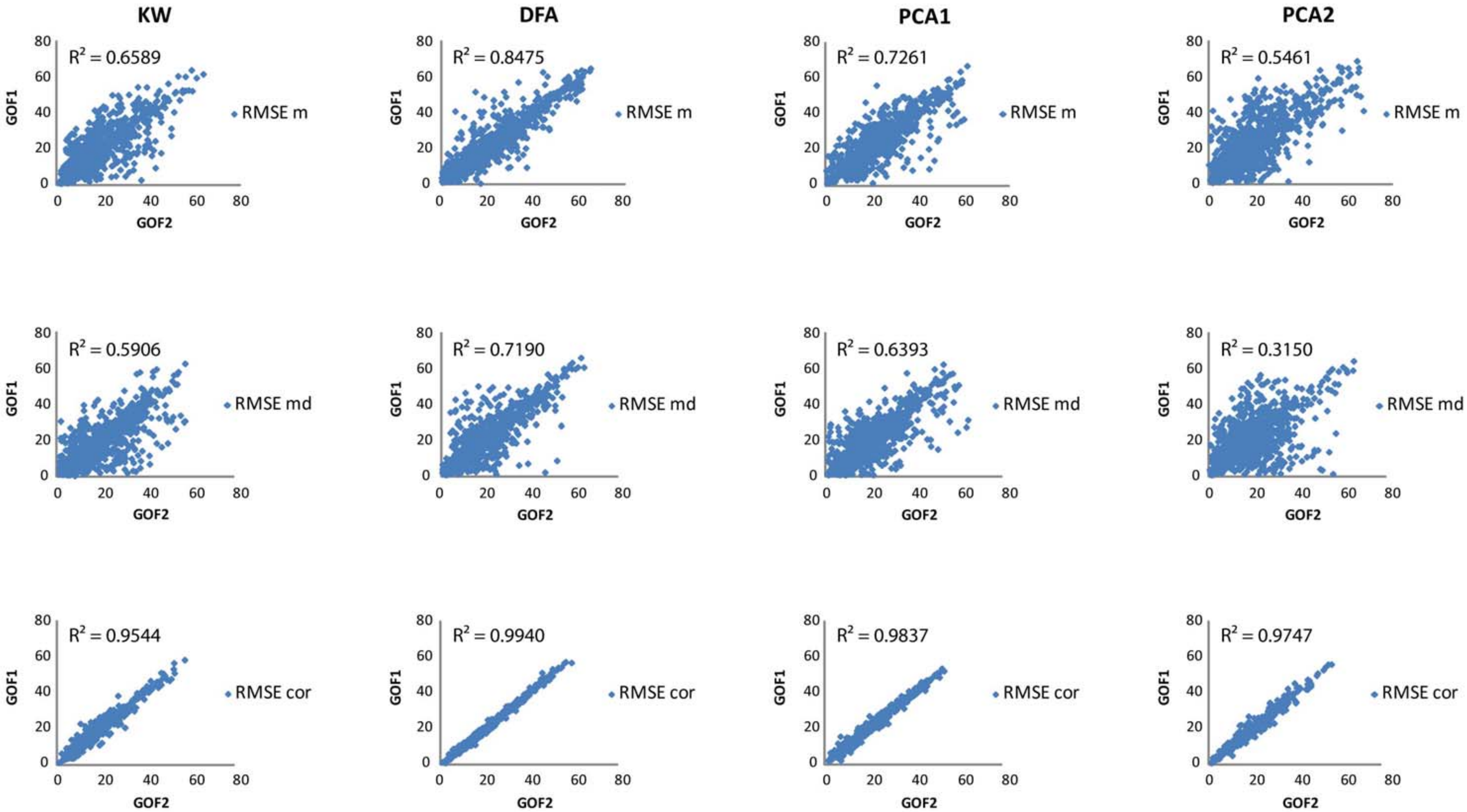


Fig. 8 Plots of the RMSE for the GOF pairs for each statistical test and source characterisations.

4. Discussion

The use of individual statistical tests to select optimum composite fingerprints for source assessment allowed the inclusion of a larger number of tracer properties. The widely used two step statistical procedure (KW and DFA) proposed by Collins et al. (1997) was not assessed as this procedure can be more restrictive in the number of tracer properties selected. Furthermore, recent work 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., 2014).

The poor separation between agricultural and forest sources based on the DFA plots (Fig. 4) was not unexpected due to changes in land uses that occurred in the past century. This reflects likely succession states between former agricultural areas that are partly reverting to natural forests after land abandonment (e.g. López-Vicente et al., 2011) which could contribute to overlapping source data. Also the influence of similar lithological characteristics of the three overlapping points from forest source with those from the agricultural source may also account for the lack of discrimination between these two sources.

The common selection of Bi and Ni for all optimum composite fingerprints could be due to a closer link with the mineral components of the substrate. The highest contents of both elements in sedimentary rocks are related with argillaceous materials (Kabata-Pendias and Pendias, 2001) which are the dominant lithology of the substrate in the subsoil sources. Moreover, differences between sources also indicated a possible weathering control related to the types of land uses. ^{137}Cs was selected in two fingerprints because of its higher concentrations in undisturbed areas such as scrublands and low ones concentrations in eroded areas represented by the subsoil source.

Similar to findings reported by Haddadchi et al. (2013; 2014) and Laceby and Olley (2014), we observed differences in source contributions obtained for the same virtual sample mixture when using different fingerprinting procedures. This fact strengthens the need to be careful when selecting fingerprinting procedures for catchment applications and also supports the need to test the accuracy of the fingerprinting procedures prior to application to field samples. Virtual sample mixtures have a potential advantage over 'real' artificial mixtures as the latter need to be mixed and analysed, involving a greater consumption of time and cost. Virtual sample mixtures are, however, limited where different sources might have contrasting texture distributions that bias the finer fraction of mixtures.

The approach taken here aims to simulate real study cases where sample mixtures are unlikely to represent exact mixtures of the central values of source materials (mean, median and corrected mean) hence, in these simulations GOF would never reach 100 %. The finding that four source combinations had greater GOF and lower RMSE than those with fewer source combinations is related to the differences between the source samples used in the virtual mixtures and the proposed characterisation of the sources in the mixing model. Although this difference can occur with the same probability in all virtual samples, combinations with fewer sources will have lower GOF and greater RMSE due to their higher contributions in the mixture (Figures 6 and 7).

As GOF is only a normalized value of the absolute fit provided by the minimization of the objective function (Motha et al., 2003), high GOFs do not necessarily correspond to accurate predictions of source contributions and it cannot be used as a definitive index of the mixing model performance. This fact that the GOF does not necessarily confirm the accuracy of model estimates of source contributions was also reported by Laceby and Olley (2014) and, in agreement with them, an index different to GOF may be needed to assess mixing model performance.

Better source ascription (based on RMSE) was achieved by the sets of tracers selected using the KW and PCA2 than the other statistical tests, supporting the conclusion that optimum fingerprints which contain a greater number of tracer properties can produce better model performance. Discriminant Function Analysis can be seen to over simplify signatures at the expense of source ascription power. Similar to Haddadchi et al. (2014), the use of Student's t distributions to generate corrected means improved source ascription because this source characterisation better simulated source variability than mean or median source characterisations. GOF2 penalizes large differences and favours more balanced contribution selections than GOF1, therefore GOF2 had slightly lower RMSE and greater GOF than GOF1. Procedures based on the mean for the optimum composite fingerprint selected by the DFA and PCA1 with GOF1 could be directly excluded because they had almost null discriminatory capacities as they almost reached the limit of the random guess method.

A limitation which should be taken into account in this study is the small number of source samples that could restrict the applicability of the results to the assessed catchment. This is less of an issue for the analysis of virtual sample mixtures, from which the main methodological observations are made but could be challenging if this analysis was applied to assess actual source contributions to sediment samples collected from the catchment. To overcome this restriction a spatial-integration sampling approach was used to improve the representativeness of the source data, which, while supporting environmental representativeness is more limited for demonstrating statistical representativeness. More source samples are recommended in sediment fingerprinting approaches to better characterise within-source variability (Evrard et al., 2013) and to underpin more robust statistical analysis.

4. Conclusions

In this study we tested an approach which incorporates virtual sample mixtures to compare the accuracy of 24 sediment fingerprinting procedures and select the best one for subsequent application. Different source contribution estimates between procedures for the same dataset indicate that the selection of the most effective fingerprinting procedure for each specific application is fundamental to obtain reliable source contribution results. Catchment source samples can be used to generate virtual sample mixtures to assess the accuracy of fingerprinting procedures. The auto-evaluation of the accuracy of the different fingerprinting procedures could serve as a verifiable approach for optimising the process of selecting the best procedure for discriminating and un-mixing catchment sediment source contributions. Furthermore, the assessment showed that high GOF values were not always indicative of accurate source apportionment results and, therefore, care should be taken when using GOF as an index of mixing model performance.

A simple and flexible Monte Carlo global routine, which was configured to sample the entire parameter space by the generation of uniformly distributed values, was used to solve the mixing model and ensure the best optimal apportionment solution for the generated virtual mixture samples to test the fingerprinting procedures. From the assessed options, the procedure which yielded the most accurate source apportionment results were the composite fingerprints that included the largest number of tracer properties, used the corrected mean for source characterisation and the GOF based on the objective function with the sum of squares of the relative errors. Several other statistical tracer selection procedures produced optimum composite fingerprints that had almost null discriminatory capacities as these approached the limit defined by a random guess method.

For the same virtual sample mixtures, the compared fingerprinting procedures produced different source ascriptions and different RMSE, highlighting the need to test and compare fingerprinting procedures with known datasets prior to applying them to real field samples. The large variation from the best procedures (RMSE = 0.1 %) to the worst ones (RMSE = 69 %) demonstrates that the auto-evaluation test of the fingerprinting procedures could improve the reliability of source apportionment results as well as providing information on mixing model performance.

Acknowledgements: This research was financially supported by the project CGL2014-52986-R. Reviews by Fernando A.L. Pacheco and two anonymous referees improved the manuscript.

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