Testing the sensitivity of a multivariate mixing model using geochemical fingerprints with artificial mixtures

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Graphical abstract

Highlights

- Relevant lab approach to validate an unmixing model using artificial samples
- Source apportionment results are sensitive to tracer selection
- Model sensitivity depends on the elemental composition of sources
- High GOF values do not necessarily ensure accurate source apportionments
- Different size fraction for sources and mixtures lead to inconsistent results

Abstract

Sediment source fingerprinting is increasingly used to provide insight into the dynamics of catchment sediment transfer processes, yet relatively few studies seek to validate source apportionments obtained from unmixing models. Our work focuses on simulating natural processes to test the accuracy of source apportionments obtained using a multivariate unmixing model called FingerPro. A relevant laboratory experiment is proposed to test the sensitivity of the model, using as experimental sediments 14 artificial mixtures composed of different proportions and numbers of sources selected from five soils as experimental sources. Twelve artificial mixtures were created by mixing a known proportion of source soils sieved to $<63\ \mu\text{m}$ in different proportions obtaining experimental sediments with three or four sources (experiment 1), while two additional artificial mixtures were prepared by combining mixing and sieving to obtain experimental sediments sieved to <40 and $<15\ \mu\text{m}$ (experiment 2). This research aims to test the sensitivity of the model by comparing the estimated source contributions for three sets of selected tracers (experiment 1) and for variations in particle size of the sources and mixtures (experiment 2). Experiment 1 show that source apportionments estimated by the FingerPro model for the same mixture reached maximum differences of 10% by using different tracers, with significantly different GOF and RMSE values between tracer sets (GOF means: 90% set A, 94% set B and

96% set C; RMSE means: 1.9% set A, 3% set B and 2.7% set C). Experiment 2 showed the inconsistency of model outputs when sources and mixtures had different particle size fractions. The accuracy of the model declined as the sediment become finer, and the mean RMSE increased from 2% to 4% up to 12% for mixtures at < 63 , < 20 and < 15 μm , respectively. The source apportionments estimated using a particle size correction factor improved slightly but not in all cases, with a maximum improvement of around one-third of the RMSE (mixture 10-B). Our results highlight the usefulness of employing artificial mixtures to test the accuracy of model simulations based on different tracer selections, source combinations and particle size fractions.

Keywords

Sediment tracing; Laboratory mixtures; FingerPro unmixing model; Geochemistry; Particle size

1. Introduction

Sediment fingerprinting is an increasingly used technique that can provide information to quantify the sources of mobilised sediments in catchments. Discriminating the potential contribution of sediment sources is necessary for understanding soil redistribution processes. The results obtained from fingerprinting unmixing models are becoming valuable data to support soil and water resources conservation and catchment management strategies (e.g. Wallbrink, 2004; Walling, 2005; Porto et al., 2010). Unmixing models, also known as mixing or source apportionment models, are tools that quantitatively link sources and sediment in terms of the proportion of sediments derived from each potential source. As the questions being asked of fingerprinting datasets become increasingly complex, validation of unmixing model outputs is increasingly important. This is particularly essential for

understanding sediment dynamics in complex landscapes where the intricate topography and the impact of different land uses represent important factors affecting the processes of soil particle generation and erosion, as well as the storage and export of sediments (Gaspar et al., 2013; Navas et al., 2013).

Different sediment fingerprinting studies have focused on sample location and collection (e.g. Smith et al., 2013; Owens et al., 2016) and explored the potential of fingerprinting tracers like geochemistry, fallout radionuclides, magnetic susceptibility or colour properties (e.g. Collins and Walling, 2002; Blake et al., 2006, 2012; Gellis and Noe, 2013; Taylor et al., 2013; Alewell et al., 2014; Navas et al., 2014; Barthod et al., 2015). Recent studies have examined other promising new tracers such as compound specific stable isotope traces (e.g. Gibbs, 2008; Alewell et al., 2016; Reiffarth et al., 2016; Upadhayay et al., 2017; Mabit et al., 2018). There is a need to revisit assumptions associated with tracer selection (e.g. Laceby et al., 2015; Collins et al., 2017; Smith et al., 2018), the conservative behaviour of tracers (e.g. Koiter et al., 2015; Sherriff et al., 2015; Laceby et al., 2017), mixing model selection or the accuracy of source apportionments obtained (e.g. Palazón et al., 2015a; Pulley et al., 2015; Haddadchi et al., 2016), as well as the effects of particle size (Laceby et al., 2017) and temporal sediment source dynamics and residence times (e.g. Wallbrink et al., 1998; Evrard et al., 2011; Smith et al., 2014; Gellis et al., 2016).

In order to validate fingerprinting models, the use of artificial mixtures of known proportions of sediment sources has gained increasing interest in recent years. Early studies using artificial mixtures include the work by Lees (1997) who identified non-linear additivity associated with the use of the mineral magnetic properties of sediment. Franks and Rowan (2000) used five artificial mixtures consisting of five source types based on major chemical groups to assess a source tracing procedure. Small et al. (2004) used a Bayesian modelling approach and artificial mixtures to explore source sampling

related uncertainties and the number of source samples required to limit uncertainty in modelling results. Given the laboratory work associated with generating and analysing the tracer content of artificial source mixtures, some recent studies have introduced synthetic or virtual mixtures based on Monte Carlo routines (Palazón et al., 2015b; Sheriff et al., 2015) as an alternative. Additional studies using artificial mixtures to assess unmixing model outputs include those by Hughes et al. (2009), Poulenard et al. (2012), Legout et al. (2013), Brosinsky et al. (2014), Haddadchi et al. (2014), Cooper et al. (2014) and Laceby et al. (2015) that shed light on the response of unmixing model using virtual and experimental samples and different numbers and types of tracers.

One of the most important limitations of fingerprinting research is the validation of unmixing model outputs, and further strengthening of unmixing models is required to include a measure of robustness of their predictive source apportionments. Once the source proportions are estimated by unmixing models these results need to be compared with some evidence for validation. The use of field data for validating source apportionments is challenging due to difficulty in obtaining spatially and temporally comparable data on sediment contributions from sources across a catchment (Collins and Walling, 2004).

Testing the sensitivity and accuracy of the results provided by unmixing models with experimental sediment mixtures depends on the use of different sets and numbers of tracers and different particle size fractions for sources and sediments (Rowan et al., 2000). There have been only a few attempts to explore and validate unmixing model outputs using real soils and artificial mixtures prepared manually in the lab (e.g. Haddadchi et al., 2014). However, there is a need to validate model outputs using samples of different proportions of source concentration and of different grain size fractions in order to simulate the effect of selective fluvial transport of fine particles, as

well as to test different approaches for assessing the accuracy of sediment fingerprinting procedures.

To this end, we report our examination of the sensitivity of unmixing model outputs to the number and type of elemental geochemistry tracers selected and the influence of different particle size fractions of artificial mixtures. Our main objective was to adopt a lab-based approach exploring two experiments: 1) the sensitivity of model output to different tracer selections and 2) the influence of different particle size fractions for sources and sediment mixtures (Figure 1).

2. Materials and Methods

2.1. Artificial mixtures

Five soils characterized by different colour (visual observation) and different geochemistry, soil organic carbon (SOC) content and particle size distributions were selected as experimental source soils (hereafter, sources) for this study. The soils used in these experiments were collected from locations in Devon, south-west England, UK. Agricultural activities contribute to sedimentation problems within many catchments from which samples were collected (sources #1 to #4) and some areas are also impacted by industrial activities. For instance, extraction of China Clay (source #5) is an important mining activity in this area, producing large amounts of fine sediment waste.

A total of 14 artificial mixtures (hereafter, mixtures) were manually prepared in the laboratory by combining different known proportions of sources (Table 1). Figure 1 summarizes the laboratory experiments setup used to test the sensitivity of the FingerPro multivariate unmixing model to different tracer sets (Experiment 1), and the effect of the particle size fraction (Experiment 2). For experiment 1, 12 mixtures (mixtures 1 to 12) were obtained after a mixing process using different proportions of soils sieved to $< 63 \mu\text{m}$, resulting in sources and mixtures with a comparable grain size

fraction (e.g. Walling, 2005). For experiment 2, mixture 9 (hereafter mixture 9a) was manually sieved to $< 40 \mu\text{m}$ (mixture 9b) and $< 15 \mu\text{m}$ (mixture 9c) to mimic the expected grain size fraction of sediments. A total of three mixtures with different particle size fractions were obtained using the same contributions of sources sieved to $< 63 \mu\text{m}$.

2.2. Laboratory analysis

Sources were dried, gently disaggregated using a mortar and pestle and sieved to $< 63 \mu\text{m}$. Sources and mixtures were analysed for elemental geochemistry (major and trace elements), SOC and particle size at the ISO-certified Plymouth University Consolidated Radio-isotope Facility (CoRIF).

Elemental geochemistry was analysed by X-ray fluorescence (XRF) using a Thermo Fisher Scientific Niton XL3T 950 He GOLDD XRF analyser, equipped with different excitation filters (main, low and high range) that optimize the analyser's sensitivity for various elements. Helium was used to allow measurement of light elements. All sources and mixtures ($n = 19$) were packed into XRF sample cups with a 38.2-mm exposure diameter in which the laser pulse (3-mm diameter) strikes the surface of the sample. During analysis, sample cups were moved 10 times to change the position of the laser, thereby obtaining 10 different measures per sample to produce a dataset of 190 measurements. To assess the accuracy of the analysis and the XRF analyser drift three repetitions were obtained for each measurement, recording a very low drift of less than 1%. A total of 18 elements returned measurements above the limit of detection: Ba, Nb, Zr, Sr, Rb, Pb, Zn, Fe, Cr, V, Ti, Ca, K, Al, P, Si, S and Mg.

Particle size distribution was measured using a Malvern 2000 series laser granulometer for the five sources ($< 63 \mu\text{m}$) and for mixtures 9a ($< 63 \mu\text{m}$), 9b ($< 40 \mu\text{m}$) and 9c ($< 15 \mu\text{m}$), respectively. A sub-sample was digested in hydrogen peroxide

over 24 h to remove organic matter and disaggregated in an ultrasonic bath prior to particle size analysis. Particle size data were used to calculate the specific surface area (SSA, $\text{m}^2 \text{g}^{-1}$) by assuming particle sphericity (Smith and Blake, 2014). SOC content for the five sources ($<63 \mu\text{m}$) was obtained by calculating the difference between total carbon and inorganic carbon using a Skalar Primacs Carbon Analyser.

2.3. Tracer selection

The fingerprinting procedure employs statistical testing of a range of tracer properties to select the optimum subset that discriminates sources, to eliminate redundant fingerprint properties (Collins and Walling, 2002). Three different tracer sets (A, B and C) were selected in order to identify an optimum composite group of tracers that provides the greatest discrimination of sources for the modelling process. Tracer sets were based on statistical procedures to eliminate redundant fingerprint properties. In order to verify the conservative behaviour of the potential tracers and before applying statistical tests, a range test was applied. Thus, mixture properties having values outside the minimum and maximum values of the sources were excluded.

Tracer set A used a Kruskal–Wallis H test (KW), a non-parametric equivalent to one-way analysis of variance (ANOVA) that includes the unequal variances of the data set. It is based on those properties which produce contrasts between the different sources at the 5% confidence level. The KW test is a traditional procedure of fingerprinting selection that confirms inter-category contrast of the sources; however, this does not satisfy statistical testing between possible pairs of categories (Collins and Walling, 2002).

Tracer set B used principal component analysis (PCA) which provides useful means to analyse variance in tracer data sets and reduce dimensionality (D’Haen et al., 2012). The principal components identified with eigenvalues above 1 were used to

identify tracer elements with the highest component loadings (higher than 0.9) after a Varimax rotation.

Tracer set C used discriminant function analysis (DFA), coupled with a multivariate stepwise algorithm based on the minimization of Wilks' Lambda, to identify a composite fingerprint that comprises the minimum number of tracers that provide the greatest discrimination between sources. The test creates a composite fingerprint by drawing the smallest number of tracers selected from the tracers that pass the KW test, providing the maximum discrimination of source properties (Collins and Walling, 2002).

For experiment 1, 12 artificial mixtures were unmixed using the three tracer sets, resulting in a total of 360 simulations as 10 different replicates of artificial mixtures were modelled. For experiment 2, the unmixing model was run using sources at $< 63 \mu\text{m}$, and mixtures with a lower size fraction, at < 40 and $< 15 \mu\text{m}$. In addition, a particle size correction (PSC) factor was applied using SSA, assuming enrichment of the soil as the SSA increases, resulting in a total of 120 simulations.

2.4. Multivariate unmixing model

A standard linear multivariate mixing model, FingerPro (CRAN; Lizaga et al., 2018), based on the work of Palazón et al. (2015b) was used to carry out these experiments. This model employs a Monte Carlo random sampling system to identify the relative contribution of different sources exploring the entire parameter space.

The model was developed as an R package within the CRAN platform and the main assumptions are that tracer properties must be conservative. Concentrations of the selected fingerprint properties in the sediment samples directly reflect i) the corresponding concentrations in the original sources and ii) the relative proportions of sediment contributed by those sources.

The relative contribution of each sediment source was determined following:

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

which satisfies the subsequent constraints:

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

$$0 \leq \omega_j \leq 1,$$

where b_i is the tracer property i ($i = 1$ to n) of the sediment mixture, $a_{i,j}$ represents the tracer property i in the source type j ($j = 1$ to m), ω_j is the unknown relative contribution of the source type j , m represents the number of potential sediment sources and n is the number of tracer properties selected.

The procedure tries to find the source proportions that conserve the mass balance for all tracers. The quality of each candidate is measured using the following function or goodness of fit (GOF), based on the sum of the squares of the relative error (Motha et al., 2003):

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

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

In this study the optimized solution among the three tracer sets tested was obtained by comparing the GOF values reported by the software, while the sensitivity of the model outputs was evaluated by the root mean squared error (RMSE) between the predicted and real apportionments used to create the artificial mixtures in the lab for each un-mixing case. The accuracy of each source contributions was evaluated with the absolute value of the difference between the real and estimated contributions, absolute error (AE), obtaining a standard deviation (SD) value for the 10 replicates simulated.

3. Results

3.1. Experiment 1: effect of tracer selection

3.1.1. Characterization of sources and mixtures

The SOC content was significantly higher for the brown and red soils (source #4, #3 and #1), reaching 3.5% SOC in source #3 (ANOVA test, $p \leq 0.05$). Sources #2 and #5 were characterized by the lowest values for SOC, close to 1%, and no significant differences between them. Particle size composition for the five sources was similar, with a predominance of silt fraction (mean $\pm$ SD: $90 \pm 2.7\%$). The mean values of SSA varied little but were significantly different between the sources (Table 2).

The geochemical composition for all sources and mixtures showed that only 18 elements returned measurements above the detection limit (Ba, Nb, Zr, Sr, Rb, Pb, Zn, Fe, Cr, V, Ti, Ca, K, Al, P, Si, S and Mg). For most of the elements, the coefficients of variation (CV) were around 10% and did not exceed 5% for V and P. Exceptionally in source #3 the CV for Mg, S and Ba reached a maximum of 20% (Figure 2a and 2b). Apart from Si, the most abundant elements were Al, Fe and K, followed by Ti, Ca, Mg and P. while the concentrations of S, Zr, Ba, Cr, V and Pb were lower than 1000 ppm and Sr, Rb, Zn and Nb (Figure 2a and 2b) had mean values lower than 100 ppm.

Source #1 was characterized by significantly higher Fe, Sr, Cr and V content, while source #2 had significantly higher Si and Pb content but the lowest Zn content. Even though sources #3 and #4 were the most similar, with no significant differences in Nb, Sr, Cr, V, Pb and Ti content and similar colour, the Ba, Zr, Zn, Fe, P, K, Ca and Mg content was significantly different between them. Source #5 had significantly higher Nb, Al and Rb content and the lowest Zr, Cr, V, Pb, Ti and S content. Comparison using bi-plots between the 18 elements showed that all mixtures presented content within the range of the source concentrations, except Ba for mixtures 6, 7 and 8 (Figure 2a and 2b).

3.1.2. Optimum tracer selection

The elements included in each tracer set for each mixture are listed in Table 3. Tracer set A (KW) identified the same 18 elements for all mixtures, with a p-value ≤ 0.05 , which provided contrast between the sources at the 95% confidence level. However, the range test failed for Ba in mixtures 6, 7 and 8, and it was removed as a potential fingerprint in further analysis of these three mixtures (Figure 2a and Table 3).

Tracer set B (KW + PCA) resulted in three different combinations of elements for the mixtures. The four PCA tests showed that for mixtures 1, 4, 5, 6, 7 and 8, the first two components with eigenvalues greater than 1 explained 97.2% of cumulative variance, while for mixture 2 they explained 96.7% of variance. For mixtures 9, 10, 11 and 12, the percentage variance explained by the first three components was 98.7%, and it was 81.3% for mixture 3 (Figure 3). After a varimax rotation, 11 elements (mixtures 1, 4, 5, 6, 7 and 8), seven elements (mixture 2) and the same eight elements for mixtures 3, 9, 10, 11 and 12 were identified, with component loadings higher than 0.900 (Table 3). The 3D scatter plot of the first, second and third components provided good discrimination between the sources (Figure 3).

Tracer set C (KW + DFA) resulted in three different combinations of elements, and for most mixtures included fewer elements than in tracer sets A and B. The four stepwise DFA tests provided very good discrimination between the sources; the percentage of samples correctly classified was 100%, with a Wilks' lambda value of 0.001. Four elements were selected for mixtures 1, 4, 5, 6, 7 and 8, the same six elements for mixtures 2 and 3, and nine elements were chosen for mixtures 9, 10, 11 and 12 (Table 3).

3.1.3. Sensitivity of model output

The unmixing model results for the 360 simulations were highly consistent (Figure 4 and Table 4). The GOF values were never lower than 86% (e.g. mixture 2-A), reaching values close to 99% (e.g. mixture 1-C). The mean value of RMSE was 2.5%, with a range from 0.4% to 5.6%, and for as much as 75% of the simulations, RMSE values were lower than 3%.

The AE between predicted and real source contribution had a maximum of 8.2% (e.g. source #1, mixture 8-C) and a mean of 2%. Source #2 showed the largest variations, with a significantly higher mean AE (mean $\pm$ SD: $3.0 \pm 1.7\%$) than the other sources (#1: $2.2 \pm 1.7\%$; #3: $1.7 \pm 1.5\%$; #4: $1.9 \pm 1.3\%$). Source #5 had the lowest mean AE ($1.2 \pm 0.7\%$) and the smallest variation.

Tracer set C had significantly higher means of GOF but means of RMSE were not as low as might be expected. However, tracer set A had the lowest RMSE means despite the lowest means of GOF. Tracer set B, incurred the highest RMSE (Table 5). GOF generally decreased with an increasing number of tracers but RMSE improved. When analysed separately, similar results were obtained for mixtures with three or four sources, although differences were not significant for means of GOF and RMSE for mixtures of four sources.

The accuracy of source contribution predictions varied between tracer sets, with mean AE significantly different for sources #3 and #4, and mean SD significantly different for sources #1, #2 and #3 (Table 5). Tracer set C provided less variable results (SD range: 0.4–4.6%), and AE ranged from 0.1% to 8.2%, depending on the source type. Tracer set A increased the variability in the predictions (SD range: 1.1–8.6%) against tracer set C; however, the former had the lowest AE that ranged from 0% to 4.7%. When using set B, the results were less consistent, incurring the greatest variation (SD ranges 1.3–14.8) and a high AE ranging from 0.2% to 6.7%.

The relationship between GOF and RMSE was not significant for all modelled mixtures ($r = 0.1067$). Similar results were found when the three tracer sets were grouped separately (A: $r = 0.1199$; B: $r = 0.231$; C: $r = -0.4374$).

3.2. Experiment 2: effect of particle size fraction

3.2.1. Characterization of mixtures

Comparing the mixtures at 63, < 40 and < 15 μm , the finest fraction was gradually enriched as result of sieving, with < 10 μm mean content of $53.2 \pm 0.7\%$, $60.0 \pm 0.2\%$ and $79.1 \pm 0.2\%$ for mixtures 9a, 9b and 9c, respectively. Overall, the sources had significantly lower contents of the finest fraction as compared to mixtures 9b and 9c. The SSA for mixtures 9a, 9b and 9c were 0.314, 0.338 and $0.436 \text{ m}^2 \text{ g}^{-1}$, representing a gradual increase of 8% from < 63 to < 40 μm and of 29% from < 40 to < 15 μm . The total SSA increase between mixture 9a and the finer mixture 9c was 39%. Comparing SSA between sources and mixtures, mixture 9c had a significantly higher mean SSA than the sources. However, mixture 9b had similar SSA mean to the sources.

The bi-plots between the 18 elements showed that all element concentrations in the mixtures were within the range of the sources (Figure 5).

3.2.2. Sensitivity of model output

The estimated source contributions for mixtures 9b and 9c with and without PSC factor are shown in Figure 6, and model outputs are shown in Table 6. The results for mixture 9a are those for mixture 9 in experiment 1 that had consistent GOF, RMSE and AE of source apportions for the three tracer sets.

Apportions estimates worsened as mixtures became finer (9a to 9c), especially when no PSC factor was applied. Thus, mixture 9b showed GOF higher than 88% and RMSE lower than 7% for all tracer sets. Tracer set B had the highest AE that reached up

to 10% for source #1. However, even the best results obtained with tracer sets A and C, were not as good as the estimate for mixture 9a. Mixture 9c showed the most inconsistent source contributions for the three tracer sets. GOF decreased to 78% for set B, and RMSE reached values up to 15% (Table 6).

After applying a PSC factor to mixtures 9b and 9c, the results changed, and the source apportionments were slightly closer to the theoretical source contributions, but not as close as the source contribution estimated for mixture 9a. However, a consistent trend was not found, and some results did not improve after applying the PSC factor. Despite there being a general increase in GOF values, and lower RMSE for all tracer sets, AE values for each source were not good, especially for mixture 9c (Table 6). After applying a PSC factor for mixture 9c, AE for sources #2 and #5 using tracer set B was reduced by half, but reached a maximum value of 10.2% and 11.2%, respectively, and the estimate for source #2 contribution was only 19.5% when the real contribution was 30%.

Comparing the three tracer sets for mixtures 9b and 9c, more inconsistent results were obtained with tracer set B while tracer sets A and C reported more robust results with a PSC factor. Tracer set A recorded a better AE for the sources, even though source #3 for mixture 9c could not be modelled correctly, obtaining a contribution of 22% instead of 30%. When using tracer set A, RMSE values improved up to 1.9% for mixture 9b with a PSC factor but for mixture 9c, improvement was not as good, and the minimum RMSE was around 6% (Table 6 and Figure 6).

4. Discussion

4.1. Experiment 1: effect of tracer selection

Source apportionments with the FingerPro model are sensitive to tracer selection. All simulations show a weak relationship between RMSE and GOF ($r = 0.254$), which

suggests that GOF does not necessarily validate the ability of the model to accurately estimate source contributions. A low GOF likely denotes a modeling error or random behaviour rather than good unmixing of the mixture. However, as GOF is only a normalized value of the absolute fit provided by minimization of the objective function (Motha et al., 2003), high GOF values are not by themselves a good enough index of model performance, as also found by Laceby and Olley (2015) and Palazón et al. (2015b). Recent research supports the need to find a complementary index to test the sensitivity of model results (Laceby and Olley, 2015) or to apply an auto-evaluation procedure by creating virtual mixtures (Palazón et al., 2015b). To this end, our artificial mixtures also support this and provide valuable complementary information for better understanding unmixing model outputs.

Comparing the results obtained with tracer sets A, B and C, some source apportionments were more accurate using tracer set A which had the lowest GOF but the best RMSE, while tracer set C with the highest GOF did not record the best RMSE. This is likely due to the fewer tracers in tracer set C that might simplify the model calculations thus improving GOF values. This finding is in agreement with Sherriff et al. (2015), who suggested that the inclusion of a larger number of tracers can decrease uncertainty ranges in source apportionments estimated by the model. We found that the most accurate source apportionment was achieved by tracer sets A and C in comparison with tracer set B (KW + PCA) that was less accurate and had greater uncertainty, despite tracer set B having double the number of tracers in set C for some mixtures. Palazón et al. (2015b) also found relatively poorer results when using PCA in comparison with other statistical tests.

Mixtures with a proportional composition of sources (mixtures 1, 2 and 3) tended to reproduce similar source apportionments with tracer sets A and C. Moreover, if there were similarities between two sources as in mixture 3 (sources #3 and #4),

apportionments were very accurate. However, when using tracer set B, FingerPro was sensitive to the number and type of tracers. Differences were also observed depending on the characteristics of the sources. This was especially the case for source #2 (mixtures 1 and 3). Source apportionments for mixtures in which one of the sources predominated (e.g. source 5 in mixtures 11 and 12) and the remaining sources had similar low percentages, were consistently modelled and again in this case, greater variations were obtained for tracer set B. This supports that the model is capable of identifying all source signals, even those that have similar low contents and could be masked by other much more abundant sources.

Our results confirm the differences in source contributions obtained by the model for the same mixture when using different optimum tracers, in agreement with findings by other authors (e.g. Haddadchi et al., 2014; Laceby et al., 2015; Palazón et al., 2015b). In contrast, Smith et al. (2018) presented a new approach to tracer selection based on identifying and removing tracers that exhibit non-conservative behaviour during transport. The authors provided further evidence to support the use of more rather than fewer tracers, subject to the key requirement of conservative tracer behaviour.

4.2. Experiment 2: effect of particle size fraction

Our results prove that as the experimental mixtures became finer, the source contributions estimated by the model worsened. One of the key assumptions of the sediment fingerprinting approach is the conservative behaviour of sediment mixtures, assuming that soil properties used as tracers of the potential sources do not change during erosion, delivery and transport processes (Walling et al., 1993). However, in reality, many soil properties are sensitive to changes in particle size.

The geochemical signature observed in mixtures 9a, 9b and 9c is likely affected by the mineralogical control of particle size. When comparing mixtures and sources, a

comparable size fraction is desirable, as the results obtained for mixture 9a demonstrate. Koiter et al. (2017) showed similar findings using rainfall simulation runoff plots indicating that sieving to $< 63 \mu\text{m}$ to avoid enrichment reduces though not fully eliminates the difference between the sources and the mobilized soil. Therefore, the greater deviations observed for the largest differences in particle size between source ($< 63 \mu\text{m}$) and mixture ($< 15 \mu\text{m}$) supports the application of a PSC factor in this case.

Our findings show that application of a PSC factor in general improves the accuracy of the model estimates, thus reducing the effect of the sorting process simulated in our experiment. Corrections of particle size may help to mitigate differences in the particle size of sources and sediments, reducing the impact of different particle size distribution on tracer parameters prior to quantifying source contributions as recommended by Collins et al. (1997) and Walling et al. (1993). The SSA of our sources and mixtures presented a narrow range with values lower than $1 \text{ m}^2 \text{ g}^{-1}$. This, combined with different behaviour of elemental geochemistry for different experimental sources and mixtures could be the reason why the PSC factor based on a linear response between particle size and tracer concentration did not improve as much as expected from the source contribution. Thus, the best results are obtained when source and mixture are modelled with the same size fraction (mixture 9a).

Different approaches have been used assuming the fundamental assumption of a linear and positive relationship between particle size, SSA and tracer concentration. However, Horowitz and Elrick (1987) observed that these relationships are often non-linear, particularly over $1.0 \text{ m}^2 \text{ g}^{-1}$, while Russell et al. (2001) reported that for a large range of SSA, linear particle size correction may be inappropriate. Smith and Blake (2014) demonstrated that this assumption does not apply to all tracer properties and showed how the relationship between individual tracers and SSA may be positive or negative or that, in some cases, no relation may be observed.

Regarding a direct comparison between source and sediment in order to reduce the particle size effect, all source and sediment samples are usually sieved to a size that closely represents the sediment being transported in a catchment. However, in most studies, a compromise between the availability of enough sample and the time and cost of sample preparation limits sieving to $< 63 \mu\text{m}$. At this point, it is important to highlight that in different types of sediment, including suspended sediments, channel bed, floodplain and lake sediments, there is a high possibility of finding sediments much finer than $< 63 \mu\text{m}$. Nevertheless, the idea to sieve the sources to the size fraction of sediments, especially when sediments are very fine, raises interesting questions regarding how representative the fraction is of the whole sediment system. Given the challenge related to the variety of relationships between sediment biogeochemistry and particle size, Motha et al. (2003) proposed comparing like with like between sources and sediments, even if that means extracting a finer sediment particle size (e.g. $< 20 \mu\text{m}$). Motha et al. (2003) estimated that for suspended sediments composed of $< 63 \mu\text{m}$ particle sizes, more than 90% is accounted for by sediments $< 20 \mu\text{m}$ in size (clays and fine silt), while Collins et al. (1997) observed that for source soils $< 20 \mu\text{m}$ particle sizes account for a much smaller percentage.

5. Conclusions

The lab experiments presented in this work represent a useful approach for further developing the sediment fingerprinting technique. We simulated natural sediment mixing processes and the effect of the fluvial transport and sorting process on fine particles, providing an opportunity to assess the performance of a multivariate unmixing model (FingerPro). Our experiments show the different accuracy levels in source apportionment depending on tracer selection.

Different numbers and types of tracer deliver different source contributions and may thus lead to inconsistent results. Source apportionment based on KW + PCA tests was less accurate and had significantly higher uncertainty than KW and KW + DFA tests. Our results give further evidence to support that high GOF values do not necessarily correspond to accurate predictions of source contributions, and care should be taken when using only this parameter to assess the performance of unmixing models where source apportionments results predicted by models are inconsistent with prior knowledge of the study catchment or in the absence of independent data for comparison. To this end, the benefit of using known artificial mixtures for testing may provide improved confidence in model outputs.

PSC factors slightly improved simulation accuracy but did not always provide consistent results, suggesting that PSC factors require careful scrutiny. If PSC factors are used, then they should be applied on a tracer-by-tracer basis. The assumption that there is enrichment in tracer concentrations when SSA increases with decreasing particle size deserves further research, exploring in more detail the relationships between particle size and tracer concentrations using experimental mixtures. The role of particle size selectivity in fingerprinting techniques, and the need to include detailed information on particle size characteristics of both source and sediment mixtures as essential information for fingerprinting studies, is recommended for future studies.

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Fig 1 Lab experiment setup: Testing the sensitivity of multivariate unmixing model to different tracer sets (Experiment 1) and to different particle size fraction of sources and sediments (Experiment 2).

Lab Experiment

Experiment 1 | Mixing process | Tracers selection effect

Experiment 2 | Mixing and Sieving process | Particle size fraction effect

* See Table 1 To know the real source contribution for each mixture

Fig 2 2D scatter plots for the major and trace element concentrations of sources and mixtures. Dotted line defines the region that contains all sources.

Sources < 63 μ m

Source #1 ●
Source #2 ●
Source #3 ●
Source #4 ●
Source #5 ●

Artificial mixtures < 63 μ m

Mixtures 1 ✕ 4 ✕ 5 ✕ 6 □ 7 ● 8 ○
Mixture 2 ○
Mixtures 9 □ 10 ○ 11 ✕ 12 ✕
Mixture 3 +

Major and trace elements: Ba, Nb, Zr, Sr, Rb, Pb, Zn, Fe, Cr, V, Ti, Ca, K, Al, P, Si, S, Mg

Fig 3 2D and 3D principal components scatter plots PC_i with the area for each source.

Fig 4 Estimated source contributions for the 12 artificial mixtures using tracer sets A, B and C. Solid line in orange represents the real proportion of each source.

Fig 5 Scatter plots for geochemical data of sources #1, #2, #3, #5 and mixtures 9a, 9b and 9c. Dotted line represents the 95% confidence ellipse of the sources.

Fig 6 Estimated source contributions for mixtures 9b (< 40 μm) and 9c (<15 μm) using tracer sets A, B and C, a) without and b) with particle size correction factor. Solid line in orange represents the real proportion of each source.

Table 1 Real source contribution for the artificial mixtures created manually at the Lab.

PSF, *particle size fraction*

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Artificial mixtures				Source contributions % <63 µm				
	PSF			#1	#2	#3	#4	#5
	n	µm	n sources	n=10	n=10	n=10	n=10	n=10
Experiment 1								
Mixture 1	10	<63	3	33.3	33.3	33.3	0.0	0.0
Mixture 2	10	<63	3	33.3	33.3	0.0	33.3	0.0
Mixture 3	10	<63	4	25.0	25.0	25.0	25.0	0.0
Mixture 4	10	<63	3	10.0	45.0	45.0	0.0	0.0
Mixture 5	10	<63	3	20.0	40.0	40.0	0.0	0.0
Mixture 6	10	<63	3	30.0	35.0	35.0	0.0	0.0
Mixture 7	10	<63	3	40.0	30.0	30.0	0.0	0.0
Mixture 8	10	<63	3	50.0	25.0	25.0	0.0	0.0
Mixture 9	10	<63	4	30.0	30.0	30.0	0.0	10.0
Mixture 10	10	<63	4	23.3	23.3	23.3	0.0	30.0
Mixture 11	10	<63	4	13.3	13.3	13.3	0.0	60.0
Mixture 12	10	<63	4	3.3	3.3	3.3	0.0	90.0
Experiment 2								
Mixture 9a	10	<63	4	30.0	30.0	30.0	0.0	10.0
Mixture 9b	10	<40	4	30.0	30.0	30.0	0.0	10.0
Mixture 9c	10	<15	4	30.0	30.0	30.0	0.0	10.0

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Table 2 Characterization of the five sources: visual colour, SOC mean values and sand, silt and clay content. Different letters indicate significant differences between sources at the p-level 0.05 based on SOC content.

SD, *standard deviation*; SSA, *specific surface area*

	Colour	SOC %			Sand %	Silt %	Clay %	SSA m ² gm ⁻¹
		mean	SD		mean	mean	mean	mean
source #1	Red	2.11	0.06	b	5.7	89.2	5.1	0.378
source #2	Yellow	1.12	0.03	a	2.7	91.9	5.3	0.344
source #3	Brown dark	3.43	0.05	d	6.2	88.0	5.8	0.352
source #4	Brown light	2.90	0.46	c	8.1	86.9	5.0	0.287
source #5	Grey	1.05	0.14	a	3.6	93.3	3.1	0.258

722 **Table 3** Elements included as optimum tracers in tracer set A, B and C.

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Tracers set	Mixtures	Sources	<i>n</i>	Selected tracers
A KW	1 - 4 - 5 - 6 - 7 - 8	#1 #2 #3	18	Ba, Nb, Zr, Sr, Rb, Pb, Zn, Fe, Cr, V, Ti, Ca, K, Al, P, Si, S, Mg
	2	#1 #2 #4	18	Ba, Nb, Zr, Sr, Rb, Pb, Zn, Fe, Cr, V, Ti, Ca, K, Al, P, Si, S, Mg
	9 - 10 - 11 - 12	#1 #2 #3 #5	18	Ba, Nb, Zr, Sr, Rb, Pb, Zn, Fe, Cr, V, Ti, Ca, K, Al, P, Si, S, Mg
	3	#1 #2 #3 #4	18	Ba, Nb, Zr, Sr, Rb, Pb, Zn, Fe, Cr, V, Ti, Ca, K, Al, P, Si, S, Mg
B KW + PCA	1 - 4 - 5 - 6 - 7 - 8	#1 #2 #3	11	Zr, Sr, Rb, Pb, Zn, Fe, Cr, Ti, Ca, S, Mg
	2	#1 #2 #4	7	Ba, Sr, Zn, Cr, Ca, K, S
	9 - 10 - 11 - 12	#1 #2 #3 #5	8	Zr, Rb, Zn, Fe, Cr, Ca, S, Mg
	3	#1 #2 #3 #4	8	Zr, Rb, Zn, Fe, Cr, Ca, S, Mg
C KW + DFA	1 - 4 - 5 - 6 - 7 - 8	#1 #2 #3	4	Sr, Ti, Ca, K
	2	#1 #2 #4	6	Sr, Zn, Fe, Ti, Ca, K
	9 - 10 - 11 - 12	#1 #2 #3 #5	9	Sr, Rb, Fe, Ti, Ca, K, Al, P, Si
	3	#1 #2 #3 #4	6	Sr, Zn, Fe, Ti, Ca, K

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Table 4 Summary of GOF, RMSE and AE between the estimated and real source contribution for the 12 artificial mixtures using tracer sets A, B and C. In *Italics* the source contributions underestimated; in regular the source contributions overestimated.

Mixtures	n	Tracer		GOF %	RMSE %	Source contribution AE %				
		set	n			AE #1	AE #2	AE #3	AE #4	AE #5
Mixture 1	10	A	18	87.3	2.0	0.7	2.0	2.7		
		B	11	92.8	2.4	1.2	3.3	2.2		
		C	4	98.3	1.4	0.8	2.0	1.2		
Mixture 2	10	A	18	86.6	1.0	1.4	0.9		0.6	
		B	7	94.6	2.3	2.6	0.5		3.1	
		C	6	97.2	1.1	0.1	1.3		1.3	
Mixture 3	10	A	18	87.8	1.8	1.8	0.9	2.4	1.6	
		B	8	92.7	3.7	2.8	5.7	0.9	3.8	
		C	6	97.8	2.2	1.2	3.7	1.6	0.8	
Mixture 4	10	A	18	90.4	1.8	1.5	2.6	1.1		
		B	11	92.9	1.4	0.6	2.0	1.3		
		C	4	95.8	3.6	5.0	3.5	1.4		
Mixture 5	10	A	18	86.0	3.0	0.9	4.0	3.2		
		B	11	92.7	4.4	0.2	5.5	5.3		
		C	4	97.2	2.4	3.4	1.6	1.8		
Mixture 6	10	A	18	89.7	0.8	0.8	0.3	1.1		
		B	11	92.9	2.6	0.2	3.0	3.2		
		C	4	97.2	2.8	3.8	2.6	1.2		
Mixture 7	10	A	18	87.5	0.4	0.5	0.3	0.2		
		B	11	92.4	4.2	1.1	4.5	5.5		
		C	4	97.4	3.0	3.8	3.5	0.3		
Mixture 8	10	A	18	88.0	3.2	4.3	3.5	0.8		
		B	11	90.0	3.7	2.1	3.1	5.3		
		C	4	94.5	5.9	8.2	5.0	3.2		
Mixture 9	10	A	18	94.7	2.8	1.8	4.7	0.3		2.6
		B	8	96.0	2.0	2.2	2.8	1.0		1.6
		C	9	95.5	3.6	2.7	6.0	2.9		0.4
Mixture 10	10	A	18	91.6	2.9	3.6	4.4	0.0		0.8
		B	8	95.5	4.7	6.4	6.7	0.8		1.1
		C	9	92.4	2.9	3.8	3.9	1.4		1.3
Mixture 11	10	A	18	96.0	2.0	1.8	3.2	1.4		0.1
		B	8	97.5	3.4	3.3	5.6	1.3		1.0
		C	9	96.6	2.0	2.9	2.6	0.7		1.0
Mixture 12	10	A	18	95.3	1.5	0.5	2.0	0.3		2.2
		B	8	97.2	1.3	2.0	0.4	0.8		1.6
		C	9	95.1	1.1	1.1	1.5	0.7		1.1

Table 5 Summary statistics for GOF, RMSE and AE and SD for each source contribution using tracer set A, B and C.

	Set A	Set B	Set C
	KW	KW + PCA	KW + DFA
GOF %	90.1 a	93.9 b	96.2 c
RMSE %	1.9 a	3.0 b	2.7 ab
AE % source #1	1.6 a	2.1 a	3.1 a
AE % source #2	2.4 a	3.6 a	3.1 a
AE % source #3	1.2 a	2.5 b	1.5 ab
AE % source #4	1.1 a	3.4 b	1.1 a
AE % source #5	1.4 a	1.3 a	1.0 a
SD % source #1	2.8 ab	4.1 b	1.7 a
SD % source #2	2.9 a	4.9 b	1.3 a
SD % source #3	2.4 b	2.8 b	1.5 a
SD % source #4	2.8 a	3.3 a	1.5 a
SD % source #5	1.3 a	1.4 a	1.2 a

Table 6 Summary of GOF, RMSE and AE between the estimated and real source contribution for the artificial mixtures 9b and 9c using tracer sets A, B and C. Model outputs after applying PSC factor are shown with an asterisk. In *Italics* the source contributions underestimated; in regular the source contributions overestimated.

Mixtures	<i>n</i>	Tracer		GOF %	RMSE %	Source contribution AE %				
		set	<i>n</i>			AE #1	AE #2	AE #3	AE #4	AE #5
Mixture 9b	10	A	18	89.4	2.6	<i>0.5</i>	<i>1.4</i>	4.3		2.4
		B	8	88.2	6.9	9.8	<i>9.0</i>	2.5		3.2
		C	9	92.9	3.2	4.0	<i>4.7</i>	1.1		0.4
		A *	18	91.3	1.9	<i>0.5</i>	<i>1.1</i>	3.1		1.6
		B *	8	92.1	4.3	8.8	<i>7.9</i>	1.0		1.9
		C *	9	96.7	2.7	1.5	<i>2.7</i>	1.5		0.3
Mixture 9c	10	A	18	81.0	8.4	<i>11.0</i>	2.9	12.2		1.7
		B	8	78.7	15.5	<i>11.3</i>	20.2	9.3		18.2
		C	9	91.1	12.4	<i>14.5</i>	9.9	14.7		9.7
		A *	18	89.3	6.0	7.5	<i>1.3</i>	8.2		0.7
		B *	8	87.9	11.4	4.2	10.2	5.3		11.2
		C *	9	91.1	9.3	9.5	<i>6.9</i>	11.7		4.7

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