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Accounting for inter-tracer dependence in sediment source fingerprinting: a copula-based uncertainty framework

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Abstract

Purpose Uncertainty in sediment source fingerprinting is normally propagated by Monte Carlo simulation, each tracer drawn independently from its own distribution. Geochemical tracers are seldom independent, yet what this assumption costs the apportionment has not been tested. We asked whether preserving the observed dependence changes which unit emerges as the leading sediment source.

Methods Time-integrating samplers collected suspended sediment over one year in the Tool-Baneh watershed of northern Iran, alongside 41 source samples from five geological units.

Sequential screening narrowed 34 candidate tracers to 15. Three schemes propagated uncertainty through the same mixing model: Monte Carlo sampling with tracers drawn independently, and normal and t copulas retaining the dependence structure. Thirty-six virtual mixtures provided an external check.

Results Tracers covaried strongly: mean absolute Kendall's tau across 525 pairs was 0.50, and every source group departed from its permutation null. Independent sampling gave the Shemshak Formation a mean of 41.2% and the Quaternary alluvium 29.8%; under the normal and t copulas this 11.4-percentage-point gap narrowed to 0.6 and 1.6 points. On the virtual mixtures the copulas erred less (root mean square error 11.8% against 15.1%) and their 95% intervals contained the true value 96.7% of the time against 82.8%; goodness of fit separated them by 0.1 point where their errors differed by 22%.

Conclusion Independence is not a harmless simplification here: dropping it shifts the apparent ranking of sources. Goodness of fit cannot tell accurate apportionments from inaccurate ones, and mixtures of known composition belong alongside any figures reported.

Keywords: Sediment fingerprinting · Copula · Inter-tracer dependence · Uncertainty propagation · Virtual mixtures · Geochemical tracers

1. Introduction

Sediment tracing has become a widely adopted technique for determining sediment sources in watersheds (Collins et al. 2020), with a significant number of studies utilizing this approach for watershed management purposes (Gellis and Walling 2011; Miller et al. 2015; Collins et al. 2017; Collins et al. 2020). Despite its popularity, there is still room for improvement in the use of sediment tracing as a research tool (Pulley and Collins 2018), and recent studies have employed different uncertainty methods and tracers to address this issue (D'Haen et al. 2013; Koiter et al. 2013; Smith and Blake 2014; Laceby and Olley 2015; Pulley et al. 2015).

Methodological development has proceeded along three main lines. The first concerns the selection of tracers, where procedures such as conservativeness screening, tracer corrections and statistical operations have been introduced to reduce the uncertainty inherent in sediment tracing (Koiter et al. 2013; Smith and Blake 2014; Laceby and Olley 2015; Pulley et al. 2015; Collins et al. 2017), and where Latorre et al. (2021) have investigated the efficiency of a consistent tracer selection approach and Chalaux-Clergue et al. (2024) have shown that the choice of selection method materially affects the apportionment obtained. The second concerns the un-mixing model itself: Haddadchi et al. (2013) employed the goodness of fit (GOF) method to compare model formulations, identifying the modified Collins and Hughes models as the most effective for determining the relative contribution of sediment sources, and Pulley and Collins (2018) have utilized the Sediment Fingerprinting Tool (SIFT) approach to implement the tracing technique. The third, and most recent, concerns how apportionments should be evaluated. Batista et al. (2022) have argued that evaluation against artificial mixtures of known composition is essential for supporting decision-making, and Vale et al. (2022) and Williamson et al. (2025) have shown that accuracy depends strongly on tracer type, source configuration and sampling design. Tracing studies involve a combined multivariate model to determine the contribution of various sources after measuring the tracers in the source and sediment. The accuracy of the results depends on the capability and power of the statistical model used. In this regard, it is appropriate to specify a set of answers whose distribution and prediction intervals are determined to achieve more accurate results, particularly where the sample size is limited. The concentration of tracers in sediment tracing studies is subject to numerous factors, including geology (Laceby and Olley 2015), hydrology, soil type, topography and land use, so an index that indicates the model's accuracy for various inputs is essential; a model with slight bias but high accuracy is more practical than an unbiased model with low accuracy. In sediment tracing, the Monte Carlo method is widely

utilized, where a normal distribution function or other univariate distribution is typically considered for each tracer in each source. Nevertheless, this approach does not account for the correlation between different tracers in each source. The consequences of neglecting this correlation have been recognised (Lacey and Olley 2015), and although some studies have utilized a multivariate normal distribution to account for it, this imposes both linear dependence and normal margins, which is unsuitable for most cases. In light of this, it is better to fit a univariate distribution to each tracer in sources and subsequently use copula functions to account for the correlation between tracers in each source.

Copulas provide exactly this separation. Introduced by Sklar (1959), a copula links a set of univariate marginal distributions to their joint distribution, so that the marginal behaviour of each variable and the dependence structure between variables can be specified independently of one another (Genest and Favre 2007). This makes it possible to retain the skewed, strictly positive distributions that geochemical concentrations require while still reproducing the dependence observed between them. Copulas are now standard in hydrological applications such as flood, drought and rainfall frequency analysis, and software for fitting them in high dimensions is well developed (Sadegh et al. 2017; Hofert et al. 2018). To our knowledge, however, copula functions have not previously been applied in sediment source fingerprinting, despite the neglect of inter-tracer correlation having been identified as a limitation of current uncertainty analysis in this field. The present study addresses this gap using geochemical tracers and lithological source units in the Tool-Baneh watershed, northern Iran. The specific objectives are: (i) to quantify the extent of dependence between geochemical tracers within source groups; (ii) to compare the source apportionment obtained from conventional Monte Carlo sampling, in which tracers are drawn independently, with that obtained from normal and t copulas, in which the dependence structure is retained; and (iii) to evaluate all three approaches against virtual mixtures of known composition,

so that their accuracy, bias and interval coverage can be measured directly rather than inferred from goodness of fit alone.

2. Materials and Methods

2.1 Study Area

The Tool-Baneh watershed lies south of Gorgan in Golestan Province, northern Iran, between $36^{\circ}36' - 36^{\circ}59'N$ and $54^{\circ}23' - 54^{\circ}27'E$ (Fig. 1). It covers 30 km^2 and forms a sub-basin of the Qareh Su catchment, draining generally from south to north. Elevation ranges from 1094 to 3026 m over this distance, giving the steep relief characteristic of the northern flank of the Alborz range. Mean annual precipitation is 538 mm, with a monthly maximum of 49.7 mm in December and a minimum of 18.8 mm in August. Forest covers 56.4% of the catchment and rangeland a further 39.0%, with cultivated land restricted to 4.6% (139 ha), mostly on the lower slopes.

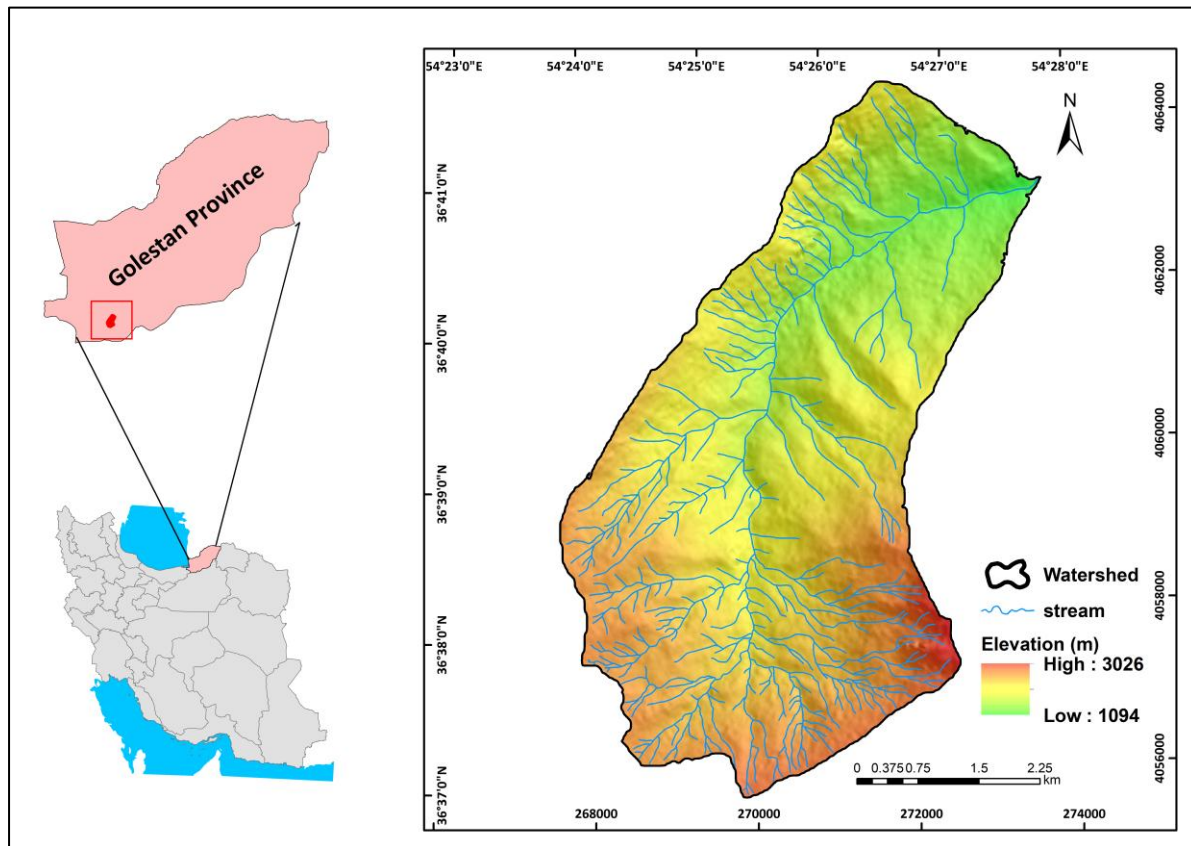


Fig 1. Location of the Tool-Baneh watershed

2.2. Suspended sediment sampling

A sampler designed by Phillips et al. (2000) was utilized to obtain suspended sediment samples for this study. This sampler provides a time-integrated sample of the suspended load passing the river section. A sufficient quantity of samplers (as depicted in Fig. 2a) was produced and deployed at suitable locations and depths (at 0.6 of the total flow depth below the water surface) across the river cross-section (as depicted in Fig. 2b, c) at five distinct points (Fig. 4). Two samplers were deployed at each point so that material would still be recovered if one were damaged during a flood. The sediment samples were collected in a manner such that each rainfall event and flood recession was sampled by referencing the area where sediment was collected (Fig. 2e). Sediments were sampled and deposited inside the sampler over the course of one year (from March 2021 to March 2022) during various seasons. A total of 25 event composites were collected throughout the year, each combining all material recovered from the paired samplers and from the five points across the section. These were then merged within each season, and eight sediment samples were ultimately obtained (two samples in each season, defined according to the Iranian calendar in which spring begins on 21 March) for the purpose of conducting the desired analysis. Because the entire recovered mass entered each composite, the seasonal samples are mass-weighted and therefore reflect the relative magnitude of the contributing events.



Fig. 2 Time-integrating suspended sediment sampler. (a) Dimensions; water enters at the inlet (1) and leaves at the outlet (2), each a 5 mm aperture, (b) Installation, (c) Sampler anchored in the cross-section, (d) Inlet detail, (e) Sediment retained after a flood.

2.3. Source sampling

The geological diversity of the watershed under investigation comprises five distinct geological units as sources, as shown in Table 1. Potential sources of sedimentation were identified by conducting repeated reconnaissance and observing different geological units in areas subjected to erosion (Fig. 3). At each sampling point, material was collected with a trowel from the upper 5 cm of the exposed, weathered surface of the unit, and each sample was a composite of several

subsamples taken around the point. The same procedure was applied to the Qal unit, which forms the channel banks. Because the sources were defined by geological unit rather than by land use, no distinction was made between surface and subsurface material. Sampling intensity was guided by the extent of active erosion observed within each unit rather than by its area alone; the Qal unit, although covering only 1.67% of the catchment, forms the actively eroding channel banks and was sampled accordingly. A total of 41 samples were collected from the geological units, with 8 from the Qal unit, 9 from the Jsl s.sh unit, 12 from the Pdl unit, 6 from the Dkh unit, and 6 from the Kul ml unit. Fig. 4 depicts the sampling points for the geological units.

Table 1. Description of geological units in the study area

Geological symbol	Formation	Age	Features	Area (ha)	Area (%)	Samples
Qal	-	Quaternary	Alluvial deposits	49.93	1.67	8
Kul ml	-	Upper Cretaceous	White marl limestone	479.48	16.00	6
Jsl s.sh	Shemshak	Lower Jurassic	Sandstone and shale	1422.24	47.46	9
Pdl	Dorud	Lower Permian	Oolitic limestone, medium to massive bedded	468.32	15.63	12
Dkh	Khoshyeilagh	Devonian	Dark grey shale	577.02	19.25	6
Total	-	-	-	2997	100	41



142 **Fig. 3** Source sampling. (a) Actively eroding alluvial bank of the Qal unit; (b) sampling an exposed
143 weathered face; (c) bedded exposure in a bedrock unit; (d) composite subsampling with a trowel.

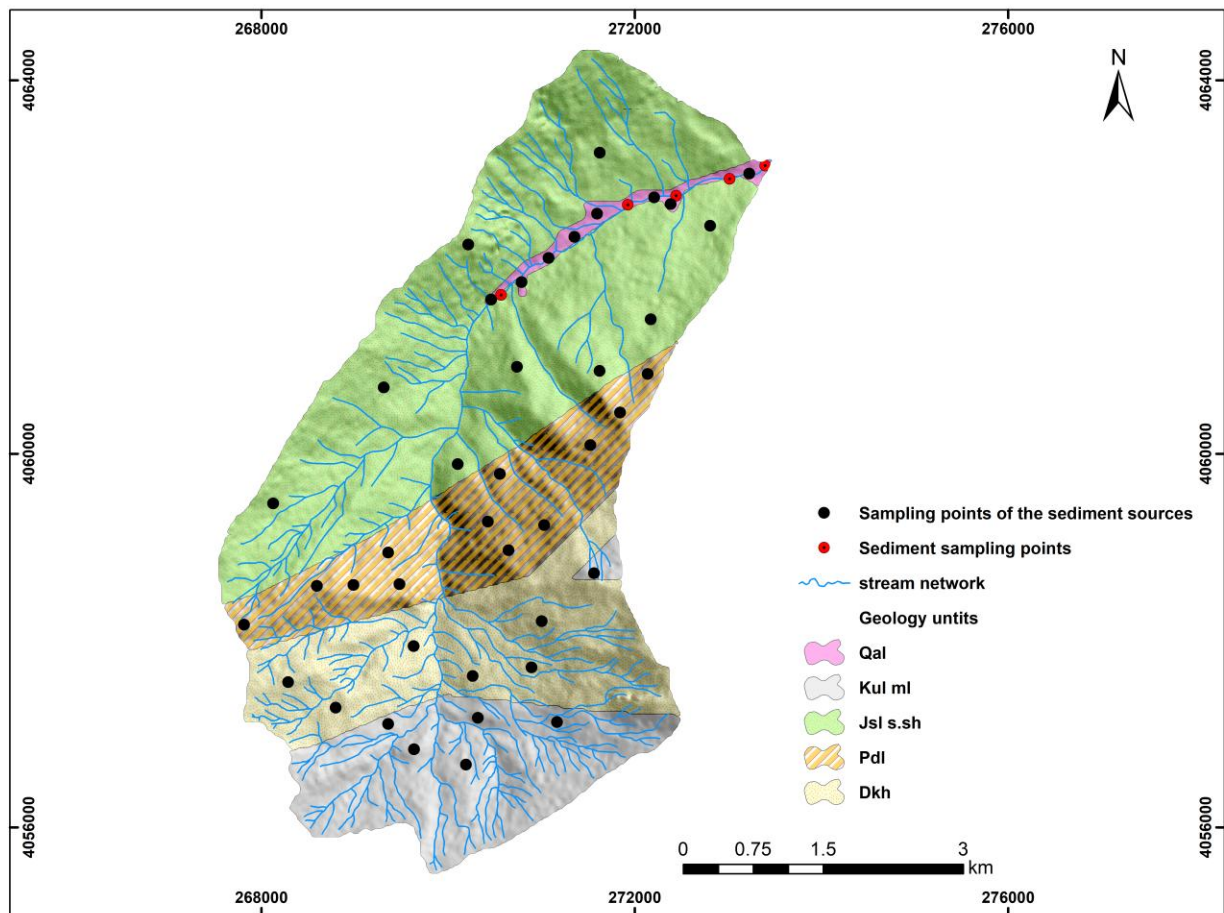


Fig 4. Distribution of the source sampling points across the geological units of the Tool-Baneh watershed, and the location of the suspended sediment sampling section.

2.4. Laboratory analyses

All source and sediment samples were air-dried, gently disaggregated and dry-sieved to $<63 \mu\text{m}$ prior to analysis, so that the same size fraction was compared across sources and target sediment and the influence of particle size on tracer concentrations was minimized (Smith and Blake 2014; Owens et al. 2016; Collins et al. 2017). The present study employed 34 primary geochemical tracers (Table 2). A four-acid digestion using HNO_3 , HClO_4 , H_2SO_4 and HF was applied to break apart all existing bonds, including silicates. The samples were prepared by placing 2 g of material into polyethylene containers, followed by adding 25 cm^3 of distilled water and 2 cm^3 of nitric acid. The

samples were then heated below 100 °C until they were dry. Subsequently, 3 drops of sulphuric acid and 10 cm³ of hydrofluoric acid were added, and the samples were gradually heated to 200 °C until all the liquid evaporated. Then, 15 cm³ of nitric acid, 2 cm³ of sulphuric acid, and 5 cm³ of perchloric acid were added, and heating continued until SO₃ vapour was emitted from the containers. Finally, after cooling, the samples were diluted to 50 cm³ with distilled water. The solution from each sample was filtered using syringe filters with a pore size of 0.45 µm. The concentrations of the elements were then determined by ICP-OES at the Geological Survey and Mineral Exploration of Iran (GSI), Karaj, and are reported in mg kg⁻¹. Detection limits ranged from 0.1 mg kg⁻¹ for silver and cadmium to 100 mg kg⁻¹ for the major elements. Calcium and uranium fell outside the reporting range of the method in 16 of the 49 samples, being returned as >10% and <5 mg kg⁻¹ respectively, and were therefore excluded before the statistical screening; all other elements were above their detection limits in every sample.

2.5. Tracer selection

The sediment tracing technique is commonly used for differentiating between sediment sources. A crucial step in this method is the selection of conservative tracers, which can maintain their properties during transport. The selection of optimal tracers is necessary to ensure the reliability and accuracy of the results obtained. In this regard, Nosrati et al. (2018) have emphasized the importance of selecting suitable tracers for sediment tracing.

The range or bracket test determines whether the concentrations measured in the target sediment fall strictly inside the range spanned by the source samples: a tracer is accepted when the minimum sediment concentration exceeds the minimum source concentration and the maximum sediment concentration is below the maximum source concentration. Tracers that pass this test are accepted, while those that fail are rejected (Foster and Lees 2000; Mukundan et al. 2010; Navratil et al. 2012; Schuller et al. 2013; Smith and Blake 2014; Haddadchi et al. 2015). The Kruskal-Wallis test was

then conducted to determine whether there are significant differences between the medians of two or more groups of sediment sources. Tracers with a p -value of less than 0.05 were retained to distinguish sediment sources, while the rest were discarded.

Stepwise discriminant function analysis was employed in the final step to reduce the initial set of selected tracers. The forward method is used to enter tracers that maximize the F-statistic based on Wilks' lambda. This approach enhances the discrimination of the selected tracers. Conversely, the backward method involves removing tracers based on the partial F statistic until the discrimination of the set of tracers is not affected. The stepwise method combines both methods, wherein a new variable is added in each step until the algorithm reaches the desired threshold level. Rencher (2002) suggests that the algorithm stops when the maximum partial F value of the new variable cannot exceed the specified threshold level. Variables were entered at a significance level of 0.05 and removed at 0.10.

The discriminating ability of the retained tracers was assessed by cross-validation. Because the tracers were themselves chosen using the full dataset, the entire stepwise procedure was additionally repeated within each of 41 leave-one-out folds, so that no held-out sample contributed to the tracer selection applied to it. This provides a classification accuracy free of selection bias, together with a measure of how consistently each tracer is selected.

The Kruskal-Wallis test was performed using IBM SPSS Statistics; the range test, discriminant function analysis and cross-validation were carried out in R (v4.5) using the MASS package (Venables and Ripley 2002).

2.6. The mixing model

In the process of fingerprinting, the final step involves determining the contribution of sources by applying a multivariate mixing model after having identified the most fitting tracers. This model

assumes a linear combination and mixing of feature tracers from various sources (Foster and Lees 2000; Walling 2013). For each source characteristic, the model can be expressed as follows:

$$\hat{X}_i = \sum_{j=1}^n a_{ij} b_j \quad (1)$$

Where $\hat{X}_i$ represents the estimated value of the i th attribute (where i is equal to the number of attributes, from 1 to m), a_{ij} is the average value of the i th attribute in the j th sediment source (where j is equal to the number of sediment sources, from 1 to n), and b_j represents the contribution of the j sediment source. To obtain the contribution of each sediment source, the above equation is repeated for each attribute of the source, resulting in a set of equations equal in number to the attributes. The contribution of each sediment source can then be obtained by solving these equations. Notably, these equations must satisfy two conditions, as stipulated by Collins et al. (2001) and reaffirmed in the methodological review of Collins et al. (2017).

1. Each sediment source's contribution coefficient must be between 0 and 1.

2. The sum of contribution coefficients for each sediment source must equal 1.

To obtain the optimal contribution of sediment sources, we need to use optimization methods rather than direct solutions (Yu and Oldfield 1993; Rowan et al. 2000; Latorre et al. 2021), as the set of equations can be overdetermined and have various solutions. Methods such as minimizing the sum of residual squares (Walling et al. 1993; Russell et al. 2001) or minimizing the sum of relative errors (Bottrill et al. 2000) can be used to attain the optimal contribution of sediment sources previously estimated by multivariate mixing models. In tracing studies, these methods play a crucial role in determining the contribution of sediment sources and should be implemented to achieve accurate results. The residual sum of squares may be defined by the following expression:

$$R = \sum_{i=1}^m (X_i - \hat{X}_i)^2 = \sum_{i=1}^m [X_i - (\sum_{j=1}^n a_{ij} b_j)]^2 \quad (2)$$

In this equation, R represents the residual sum of squares and X_i corresponds to the measured value of the i th attribute in the sediment sample, so that each residual is the difference between the measured value and the value predicted by Eq. 1. Here m is the number of tracer characteristics, n is the number of grouping variables (geological formations), b_j represents the contribution coefficient of each sediment source, and a_{ij} denotes the average value of the i th tracer in the j th sediment source. To eliminate the influence of different measurement units, we may adopt the following formulation:

$$R = \sum_{i=1}^m \left[\frac{X_i - \left(\sum_{j=1}^n a_{ij} b_j \right)}{X_i} \right]^2 \quad (3)$$

In this formulation each residual is divided by the measured concentration of the corresponding tracer, so that all tracers contribute to the objective function on a comparable relative scale irrespective of the magnitude of their concentrations. This is necessary here because the measured concentrations span several orders of magnitude, from about 1 mg kg^{-1} for beryllium to several tens of thousands of mg kg^{-1} for the major elements. The optimal solution for the contribution of sediment sources was attained by minimizing Eq. 3, subject to the constraints that the sum of b_j equals 1 and that each b_j is greater than or equal to 0. The same objective function and constraints were applied throughout the uncertainty analysis described in Section 2.7 and the model evaluation in Section 2.8. The mixing model was applied to each of the eight sediment samples individually and, in addition, to a ninth target defined as the arithmetic mean of the tracer concentrations of the eight samples. This mean-composition target represents the catchment-wide annual average and is the basis of the apportionment reported in Section 3.2 and Table 4; the eight individual samples are reported in Fig. 9. The eight samples are weighted equally in this mean.

2.7. Propagating tracer uncertainty

Before propagating uncertainty, the dependence between the selected tracers was quantified. Kendall's rank correlation was computed between every pair of tracers within each source group, and the observed mean absolute correlation was compared with a null distribution obtained by permuting each tracer independently 2000 times, which removes any dependence while preserving the marginal distributions.

The Monte Carlo method has been widely used to estimate the uncertainty of the tracing method. This method has been utilized in various studies, including those conducted by Rowan et al. (2000), Small et al. (2002), Krause et al. (2003), Motha et al. (2003, 2004), Collins et al. (2010, 2012), Martínez-Carreras et al. (2010a, 2010b), Evrard et al. (2011), Mukundan et al. (2011), Rowan et al. (2012), and Ben Slimane et al. (2013).

The Monte Carlo method involves several steps in modeling uncertainty. Firstly, a marginal distribution is fitted to each tracer in each source. Gamma and log-normal distributions were evaluated for each tracer in each source, and the one with the lower AIC was retained. The same procedure was applied for the copula schemes, so that the three schemes differ only in whether the tracers are drawn independently or jointly. The selected distribution is assumed to comprise laboratory errors, as well as spatial and temporal changes of tracers during modeling. Next, each tracer is sampled independently from its fitted marginal. Because both candidate distributions are strictly positive, no negative concentrations arise. The mixing model (Eq. 3) is then solved and the contribution of each source determined. These steps are repeated a predetermined number of times; in this research the simulation was run 20,000 times, following Collins et al. (2010), Evrard et al. (2011) and Ben Slimane et al. (2013). Lastly, prediction intervals are calculated for the contribution of each source; the 95% prediction interval corresponds to the 2.5th and 97.5th percentiles of the simulated distribution. All three schemes were implemented in R. Because the objective in Eq. 3 is quadratic in the source proportions, it was solved exactly by quadratic programming under the

constraints given in Section 2.6, so that no optimiser noise enters the comparison between schemes.

A limitation of this approach is that each tracer is sampled independently, so the correlation between tracers within a source is disregarded. To address this, the simulation was repeated using copula functions.

The term "copula" was initially introduced in the fields of statistics and mathematics by Sklar (1959). A copula is a mathematical tool that connects a set of univariate marginal cumulative probability functions and produces a multivariate cumulative probability function (Nelsen 2006; Joe 2014). This technique is based on non-linear relationships and dependence between variables and considers the dynamic correlation of variables. By connecting the marginal distribution functions of the random variable P ($F_1(X_1)$, $F_2(X_2)$, ..., $F_p(X_p)$) and their joint distribution function ($F(X_1, X_2, \dots, X_p)$), copulas enable the evaluation of the set of possible marginal functions that make up the joint distribution function and vice versa (Eqs. 4 and 5).

$$F_1(X_1) = U_1, F_2(X_2) = U_2, F_p(X_p) = U_p \quad (4)$$

$$C(u_1, u_2, \dots, u_p) = \Pr(U_1 \leq u_1, U_2 \leq u_2, \dots, U_p \leq u_p) \quad (5)$$

Marginal distribution refers to the most suitable probability distribution fitted to a random variable X without considering the distribution of the random variable Y . The same is the case for random variable Y , which is expressed in two forms of the probability distribution function (PDF) or cumulative distribution function (CDF). The marginal distribution of random variables X and Y can be expressed as follows (Eqs. 6 and 7).

$$F(x) = P[X \leq x] \quad (6)$$

$$G(y) = P[Y \leq y] \quad (7)$$

The joint distribution function is a probability distribution function that provides the probability that the random variables X and Y fall within a specific numerical interval. In other words, the joint

distribution results from connecting and combining the two marginal distributions X and Y, which can be presented in the form of the following formula (Eq. 8).

$$H(x, y) = P [X \leq x, Y \leq y] \quad (8)$$

Copulas are generally divided into two categories: parametric and non-parametric. The popularity of parametric copulas stems from the use of parameters, which have been considered in various types of research. By estimating these parameters, it is feasible to fit the copula with input data, which is a limitation for non-parametric copulas. These parameters represent the intensity of dependence on variables and have a certain mathematical relationship with them. The use of different parameters in different parametric copulas can lead to different results.

The normal or Gaussian copula is a type of elliptic copula that can be calculated using Eq. 9.

$$C_{\rho}(u, v) = \int_{-\infty}^{F^{-1}(u)} \int_{-\infty}^{F^{-1}(v)} \frac{1}{2\pi(1-\rho^2)^{0.5}} \exp \left\{ -\frac{x^2 - 2\rho xy + y^2}{2(1-\rho^2)} \right\} dx dy \quad (9)$$

In this equation, F^{-1} represents the inverse of the univariate standard normal distribution, while ρ denotes the linear correlation coefficient and the normal copula parameter. On the other hand, the t copula has the following formula (Eq. 10).

$$C_{\rho, \nu}(u, v) = \int_{-\infty}^{t_{\nu}^{-1}(u)} \int_{-\infty}^{t_{\nu}^{-1}(v)} \frac{\Gamma(\frac{\nu+2}{2})}{\Gamma(\frac{\nu}{2})\nu\pi(1-\rho^2)^{0.5}} \left\{ 1 + \frac{x^2 - 2\rho xy + y^2}{\nu(1-\rho^2)} \right\}^{-\frac{(\nu+2)}{2}} \quad (10)$$

Here, ν represents the degree of freedom, while ρ denotes the linear correlation coefficient and the parameter of the copula. For large degrees of freedom (30 or more) the t copula converges on the normal copula, whereas for small degrees of freedom it places appreciably more probability on the joint tails, so that extreme values of several tracers are more likely to occur together. The degrees of freedom were fixed at four rather than estimated, because the source group sizes available here are too small to estimate this parameter reliably alongside the dependence matrix. A low value was chosen deliberately, so that the t copula would differ as much as possible from the normal copula

and the comparison between them would be informative; that the two nevertheless produced almost identical apportionments (Section 3.2) indicates that the result is insensitive to this choice.

Several software packages have been developed to implement copula functions, including copula, MvCAT (Sadegh et al. 2017), VineCopula, and copulaedas. However, copula (Hofert et al. 2018) is the most comprehensive package that can model copula structures in high dimensions. It comprises two significant classes, namely copula and mvdc. The copula class constructs copula functions irrespective of the type of marginal function, while the mvdc class creates copula functions with specified marginal distributions. This research adopted the mvdc class to run copula functions for tracer values in sources. To this end, a copula function was considered for all tracers of each source, and a marginal function was considered for each tracer in each source. The appropriate marginal function for each tracer in each source was selected, with only two probability density functions, gamma and log-normal, being evaluated, as tracer values are positive.

Marginal parameters were estimated by maximum likelihood in R and the distribution with the lower AIC retained. Following the identification of the appropriate marginal function, the parameters of copula functions were determined. Multiple methods, including maximum pseudo-likelihood (MPL), itau, and irho, are available in this package for estimating parameter values. In this research, two functions, the normal copula and t copula, were examined due to the dimensions of the problem. Initially, the MPL method was utilized to estimate the parameters. However, given the number of observation samples for each tracer in each source relative to the number of copula parameters, the model was unable to identify optimal values. Therefore, the itau method was employed instead, which obtains the dependence parameter of an elliptical copula directly from the sample Kendall's tau (Genest and Favre 2007):

$$\rho = \sin\left(\frac{\pi\tau}{2}\right) \quad (11)$$

where τ is Kendall's rank correlation between a pair of tracers and ρ the corresponding copula parameter. Because this is a closed-form moment estimator, it converges where maximum pseudo-likelihood does not. Simulated tracer values were then drawn from the fitted copula and passed to the mixing model, which was solved 20,000 times for each copula as for the Monte Carlo simulation.

2.8. Model evaluation

Goodness of fit measures how closely a model reproduces the tracer concentrations of the target sediment, not whether the source proportions it returns are correct, and previous work has shown that high goodness-of-fit values are not reliable indicators of accurate apportionment (Palazón et al. 2015; Gaspar et al. 2019). Model performance was therefore assessed against virtual mixtures, in which sediment of known composition is constructed from the source samples so that the true contributions are known and each model's error can be measured directly (Batista et al. 2022).

Thirty-six mixtures were used: five single-source mixtures, ten equal two-source mixtures, one equal five-way mixture and twenty random compositions. Single-source mixtures were included deliberately, because the extent to which a model recovers a 100% contribution from one source is a direct measure of how separable that source is from the others. Two designs were tested. In the first, mixtures were constructed from the source group means. In the second, each mixture was constructed from individual source samples drawn at random, one per source, which were then withheld from the source characterisation used to recover them, so that no sample contributed both to a mixture and to the distributions fitted to model it. All three sampling schemes were applied to every mixture using the same objective function and the same source data, so that any difference in performance is attributable to the sampling scheme alone.

Model performance was quantified using the following measures, where P_i is the known contribution and $\hat{P}_i$ the median estimated contribution of the i th source–mixture combination, and N is the number of such combinations:

$$\text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^N (\hat{P}_i - P_i)^2} \quad (12)$$

$$\text{MAE} = \frac{1}{N} \sum_{i=1}^N |\hat{P}_i - P_i| \quad (13)$$

$$\text{ME} = \frac{1}{N} \sum_{i=1}^N (\hat{P}_i - P_i) \quad (14)$$

$$\text{NSE} = 1 - \frac{\sum_{i=1}^N (\hat{P}_i - P_i)^2}{\sum_{i=1}^N (P_i - \bar{P})^2} \quad (15)$$

Root mean square error and mean absolute error measure the magnitude of the error and are zero for a perfect model. Mean error measures bias, and is also zero for an unbiased model; because positive and negative errors cancel, it should be read together with the error magnitudes. Nash–Sutcliffe efficiency compares the model error with the variance of the known contributions and equals one for a perfect model. In addition, the squared Pearson correlation between known and estimated contributions was calculated, together with the slope of their linear regression, for which a value below one indicates that the estimates are compressed towards equal shares. Finally, the width of the 50% and 95% prediction intervals was recorded, together with the proportion of known contributions falling inside the 95% interval; an interval that is narrow but fails to contain the true value indicates overconfidence, so interval width must always be read together with its coverage (Chaloux-Clergue et al. 2024). Goodness of fit was also calculated, using the method introduced by Collins et al. (2012), so that it could be compared with the measures above:

$$\text{GOF} = 1 - \frac{1}{n} \sum_{i=1}^n [((y_i - (\sum_{j=1}^m a_{ij} x_j))/y_i)]^2 \times 100 \quad (16)$$

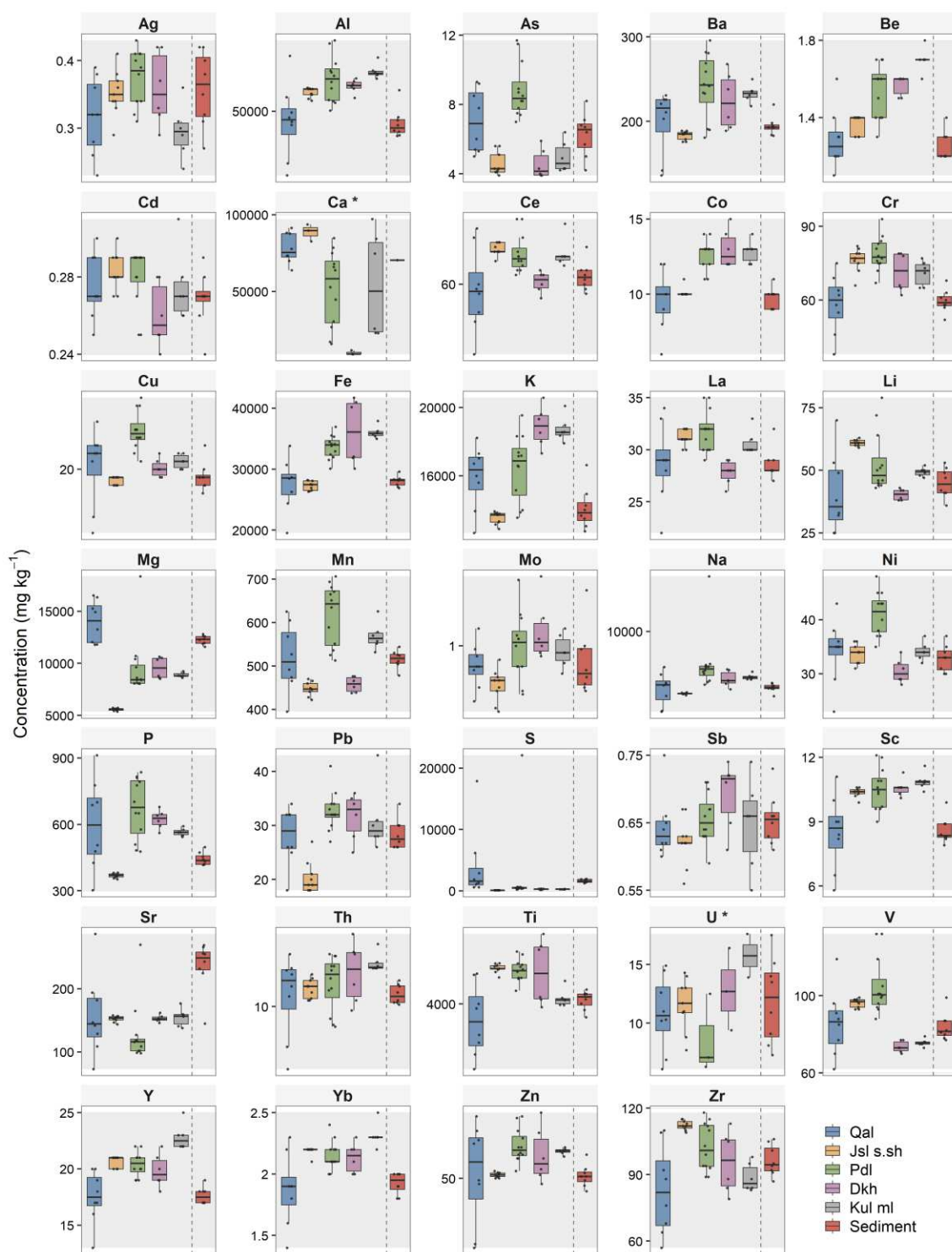
The GOF value, which ranges from 0 to 100, gauges the concordance between the predicted and observed tracer concentrations. The virtual-mixture evaluation was carried out in R.

3. Results

3.1. The results of determining the optimal combination of tracers

Concentrations of the 34 elements determined in the five source groups and in the eight target sediment samples are summarised in Fig. 5. For all but one element, concentrations in the sediment samples fell within the range spanned by the source samples, indicating that the sampled sources collectively bracket the target sediment and that no tracer showed evidence of pronounced non-conservative behaviour.

Three elements were withdrawn before the discriminant analysis. Calcium and uranium were excluded on analytical grounds, as a large proportion of their results lay outside the reporting range of the method: calcium was returned as ">10%" in 16 of the 49 samples, including seven of the eight sediment samples, and uranium as "<5 mg kg⁻¹" in 16 samples. The remaining 32 tracers were subjected to the range test, which cadmium alone failed, its minimum sediment concentration coinciding with the minimum recorded in the sources rather than falling inside that range (Table 2). The Kruskal-Wallis test was subsequently carried out on the remaining 31 tracers, and its results are also presented in Table 2. The results indicated that two tracers, antimony (Sb) and thorium (Th), were unable to distinguish between different sources and were hence removed. Consequently, 29 tracers were deemed fit for the next stage of the analysis.



398 **Fig 5.** Concentrations of the 34 elements determined in the five geological source groups and in
 399 the eight target suspended sediment samples. * Calcium and Uranium, for which a large proportion
 400 of results lay outside the analytical reporting range.

401

Table 2. Results of the range test and the Kruskal-Wallis test

Tracer	Screening	H value	P value	Tracer	Screening	H value	P value
Ca	E	-	-	Mn	P	27.04	0.000*
U	E	-	-	Mo	P	16.12	0.003*
Ag	P	11.42	0.022*	Na	P	23.02	0.000*
Al	P	16.34	0.003*	Ni	P	24.57	0.000*
As	P	27.06	0.000*	P	P	20.63	0.000*
Ba	P	19.83	0.001*	Pb	P	20.75	0.000*
Be	P	26.00	0.000*	S	P	33.54	0.000*
Cd	R	-	-	Sb	P	7.10	0.131
Ce	P	16.24	0.003*	Sc	P	13.84	0.008*
Co	P	27.08	0.000*	Sr	P	9.87	0.043*
Cr	P	18.58	0.001*	Th	P	8.01	0.091
Cu	P	25.86	0.000*	Ti	P	19.95	0.001*
Fe	P	28.51	0.000*	V	P	26.02	0.000*
K	P	27.47	0.000*	Y	P	23.98	0.000*
La	P	17.32	0.002*	Yb	P	16.30	0.003*
Li	P	19.79	0.001*	Zn	P	11.78	0.019*
Mg	P	30.16	0.000*	Zr	P	19.50	0.001*

402 * Tracers with a significance level lower than 0.05 and were considered significant in the Kruskal-Wallis test. P denotes tracers
 403 accepted in the bracket test; R denotes cadmium, rejected in the bracket test; E denotes elements withdrawn before screening because
 404 a large proportion of results lay outside the analytical reporting range.

405 In the subsequent phase of the study, stepwise discriminant function analysis was conducted to
 406 determine the optimal combination of tracers from the remaining 29 that could best differentiate
 407 the geological units. Wilks' lambda was employed to execute this analysis, with a significance level
 408 of 0.05 for entering variables and 0.10 for removing them. Consequently, 15 tracers were deemed
 409 the optimal combination, and the model Wilks' lambda fell from 0.296 after the first tracer to 5.50
 410 $\times 10^{-7}$ after the fifteenth (Table 3). Barium entered last and with the weakest contribution ($F =$
 411 4.18) and was reselected in only 9 of the 41 cross-validation folds; it was retained for consistency
 412 with the selection criterion but is the least robust member of the composite signature.

413 The discriminating ability of the selected tracers was assessed by cross-validation. Under leave-
 414 one-out cross-validation all 41 source samples were correctly classified. Because the tracers had
 415 themselves been chosen using the full dataset, the selection procedure was additionally repeated
 416 within each fold so that no held-out sample influenced the tracers applied to it; under this stricter
 417 test 38 of the 41 samples (92.7%) were correctly assigned. Fig. 6 shows the source samples and the

target sediment in the space of the first two discriminant functions, which account for 73.9% and 14.9% of the between-source variance respectively.

Table 3. Results of the stepwise discriminant function analysis (SDFA)

Step	Tracer	Wilks' λ	F to enter	Folds	Step	Tracer	Wilks' λ	F to enter	Folds
1	Mg	2.96×10^{-1}	21.43	36	9	La	9.59×10^{-5}	8.50	23
2	Be	1.03×10^{-1}	16.41	26	10	Sc	4.42×10^{-5}	7.88	24
3	V	1.69×10^{-2}	43.30	41	11	Y	1.80×10^{-5}	9.51	41
4	Li	3.98×10^{-3}	26.73	39	12	P	5.09×10^{-6}	15.81	41
5	Sr	2.11×10^{-3}	7.09	26	13	Co	2.16×10^{-6}	8.14	40
6	Zn	1.19×10^{-3}	5.96	25	14	Zr	9.68×10^{-7}	7.08	25
7	Na	5.85×10^{-4}	7.79	40	15	Ba	5.50×10^{-7}	4.18	9
8	Ti	2.12×10^{-4}	12.72	36					

* Wilks' λ is the value for the model after the tracer was entered; all entries were significant at $p < 0.05$.

** Folds give the number of the 41 leave-one-out folds in which the tracer was reselected when the stepwise procedure was repeated within each fold, and indicates how robust each selection is to the individual samples.

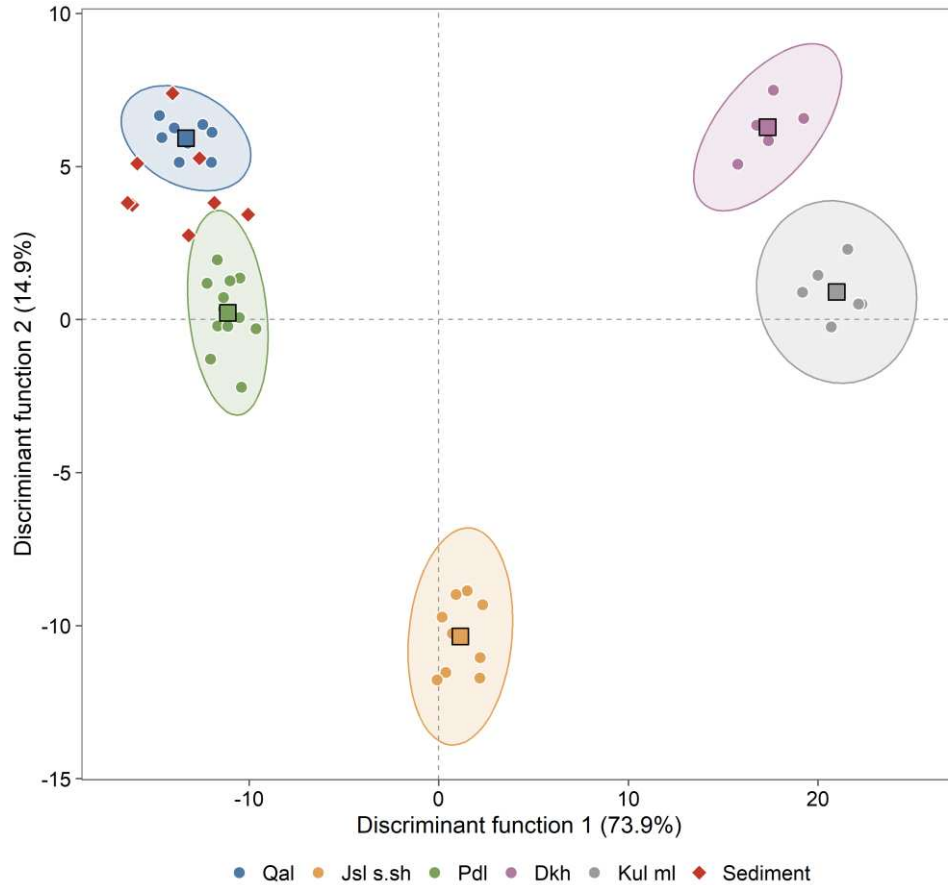


Fig. 6 Source samples and target sediment in the space of the first two discriminant functions. Circles: source samples; filled squares: group centroids; shaded areas: 95% confidence regions; red diamonds: the eight target sediment samples.

3.2. Contribution of the geological units to suspended sediment

Rank dependence between the selected tracers was widespread. Across the 525 tracer pairs examined over the five source groups, the mean absolute Kendall's tau was 0.50, and 53% of pairs exceeded 0.5 (24% exceeded 0.7). Permuting each tracer independently, which removes any dependence while preserving the marginal distributions, gave a mean absolute tau of 0.19 to 0.31 depending on group size; the observed value lay outside the permutation interval for every source ($p < 0.001$ in all cases, Fig. 7). The independence between tracers implicit in the classical Monte Carlo mixing model is therefore not supported by these data.

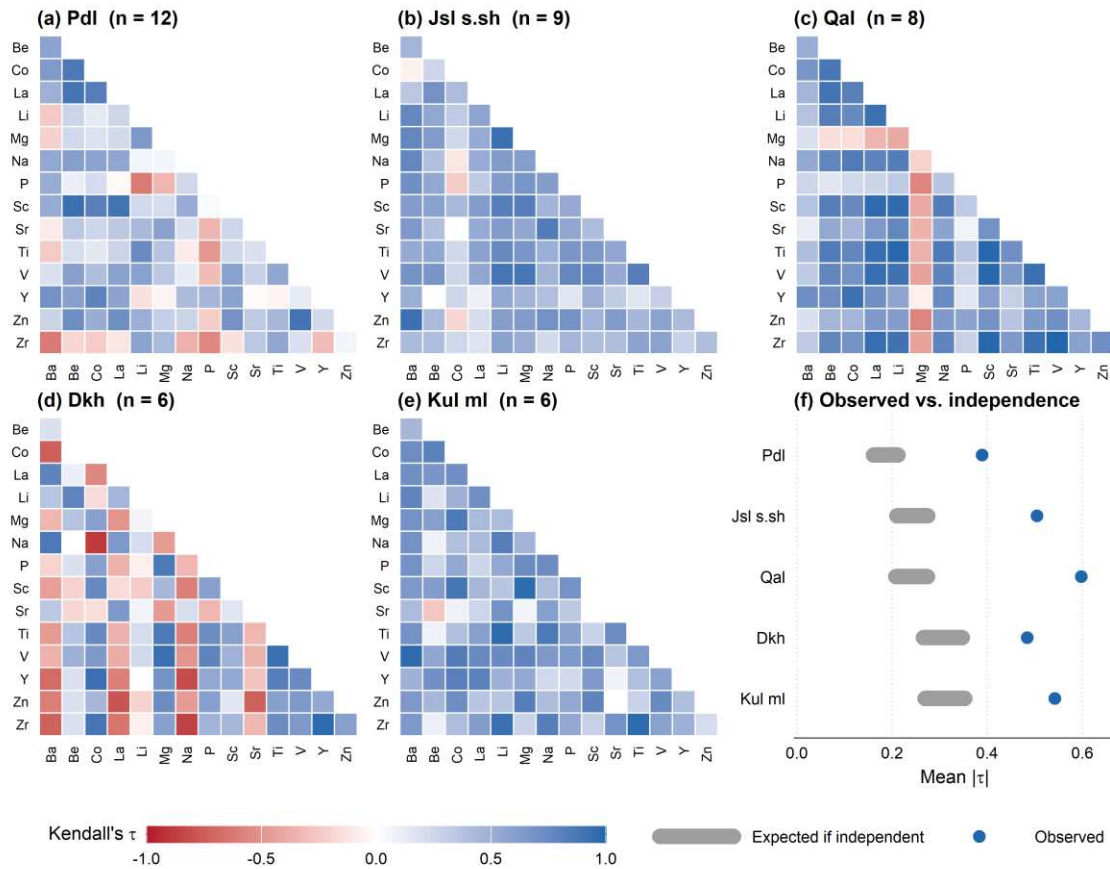


Fig. 7 Kendall's rank correlation between every pair of the 15 tracers, by source group. Panel (f): observed mean $|\tau|$ against the permutation null.

The mixing model was solved 20,000 times under each of the three approaches and the resulting distributions of source contribution are shown in Fig. 8. Under the Monte Carlo approach (Table 4), Jsl s.sh contributed a mean of 41.2% of the suspended sediment load (median 42.3%; 95% prediction interval 14.6–62.1%), followed by Qal at 29.8% (median 30.2%; 4.4–54.1%) and Dkh at 19.0% (median 18.7%; 0.0–47.6%). Pdl and Kul ml were apportioned means of 3.1% and 6.9%, with medians of zero, although their upper prediction limits reached 23.4% and 34.8% respectively. Both copulas closed the gap between Jsl s.sh and Qal (Table 4). Under the normal copula, Qal contributed a mean of 36.1% (median 35.8%; 95% prediction interval 0.0–76.7%) and Jsl s.sh 35.5% (median 36.5%; 5.4–59.0%), while Dkh fell to 14.9% (median 11.1%; 0.0–49.9%). The t copula gave a similar result, with Qal at 37.0% (median 36.7%; 0.0–78.4%), Jsl s.sh at 35.4% (median 36.0%; 5.7–58.5%) and Dkh at 14.7% (median 10.5%; 0.0–50.2%). All means and medians are reported in Table 4; the text refers to means throughout. The separation between the two leading units under both copulas is smaller than the width of their prediction intervals, so their order should not be read as a ranking.

Table 4. Estimated contribution (%) of each geological unit to the suspended sediment load

Source	Monte Carlo			Normal copula			t-copula		
	Mean	Median	95% PI	Mean	Median	95% PI	Mean	Median	95% PI
Qal	29.8	30.2	4.4–54.1	36.1	35.8	0.0–76.7	37.0	36.7	0.0–78.4
Jsl s.sh	41.2	42.3	14.6–62.1	35.5	36.5	5.4–59.0	35.4	36.0	5.7–58.5
Pdl	3.1	0.0	0.0–23.4	5.7	0.0	0.0–38.0	5.4	0.0	0.0–36.7
Dkh	19.0	18.7	0.0–47.6	14.9	11.1	0.0–49.9	14.7	10.5	0.0–50.2
Kul ml	6.9	0.0	0.0–34.8	7.8	0.0	0.0–41.4	7.5	0.0	0.0–40.4

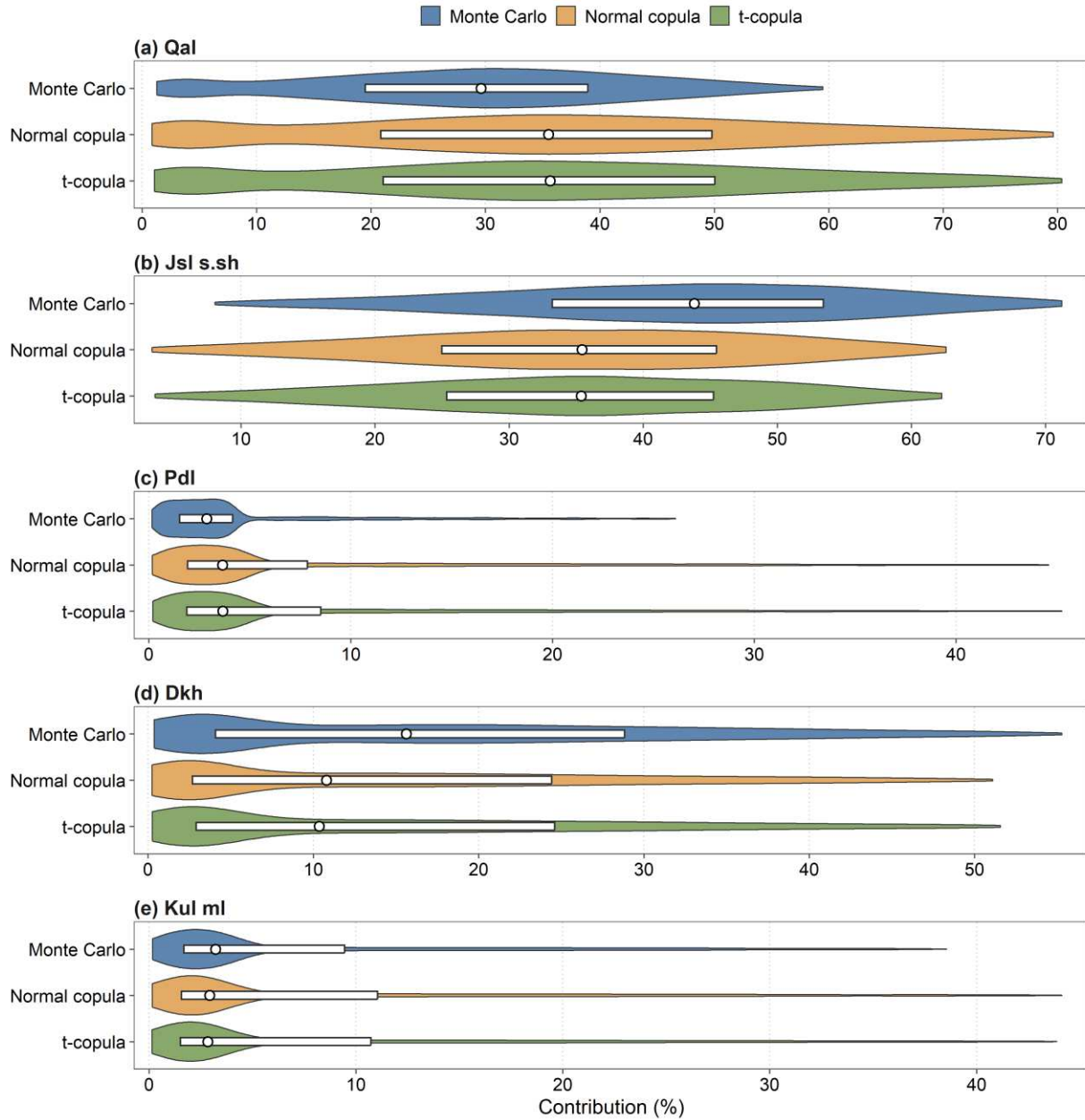


Fig.8 Distribution of the contribution of each geological unit to the mean composition of the eight sediment samples, under the three uncertainty-propagation schemes.

This convergence is the central result of the comparison. Accounting for dependence reduced the mean contribution of Jsl s.sh by approximately 5.7–5.8 percentage points and increased that of Qal by approximately 6.3–7.2 percentage points. It also reduced the mean apportionment to Dkh by 4.1 and 4.3 percentage points. removing the clear dominance of Jsl s.sh obtained under independent

sampling. The prediction intervals are wide and overlap substantially between models, so the ranking is indicative rather than resolved; those intervals are a direct consequence of the small number of source samples and are reported in full rather than being summarised by point estimates alone. Contributions varied between the eight individual sediment samples (Fig. 9). Across samples, the median contribution of Qal ranged from 21.2% to 36.6% and that of Jsl s.sh from 37.7% to 47.8%, with the two units alternating in rank between samples. The three schemes differed in the magnitude of these contributions but not in their ordering across samples. Given that each sample represents a single season and that the prediction intervals for individual samples are wider than those for the pooled sample, this variation is reported for completeness rather than interpreted as a seasonal signal.

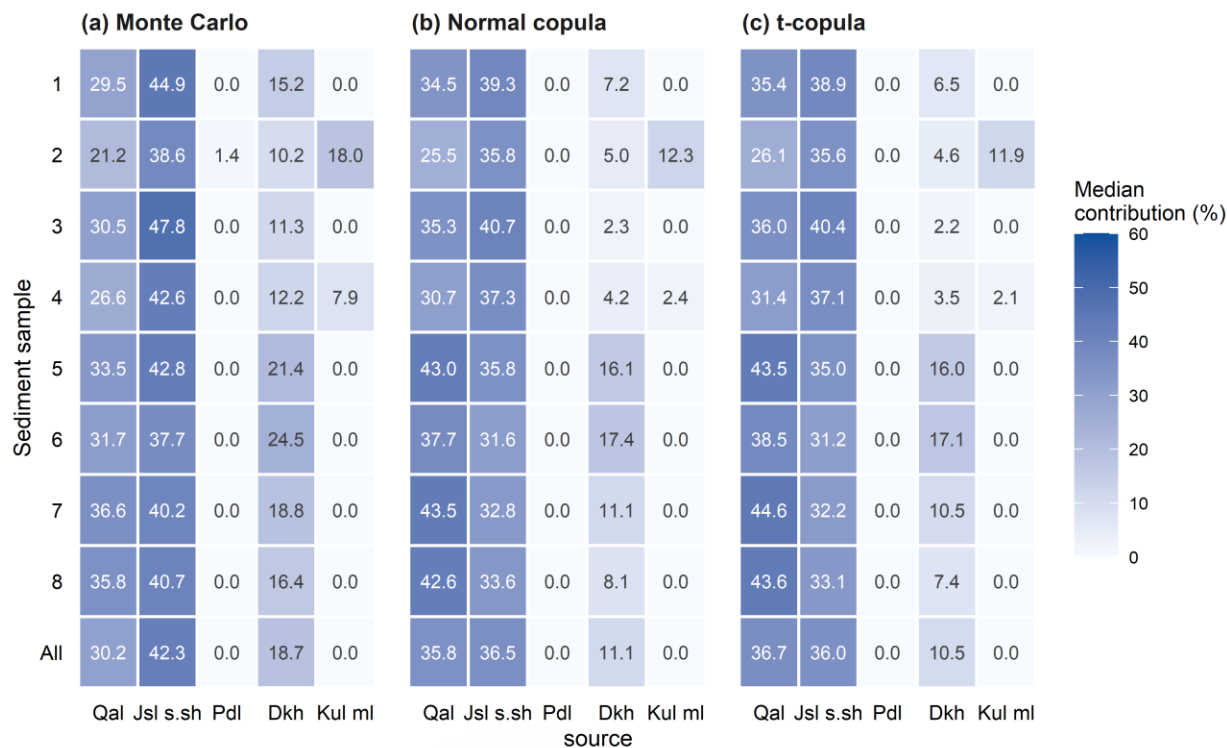


Fig. 9 Median contribution of each geological unit to each of the eight sediment samples, under the three uncertainty-propagation schemes.

3.3. Model evaluation

The two copulas were more accurate than independent Monte Carlo sampling on every measure of error (Table 5). Root mean square error fell from 15.1% to 12.2% and 11.8%, mean absolute error from 10.3% to 8.1% and 7.8%, and the coefficient of determination rose from 0.57 to 0.74 and 0.76. All three approaches compressed the estimates towards equal shares, but less so under the copulas: the slope of predicted on known contribution rose from 0.55 to 0.63 and 0.64. As a reference point, a model that ignores the tracer data entirely and assigns 20% to every source would give a root mean square error of 23.0 percentage points on these mixtures, since the mean known contribution is 20% by construction. Independent sampling improves on that reference by 6% under Design B, whereas the copulas improve on it by 19%. The gain therefore comes from the dependence structure rather than from the mixing model itself.

Table 5. Performance of the three uncertainty-propagation schemes against 36 virtual mixtures

Design	Model	RMSE	MAE	ME	r ²	NSE	Slope	Cover ₉₅	W ₅₀	W ₉₅	GOF
A	Monte Carlo	15.1	10.3	-0.7	0.57	0.57	0.55	82.8	12.0	32.1	99.6
A	Normal copula	12.2	8.1	-1.3	0.74	0.72	0.63	96.7	14.8	38.2	99.7
A	t-copula	11.8	7.8	-1.3	0.76	0.74	0.64	96.7	14.8	38.5	99.7
B	Monte Carlo	21.6	14.4	-0.7	0.22	0.12	0.37	83.3	14.8	36.1	95.4
B	Normal copula	18.6	12.4	-1.5	0.37	0.35	0.45	93.9	18.5	42.1	96.1
B	t-copula	19.2	12.2	-1.5	0.35	0.31	0.45	92.8	18.3	42.0	96.1

Design A: mixtures constructed from the source group means. Design B: mixtures constructed from individual source samples that were then withheld from the source characterisation.

Interval coverage separated the approaches most clearly. Under independent sampling the 95% prediction interval contained the true contribution in only 82.8% of cases, so the narrower intervals it produced reflect overconfidence rather than greater precision. Both copulas were correctly calibrated, with 96.7% coverage. Goodness-of-fit, by contrast, differed by less than one percentage point between the three approaches (99.6 to 99.7) while root mean square error differed by 22%, confirming that it does not discriminate between models of differing accuracy.

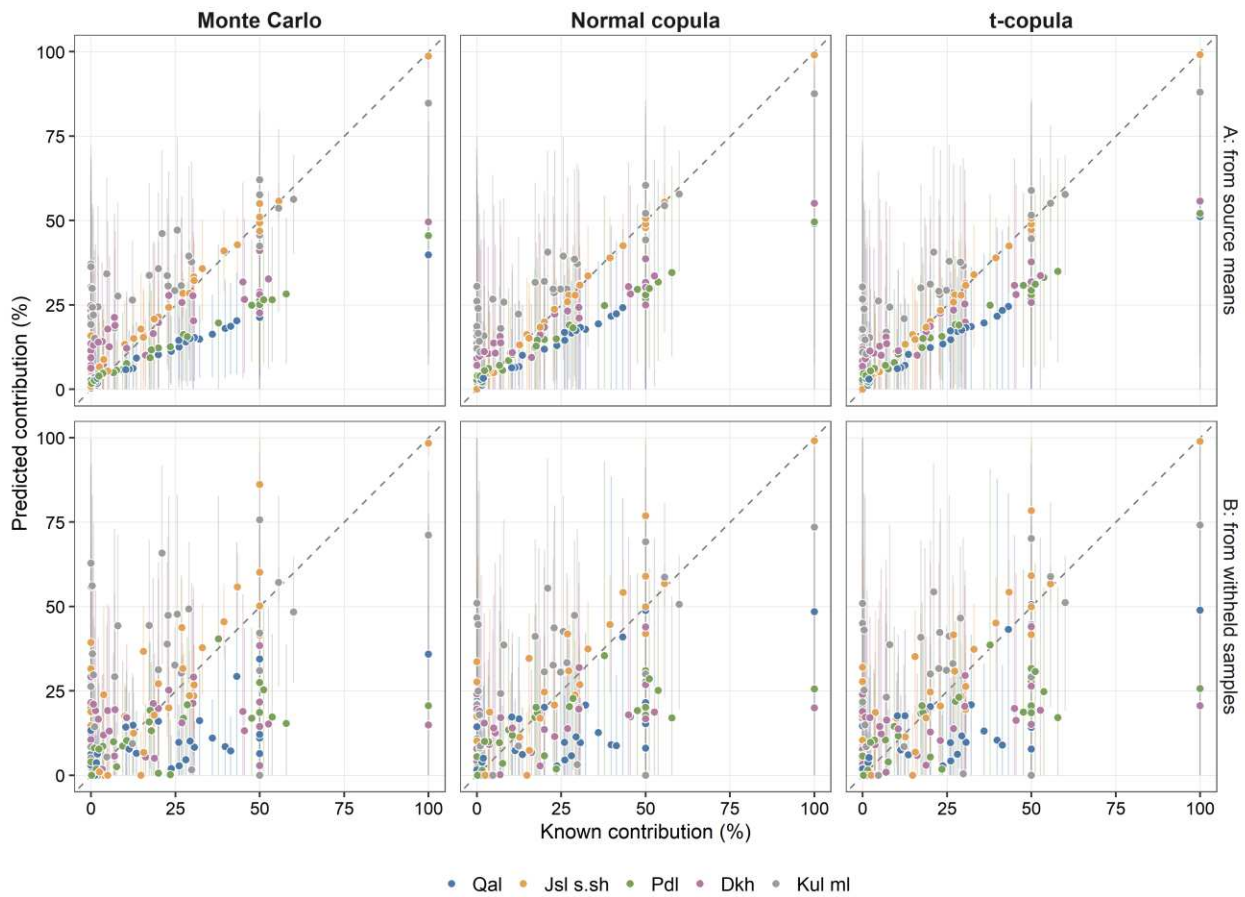


Fig. 10 Predicted against known source contributions for 36 virtual mixtures. Vertical lines: 95% prediction intervals; dashed line: 1:1. Accuracy varied markedly between sources. Jsl s.sh was recovered almost exactly (RMSE 1.7% under the t-copula) and a single-source mixture of this unit was correctly identified at 99%. The remaining sources had errors of 12 to 14% and single-source mixtures of Qal, Pdl and Dkh were recovered at only 49 to 59%. Read this way, the single-source results measure the limited separability of the alluvial and compositionally similar units rather than a failure of the mixing model: no sampling scheme can distinguish sources that carry similar signatures, and the wide prediction intervals reported in Table 4 are the appropriate expression of that limit. This reflects equifinality between compositionally similar units: Qal is Quaternary alluvium derived from

weathering of the other units in the catchment and is therefore compositionally intermediate, while Pdl and Kul ml are carbonate-dominated. Contributions from Qal and Pdl were systematically underestimated by 6 to 10 percentage points and those from Kul ml overestimated by a similar amount, in all three approaches.

A second, stricter design was also tested, in which the samples used to build each mixture were withheld from the source characterisation. Errors were larger under this design, partly because withholding a sample also reduces the number available to characterise the source, leaving only five for the two smallest groups. The ranking of the approaches was unchanged: both copulas again outperformed independent sampling on error, slope and coverage, and the goodness-of-fit values obtained under this design (95.4 to 96.1) were close to those obtained for the real sediment samples, indicating that it reproduces the difficulty of the actual apportionment problem. The two copulas could not be separated, with the normal copula marginally ahead under this design and the t-copula under the first.

4. Discussion

The concentration of thirty-four geochemical tracers was analyzed in the source and sediment samples. The results of laboratory measurements showed that the Qal geological unit exhibited the lowest concentration of Ag at 0.23 mg kg^{-1} , while the highest concentration of Al, at 68258 mg kg^{-1} , was recorded in the Pdl unit. In the sediment samples, Cd exhibited the lowest concentration of 0.24 mg kg^{-1} and Al the highest at 55403 mg kg^{-1} . Statistical screening reduced these to fifteen tracers forming the optimum composite signature. These included Sc, Y and La among the rare earth elements and Zn among the heavy elements. The stability of rare earth elements during weathering, transport and sedimentation makes them particularly useful in fingerprinting studies, and their retention here is consistent with that expectation. Cross-validation confirmed that the composite signature discriminates the five units reliably: 92.7% of source samples were classified

correctly when the tracer selection was repeated within each fold, so that no sample influenced the signature applied to it.

A prerequisite of the approach taken here is that the tracers are in fact dependent, and this proved to be the case throughout. Across the 525 tracer pairs examined over the five source groups, the mean absolute Kendall's tau was 0.50, and more than half of all pairs exceeded 0.5. The observed dependence lay outside the permutation interval for every source group. The independence assumption that underlies conventional Monte Carlo propagation is therefore not merely a simplification in this dataset; it is contradicted by the data. It is worth noting that the dependence structure differs qualitatively between units. In Dkh, 42 of the 105 pairs were negatively correlated, whereas in Kul ml only one was, which is itself an argument for fitting a separate copula to each source rather than a single structure to all of them.

The apportionment results show how much this matters. Under Monte Carlo sampling, the Jsl s.sh unit appeared to be the dominant source by a wide margin, contributing a mean of 41.2% compared with 29.8% for Qal. Once the dependence between tracers was retained, this margin largely disappeared: the normal copula returned 36.1% for Qal and 35.5% for Jsl s.sh, while the t-copula returned 37.0% and 35.4%, respectively.

The two copulas agree closely with each other and differ from the Monte Carlo result in the same direction and by a similar amount. The important point is not which of the two units is nominally ranked first: the difference between their means was 0.6 percentage points under the normal copula and 1.6 percentage points under the t copula, both far smaller than the width of the corresponding prediction intervals.

A management decision based on the Monte Carlo result would target the Shemshak Formation; a decision based on the copula result would treat the alluvial banks as equally important.

Three independent lines of evidence support the copula result. First, in the discriminant space computed from the composite signature the sediment samples plot adjacent to the Qal group rather than to Jsl s.sh, which lies in a separate region of the space. Second, evaluation against virtual mixtures showed that all three approaches systematically underestimate Qal, by between 8.5 and 10 percentage points, while Kul ml is overestimated by a similar amount; the true contribution of Qal is therefore likely to be higher than any of the models report, not lower. Third, the copula-based approaches recovered the known composition of the virtual mixtures more accurately than independent sampling on every measure of error, with root mean square error falling from 15.1% to 12.2% and 11.8% and the coefficient of determination rising from 0.57 to 0.74 and 0.76. The evaluation also exposed a limitation of the goodness-of-fit criterion, which is the measure most commonly used to compare un-mixing models. Applied to the virtual mixtures, GOF differed between the three approaches by 0.1 of a percentage point, while their root mean square errors differed by 22%. A criterion that cannot separate models whose accuracy differs by a fifth is not a basis for selecting between them, a conclusion consistent with earlier reports that high GOF values are not reliable indicators of accurate apportionment (Palazón et al. 2015; Gaspar et al. 2019). The measure that did separate the approaches was interval coverage. Under independent sampling the 95% prediction interval contained the true contribution in only 82.8% of cases, so the narrower intervals it produces reflect overconfidence rather than greater precision; both copulas were correctly calibrated at 96.7%. This result held under both mixture designs and is the most robust of the comparisons made here. It also has a practical implication: where uncertainty is being propagated in order to inform management decisions, an interval that is too narrow is more damaging than one that is too wide. These error magnitudes should be read in the context of the evaluation design. Published evaluations against laboratory mixtures report root mean square errors of a few percentage points, but they typically use three maximally distinct sources and construct

the mixtures from the same source characterisation that is then used to recover them (Gaspar et al. 2019). The present evaluation uses five geological sources, several of which are compositionally similar and one of which is derived from weathering of the others, and its second design withholds each mixture's constituent samples from the source characterisation. The errors obtained under Design A are comparable with those reported for three-source artificial mixtures, and the larger errors under Design B reflect the additional difficulty imposed by the source configuration and the withholding rather than a defect in the mixing model. Evaluation designs differ enough between studies that absolute error values are not directly comparable, which is itself an argument for reporting the design in full alongside the metrics (Batista et al. 2022).

The geological interpretation of the apportionment is consistent with field observation. The Shemshak Formation (Jsl s.sh) is a shale-rich formation known for its susceptibility to erosion, and a significant portion of it is covered by bushland and semi-dense shrubs rather than forest. During field reconnaissance, multiple debris movements were observed in this formation, associated with coal layers parallel to the sliding surface. The Quaternary deposits of the Qal unit are situated along the periphery of the primary stream, where the banks are susceptible to lateral mass movements and shallow landslides are frequently recorded (Fig. 3a). That this unit contributes on the order of a third of the sediment load while occupying only 1.67% of the catchment is the clearest illustration in these results that source contribution need not scale with source area. Anthropogenic destruction in the form of deforestation and vegetation loss has also contributed to soil erodibility in the Shemshak formation. These observations, taken together, support the apportionment obtained rather than merely accompanying it.

Comparison with other work in the region is instructive. Nosrati et al. (2018), working in a mountainous forest catchment in northern Iran, likewise found that the choice of statistical framework materially affected the apportionment obtained, in their case between Bayesian and

frequentist approaches. The present results extend that observation to the treatment of dependence within a single frequentist framework, and suggest that the sensitivity of fingerprinting results to modelling choices is not confined to the choice between model families. More broadly, the finding aligns with the growing recognition in this field that source apportionments require evaluation against mixtures of known composition rather than assessment by fit alone (Batista et al. 2022; Vale et al. 2022).

5. Conclusion

This study examined how the treatment of dependence between geochemical tracers affects sediment source apportionment. Fifteen tracers were retained from an initial set of 34 by sequential screening, and cross-validation in which the selection was repeated within each fold assigned 92.7% of source samples to the correct geological unit, confirming that the composite signature discriminates the five units reliably.

Dependence between these tracers proved to be widespread rather than incidental. Across the 525 tracer pairs examined over the five source groups, the mean absolute Kendall's tau was 0.50 and more than half of all pairs exceeded 0.5, with the observed dependence lying outside the permutation interval in every source group. The independence assumption on which conventional Monte Carlo uncertainty propagation rests is therefore not supported by these data.

Retaining that dependence changed the apportionment materially. Under independent Monte Carlo sampling, the Jsl s.sh unit appeared to dominate sediment production by 11.4 percentage points over the Qal unit. Once the dependence structure was preserved, this margin fell to 0.6 percentage points under the normal copula and 1.6 percentage points under the t-copula, and the two units became statistically indistinguishable given their widely overlapping prediction intervals. A catchment management decision taken on the basis of the first result would prioritise the Shemshak

Formation; one taken on the basis of the second would treat the actively eroding alluvial banks as equally important, despite their occupying only 1.67% of the watershed.

Evaluation against virtual mixtures of known composition showed that the copula-based schemes were the more accurate. Root mean square error fell from 15.1% under independent sampling to 12.2% and 11.8% under the normal and t copulas, and the regression slope of predicted on known contribution rose from 0.55 to 0.64, indicating less compression of the estimates towards equal shares. The clearest separation, however, was in interval coverage: the 95% prediction intervals produced by independent sampling contained the true contribution in only 82.8% of cases, whereas both copulas were correctly calibrated at 96.7%. The narrower intervals obtained under the independence assumption therefore reflect overconfidence rather than greater precision. This distinction was invisible to goodness of fit, which differed between the three schemes by 0.1 of a percentage point while their root mean square errors differed by 22%, and which cannot on its own be used to choose between un-mixing approaches.

Two limitations qualify these results. Source group sizes of six to twelve samples are small relative to the number of dependence parameters a copula in fifteen dimensions requires, so the fitted dependence structure should be regarded as indicative rather than precisely estimated, and the prediction intervals are correspondingly wide. In addition, the virtual-mixture evaluation showed that the alluvial Qal unit and the two carbonate-dominated units are not fully separable, since Qal is itself derived from weathering of the other units and is compositionally intermediate between them. Both constraints argue for larger source sample sets in future work, and for the routine use of mixtures of known composition when apportionments are evaluated. The wider implication is that where tracers are correlated, and this study suggests they usually will be, the assumption of independence does not merely widen or narrow the uncertainty bounds but can alter which source is identified as dominant.

643 **Declarations**

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647 **Competing interests**

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

650 **Ethics approval**

651 Not applicable.

652 **Consent to participate**

653 Not applicable.

654 **Consent for publication**

655 Not applicable.

656 **Data and code availability**

657 The datasets generated and analysed during the current study, together with the R scripts used for
658 data analysis and modelling, are available from the corresponding author on reasonable request.

659 **Author contributions**

660 **Meisam Samadi:** Conceptualization, Methodology, Investigation, Formal analysis, Software,
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663 **Abolhasan Fathabadi:** Conceptualization, Funding acquisition, Methodology, Formal analysis,
664 Software, Validation, Writing – review and editing.

665 **Ali Salajegheh:** Supervision, Methodology, Writing – review and editing.

666 **Majid Ownegh:** Supervision, Resources, Writing – review and editing.

Mohsen Hosseinalizadeh: Conceptualization, Investigation, Methodology, Writing – review and editing.

Christian Conoscenti: Conceptualization, Supervision, Writing – review & editing.

Benli Liu: Conceptualization, Writing – review and editing.

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