



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



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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 $< 15 \mu\text{m}$, 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.

1. Introduction

Sediment fingerprinting is an increasingly used technique that can provide information to quantify the sources of mobilized 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; Gaspar et al., 2017). 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; Gaspar and Navas, 2013; Alewell et al., 2014;

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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. Lacey 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; Lacey 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 (Lacey 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; Sherriff 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 Lacey 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 (Fig. 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). Fig. 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 $< 1\%$. 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

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