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Quantitative sediment fingerprinting using a Bayesian uncertainty estimation framework

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Abstract Numerous studies have shown how selected physico-chemical properties of sediments may be used as tracers to identify catchment sediment sources. Sediment fingerprinting has value in elucidating the linkages between erosion and downstream sediment delivery and potentially offers the opportunity to validate deterministic erosion models. However, quantitative fingerprinting is subject to considerable uncertainty throughout the research process, i.e. the inherent variability of source group properties, the number and distinctiveness of source groups, the relative discriminating power of different tracers, numerical issues associated with the un-mixing models, and further complications associated with nonlinear additivity, tracer transformation and enrichment. A Bayesian statistical framework was employed to assess two of the sampling issues using laboratory-based and synthetic data sets. The analysis shows source group contributions can be robustly derived, but source group variability and number of samples collected are key issues influencing performance.

Key words suspended sediment; sediment source; fingerprinting; uncertainty estimation; Bayesian framework

INTRODUCTION

The use of the physico-chemical properties of suspended sediments to trace linkages between soil erosion and the sediment delivered to a catchment outlet is now well established (e.g. Oldfield *et al.*, 1979). A useful tracer (sediment property) should be able to differentiate unequivocally between potential source groups and should exhibit conservative behaviour during transport (Walling *et al.*, 1993). Sediment fingerprinting studies have gained in popularity as they offer scope both to identify spatial patterns of sediment supply (Passmore & Macklin, 1994), and to distinguish between types of supply processes i.e. whether sediments have originated from sheet, rill or gully erosion (Wallbrink & Murray, 1993).

Individual properties such as colour, ^{137}Cs and particle-size distribution have offered valuable insight into sediment supply dynamics, principally at the small catchment scale. However, quantitative resolution of multiple sources can only be achieved using composite signatures (cf. fingerprints) involving several tracers deemed statistically significant (Yu & Oldfield, 1989; Collins *et al.*, 1997).

The quantification of sediment sources using a fingerprinting approach involves three stages. First, is to identify all key sediment sources relevant to the research

questions being asked. Second, is the identification of statistically significant tracers capable of unequivocally distinguishing between source groups. Third, is the implementation of a multivariate un-mixing model to apportion the "target sediment" (whether loess, flood plain or lake deposits) back to its source components. A broad range of sediment properties i.e. chemical, mineral magnetic and radiometric have been used (cf. Foster & Lees, 2000). However, quantitative fingerprinting is still subject to considerable uncertainty throughout the research process (see Table 1).

METHODOLOGICAL ISSUES AND SOURCES OF UNCERTAINTY

Sampling from source groups is typically limited in terms of sample numbers and the range of tracer properties measured, due to resource constraints and availability of analytical facilities. However, source groups are often heterogeneous in nature. Thus failure to characterize the true variability of the source groups and the sinks by inadequate sampling may introduce significant uncertainty into the multivariate un-mixing models (Franks & Rowan, 2000). In many cases such uncertainty is not propagated into the model output because the current generation of un-mixing models use mean properties only. It is therefore apparent that selected fingerprints representing individual sources should have low variability from the mean to minimize errors in model outcomes, and careful consideration should be given to the design of an appropriate sampling strategy, in order to adequately capture source group variability. McBratney & Webster (1983) suggest there is the need to account for the spatial dependence of soil properties using geostatistical techniques and variograms to optimize sample numbers.

Uncertainty is still deeply embedded within procedures of source group identification. In many studies the potential source groups are characterized on the basis of underlying geology, soil type and land use. However such groups may fail to include the entire spectra of possible sediment sources in the study catchment (i.e. farm tracks and footpaths) or seasonal/event related sources, which may contribute considerably to the supply of suspended sediment. Hence, background knowledge of the study catchment is essential to ensure that the study includes all the spatially distributed source types in the analysis. However, inclusion of too many source groups can equally cause problems, whereby groups of source samples are numerical multiples of one another (Lees, 1997; Dearing, 2000).

Additionally, there is significant uncertainty associated with the selection of appropriate tracer properties. Many tracers suffer apparent enrichment or depletion effects due to differences in particle-size distributions between the sources and the sinks (Novotny, 1980). These effects often render the use of specific tracers too uncertain. Typically, subjective corrections are made i.e. for % clay and surface area (Collins *et al*., 1998) to account for these effects. Another potential area of uncertainty is tracer transformation which, although widely perceived, has received little attention. Processes associated with this are mechanical and chemical alteration along with organic matter decomposition resulting in suspended sediments no longer reflecting original source material. Such effects must be recognized and accounted for in any robust modelling scheme (Walling *et al.*, 1993).

Table 1 Principle sources of uncertainty within sediment fingerprinting schemes.

Nature of uncertainty	Key issues (and assumptions involved)	Solutions
Problem formulation i.e. how many source groups can be distinguished	Too few source groups compromises utility of approach, too many leads to problems of source group discrimination and spurious numerical solutions	Good experimental design; field experience
Discriminating power of tracers to distinguish between source groups (dimensionality)	Depends partially on number, location and types of source groups to be distinguished, and laboratory resources available to the research team	Optimize analysis through *a priori* appreciation of the problem; obtain broadest array of property measurements possible
Tracer bias	Order of magnitude variations in tracers	Normalization procedures in un-mixing models
Characterization of source group variability	Discriminating between source groups depends on "within group" variance relative to "between group" variance	Requires sound characterization of "source groups" and appropriate sample numbers to adequately capture variability
Measurement uncertainty of tracer properties	Radiometric measurements i.e. ^{137}Cs associated with intrinsic uncertainties ±5%, clay mineralogy typically only semi-quantitative	Good laboratory practice and quality controls
Tracer transformation	During transport and particularly sediment deposition diagenetic transformations may occur i.e. synthesis of biogenic greigite in lake sediments (Dearing, 2000)	Ensure only conservative tracers (Walling *et al*., 1993) are employed in analysis
Linear additivity	Some properties, such as mineral magnetic measurements present nonlinear additivity problems (Lees, 1997)	Combine range of sediment properties i.e. radiometric, geochemical and magnetic (multi-parameter approach)
Enrichment	Preferential enrichment/selective deposition of fine/coarse fractions of the mineral sediment fraction and organic matter	Repeat measurements across selected fractions (Yu & Oldfield, 1993). Examine only specific fraction i.e. "heavy silts" following extensive sample preparation (Kelly & Nater, 2000) and particle size corrections (Collins *et al*., 1998)
Mixing models	Constrained linear programming (optimization based)—problems of equifinality in prediction of estimated source contributions	Further development of "likelihood based" modelling approaches (Rowan *et al*., 2000)

Most un-mixing models (e.g. Walling *et al*., 1993) have been based on some form of linear programme and rely on an optimized solution based on the use of mean end-member tracer values. Within these models no acknowledgement is made of sampling constraints and so this issue is the focus of the present paper. Here a Bayesian Monte-Carlo based methodology has been developed to explore sampling uncertainties permitting the objective derivation of confidence intervals on un-mixing model results. Preliminary results use laboratory-mixed and synthetic data sets to provide a rigorous examination of the scheme and assess the importance of sampling densities.

PROBLEM FORMULATION

The un-mixing model used to quantify relative source group contributions may be generalized as follows:

$$\sum_{i=1}^{m} \hat{\bar{x}}_{i,j} \cdot A_j = X_j + \varepsilon_i \qquad j = 1, m \tag{1}$$

and additionally constrained by;

$$\sum_{j=1}^{n} A_j = 1 \qquad 0 < A_j < 1 \tag{2}$$

where $\hat{\bar{x}}_{i,j}$ = estimated population mean, i = trace property, j = source group, n = number of source areas, m = number of tracers, and A_j = proportional contribution of source group, j. ε_i = error associated with the prediction of the sink trace characteristic, X_i. Equation (2) provides an additional constraint on the unknown source groups in that they must sum to unity. Consequently, if the requirement is to quantify contributions from three source groups, then there are only two unknown variables as the third is the residual term. Given the problem as expressed in equation (1), if $m > n - 1$ (i.e. more tracer properties measured than unknown source groups), then the equation is over-determined. Such over-determined problems also potentially suffer from predictive equifinality if multiple acceptable solutions can be found (see Rowan *et al.*, 2000).

ESTIMATION OF SAMPLING UNCERTAINTIES

To characterize the properties of a source group it is assumed that the mean and associated uncertainty may be represented by Students' *t*-distribution. Hence:

$$\hat{\bar{x}}_{i,j} \approx t_\nu(\mu, \sigma^2) \tag{3}$$

where i = specific source group, j = trace property, μ = true value of the population mean (mean of x_{ij}) and σ^2 = variance of the probability distribution of the population mean. The variance of the distribution is given by:

$$\hat{\sigma}^2 = \left(\frac{S}{\sqrt{d}} \right)^2 \tag{4}$$

where S = sample standard deviation, and d = number of independent samples. The derived probability distribution of the true population mean is therefore dependent upon the number of samples collected and used to represent the population mean. Using the above equations, the probability distribution of the population means of each of the trace characteristics, from each of the source areas, can be calculated.

PROPAGATING THE EFFECTS OF UNCERTAIN SAMPLE MEANS

For a given composite sediment signature, the variability associated with each component tracer must be propagated into the final model output. To achieve this, Monte-Carlo sampling of the derived probability distributions was performed and fed into an optimization scheme using the shuffled complex evolution (SCE) algorithm (Duan *et al*., 1992). The model is run iteratively until a sufficient number of realizations has been completed. The scheme is inclusive of source group variability and analytical error. Analytical errors of target sediment (suspended sediment, flood plain deposits etc.) are also included. The scheme is executed as follows:

(a) Prior to analysis, all values of tracer properties are normalized by the target sediment values.
(b) For each tracer, from each source group, an estimate of the mean value is selected from each of the derived probability distributions i.e.

$$\hat{\bar{x}}_{i,j} \leftarrow t_{\nu}(\mu_{ij}, \sigma^2_{ij}) \tag{5}$$

(c) Equation (1) is then solved through an optimal least-squares routine (SCE). This produces the optimal estimate of the source groups (A_j, j = 1, n) given the randomly sampled estimates of the true population means.
(d) Repeat steps 1–3 until sufficient realizations have been achieved.
(e) The distributions of calculated source groups for each of the sources represents the associated uncertainty. From these, confidence quartiles may be selected (e.g. 95%).

APPLICATION TO LABORATORY MIXTURES

As a validation exercise, the modelling approach was applied to experimental data generated in the laboratory. Five different rock types (sandstone, basalt, limestone, granite and slate) were milled to produce homogenized rock powders. XRF analysis (Phillips PW1400) was used to determine the major oxide composition (i.e. Si, Al, Ca, K, Na) in both the end-member samples and a series of mixtures of known composition. The mixtures were thus used to test the performance of the un-mixing scheme. The uncertainty routine was then performed for each of the five admixtures and uncertainty bounds were calculated, as shown in Fig. 1.

The model yields 95% quartiles reflecting the uncertainty associated with the inferred source contributions. The median values always lay on or near the equiline (R^2 = 0.982) indicating a "good fit" between modelled and expected values. However, broad error bands are also evident (i.e. 30–35%). These large error envelopes were

related to the relatively small number of samples (n = 3) used to characterize the source groups. This effect illustrates the importance of sample numbers as will now be discussed.

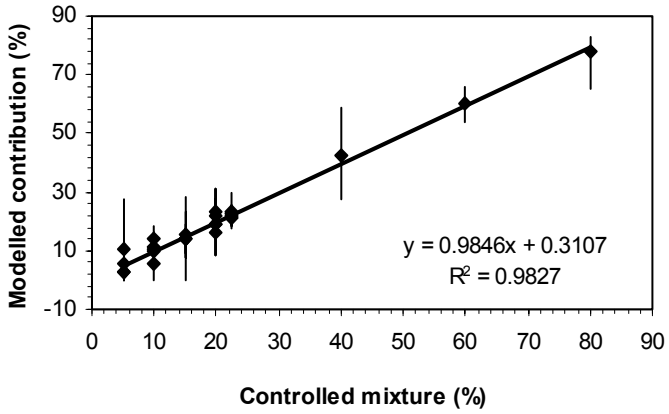

Fig. 1 Comparing modelled contributory coefficients to laboratory mixtures.

SYNTHETIC TEST DATA: CONFIDENCE INTERVALS AS A FUNCTION OF SAMPLE SIZE

To more explicitly investigate the role of value ranges and sample size with regards to uncertainty estimation, synthetic test data were created (Table 2). Four source groups (SG) were specified with known contributions to the sink (A_1 = 20%; A_2 = 30%; A_3 = 5%; A_4 = 45%). Specifying "true" mean values of seven component tracers, different combinations of sample number, and variability as expressed by the coefficient of variation, were explored to elucidate the resultant uncertainty in the modelled contributory coefficients.

The un-mixing model was run for contrived data sets comprising 3, 5, 10, 20, and 100 samples from each source group, with CV%s of 10, 20, 30, 40 and 50% respectively. In each case, 1000 realizations were achieved. The mean of the 95% CI ranges of the contributory coefficients are shown in Fig. 2. The results illustrate that the uncertainty associated with the derived contributions is large when sampling density is low, even with very low source group variability (e.g. n = 3, CV% = 10%). As more samples are used, the uncertainty associated with the group contribution is markedly reduced.

Table 2 Synthetic data set showing "true" population means.

Tracer no.	SG1 20%	SG2 30%	SG3 5%	SG4 45%
1.	50	20	110	60
2.	70	55	22	79
3.	2	6	3	8
4.	23	78	54	116
5.	5	7	9	2
6.	1	0.5	2.2	6
7.	90	10	17	57

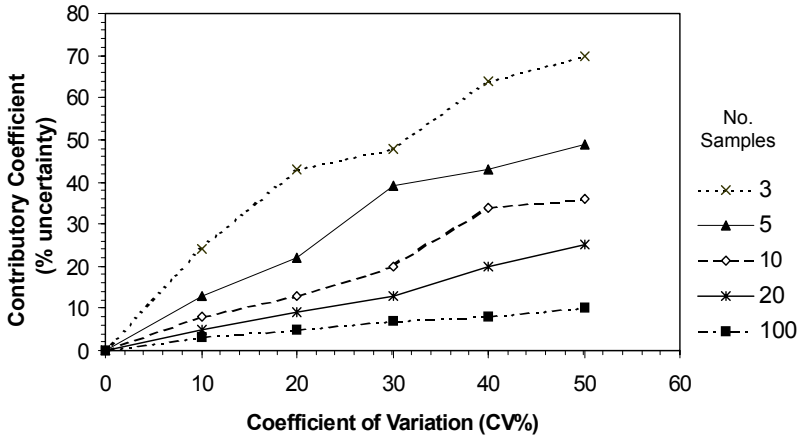

Fig. 2 Effect of source group sampling numbers and source group variability on model performance.

Sampling densities required for constrained uncertainty is also very much dependent on the variability (CV%) of the source groups. An increase in CV%, clearly also controls precision e.g. with n = 20 and CV% = 10% uncertainty was 5%, as CV% increases to 30%; uncertainty likewise increases to 13%. Thus, confidence in any particular fingerprinting application depends on both the natural variability of the source group tracer values and the number of samples used to characterize their probability distributions.

DISCUSSION AND CONCLUSIONS

A conceptually simple but robust methodology has been developed for the assessment of uncertainty in sediment fingerprinting models. By accounting for source group and analytical uncertainties, confidence limits have been calculated for inferred source group contributions. The scheme was validated using laboratory analysis and extended using synthetic admixtures. The accuracy and precision of the un-mixing clearly depends on the number of samples obtained combined with the inherent variability of tracer values within source groups.

Much of the existing literature reports relatively limited field campaigns and under reports the variability involved. The results presented indicate some directions forward in this regard. If tight confidence limits are required, then high-density sampling is likely to be needed. The number of samples needed is itself a function of the natural variability of each group.

The discussion thus far has not explored the issue of tracer numbers. Bayesian sampling implies that maximizing the number of tracers included in the analysis may also reduce uncertainty. However, it is not simply a case of including all potential tracers, as many are non-conservative and/or may be subject to enrichment/depletion processes. Current methods of tracer selection do not adequately account for sampling variability or for enrichment/depletion effects in a rigorous manner. Within the Bayesian approach, it is preferable that the worth of each individual trace property is assessed according to its influence on the inferred group contributions (rather than its ability to discriminate between groups alone). A Bayesian approach enables corrupted

tracer properties to be identified, and explicitly calculates and minimizes uncertainty (Franks & Rowan, 2000). The effects of enrichment (grain size) and organic matter remain key issues and will be reported in a future study.

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