Uncertainty assessment in suspended sediment fingerprinting based on tracer mixing models: a case study from Luxembourg

N. MARTÍNEZ-CARRERAS[1], F. GALLART[2], J. F. IFFLY[1], L. PFISTER[1], D. E. WALLING[3] & A. KREIN[1]

1 *Public Research Centre - Gabriel Lippmann, Department of Environment and Agro-Biotechnologies, Research Unit GEOSAT, 41 rue du Brill, L-4422 Belvaux, Grand Duchy of Luxembourg*
martinez@lippmann.lu

2 *Institute of Earth Sciences "Jaume Almera", CSIC, Lluis Solé Sabarís s/n, 08028 Barcelona, Spain*

3 *School of Geography, Archaeology and Earth Resources, University of Exeter, Amory Building, Rennes Drive, Exeter EX4 4RJ, UK*

Abstract The primary purpose of this paper is to explore the various sources of uncertainty associated with the use of the fingerprinting approach, based on multivariate mixing models, to establish suspended sediment sources. Model uncertainty has been investigated using a Monte Carlo simulation technique. A key aim of the study is to assess the relative importance to the uncertainty of the output of: (1) the number and type of tracers included in the mixing model, and (2) the spatial variability of the tracer signatures of individual sources. The results obtained showed that the main source of uncertainty was the number of tracers included in the model, and the spatial variability of the tracer signatures associated with an individual source, whereas the types of tracers included were shown to be of lesser importance. The various assessments of the uncertainty associated with sediment fingerprinting were, however, conditioned by the assumptions made. This study demonstrates that the precision and coherence of source ascription partitioning can be improved by: (1) incorporating tracer weightings to reflect the spatial variability of source signatures, and (2) constraining the mixing model to reflect current process understanding. Despite the uncertainties involved, the proposed methodology provides a formalized procedure by which sediment source contributions can be readily established using tracer mixing models.

Key words suspended sediment sources; fingerprinting approach; multivariate mixing models; uncertainty analysis; Grand Duchy of Luxembourg

INTRODUCTION

Sediment source ascription using the fingerprinting approach has now been applied in numerous studies in many different areas of the world (see Walling, 2005). The technique offers a valuable indirect method for establishing contemporary sediment provenance at the catchment scale. It uses mass balance equations and tracer property values for the various potential sources to determine their relative contribution to the mixed signature in a suspended sediment sample. The methodology is founded on the assumption that the properties of suspended sediment can be compared with the equivalent information for the materials identified as potential sources. An effective tracer should be able to differentiate between potential sources, exhibit conservative behaviour during erosion and transport (cf. Foster & Walling, 1994) and the tracer property values should be linearly additive. However, the ability of a tracer to distinguish sediment sources depends on the nature of the catchment (Rowan *et al.*, 2000) and there are at present no generic guidelines for pre-selecting the most useful combinations of properties for discriminating sediment sources in different catchments (Collins & Walling, 2004).

Despite the widespread application of mixing models for sediment source ascription, relatively little attention has been paid to the quality of the statistical models developed (Lees, 1997) and to the methodological uncertainties associated with the approach (Collins & Walling, 2002). However, mixing models are generally based on rather simplistic hypotheses (e.g. spatio-temporal homogeneity of source tracers, or conservative behaviour of tracers during sediment mobilization and transport) that make the approach inherently uncertain (Joerin *et al.*, 2002). Table 1 summarizes the differences between a hypothetical fingerprinting model with no uncertainty and one involving uncertainty. In the former case, it would be possible to determine exactly the amount of sediment contributed by each source. However, with an uncertain model, the results obtained would be influenced by the assumptions made beforehand. For example, the number and

Table 1 Differences between a hypothetical sediment fingerprinting model with no uncertainty and a model with uncertainty, as related to the processes of erosion, transport, mixing and mobilization/deposition.

	Model with no uncertainty	Model with uncertainty
1. Erosion	Known sediment sources No tracer spatial/temporal variability	Potential sediment sources Tracer spatial/temporal variability
2. Transport	Tracer conservative behaviour Source–river connectivity	Possible tracer transformation Source–river connectivity assumed
3. Mixing	Perfect sediment mixing Linear additive tracers	Perfect sediment mixing assumed Linear additive tracers assumed
4. Mobilization/Deposition	Completely representative samples	Representative samples assumed

nature of the potential sediment sources is commonly assumed and not known with certainty, and the tracer values used to characterize sources are likely to be spatially and temporally variable. Furthermore, all tracers may not be capable of differentiating between potential sources and they might be influenced by transformation during transport. In the same way, source–river connectivity, perfect mixing, linear additive tracer behaviour during mixing, and the representativity of source material samples cannot necessarily be ensured. As a consequence, it is not possible to determine with certainty the precise relative contributions of the individual potential sources. The uncertainty assessment should therefore be incorporated into the fingerprinting approach, even though any uncertainty assessment will always be conditional on the possibilities considered and the assumptions made (Beven, 2007).

To date, relatively few studies have explicitly considered the resulting uncertainty when using the fingerprinting approach to establish the relative contributions from a number of potential sediment sources. As a result, there is little guidance available to select an appropriate approach to incorporate consideration of uncertainty, and such selection is likely to be subjective. Rowan *et al.* (2000) considered uncertainty associated with the numerical solutions provided by the current generation of multivariate sediment-mixing models. Their methodology is based in the GLUE approach (Generalised Likelihood Uncertainty Estimation) developed by Beven & Binley (1992). Their method incorporates a user-specified efficiency tolerance which can reflect measurement error and population variability uncertainties. However, this approach focuses on the uncertainty hidden within the model structure, when using an optimisation algorithm to solve over-determined multivariate mixing models (i.e. number of tracer properties equal or higher than number of potential sediment sources) and does not consider the likely spatial variability of the tracer properties used to characterize potential sources. Other studies have attempted to take account of the uncertainty due to the spatial variability of source tracer properties (Motha *et al.*, 2003; 2004; Collins & Walling, 2007a,b). Briefly, in these studies the authors use a Monte-Carlo approach to randomly select tracer property values from the cumulative Normal distribution for each tracer, in order to establish a range of mean values for the tracer property to characterize a particular source. The mixing model is optimised for many different potential parameter sets and the uncertainty in the estimated source contributions is established by considering the range of values provided by the model output. For example, Collins & Walling (2007b) estimated the 95% confidence limits using the standard error of the mean of the results produced by 1000 iterations.

The main purpose of the study reported in this contribution is to assess model uncertainty associated with the spatial variability of source tracer properties by using the GLUE approach. We have tried to determine the relative contribution to the uncertainty associated with the model output of: (1) the number and type of tracers included in the mixing model, and (2) the spatial variability of the tracer signatures of individual sources. The possibility of improving model performance by: (1) incorporating tracer weightings to reflect the spatial variability of source signatures associated with a particular tracer property, and (2) constraining the mixing model to reflect current process understanding, is also addressed. This exercise aimed to formalize a general procedure to be used to estimate suspended sediment source contributions (with uncertainty assessment) for any number of tracers and sources.

STUDY AREA

The analysis was undertaken using data from the Wollefsbach catchment (4.4 km^2, Fig. 1). This catchment is a sub-basin of the Attert experimental river basin (254 km^2) located in the NW of the Grand Duchy of Luxembourg, which represents one of the main tributaries of the Alzette River, which drains most of the southern part of the country. The mean annual rainfall for the study area (1954–1996) is estimated to be 853 mm (Pfister *et al.*, 2000). Mean monthly temperatures are characterized by a maximum of about 18°C in July and a minimum of 0°C in January. Air temperatures below 0°C at 1.5 m above ground typically occur more than 75 days per year (up to about 110 days per year). The hydrological regime is pluvial oceanic, with low flows observed from July to September due to high summer evapotranspiration, while high flows occur from December to February (Salvia-Castellví *et al.*, 2005).

The bedrock of the Wollefsbaach catchment is predominantly Keuper sandy marl. The land use is primarily grassland and cropland (65% and 27% of the surface area, respectively). There are some areas of forest (7%), but these are situated near the catchment margin and far from the stream network. The cropland is underdrained by an extensive drainage system, but its exact layout is unknown and it is difficult to estimate its influence on discharge (Pfister *et al.*, 2006) and sediment transport. Surface water is rapidly collected by a dense surface drainage system. This results in a flashy runoff regime. However, since the slopes are gentle, some significant surface and sub-surface storage is likely (Van den Bos *et al.*, 2006). Field visits provided visible evidence of eroding stream channels. After several field inspections during storm events, channel banks, and the surface of areas under cropland, grassland and forest were identified as potential suspended sediment sources.

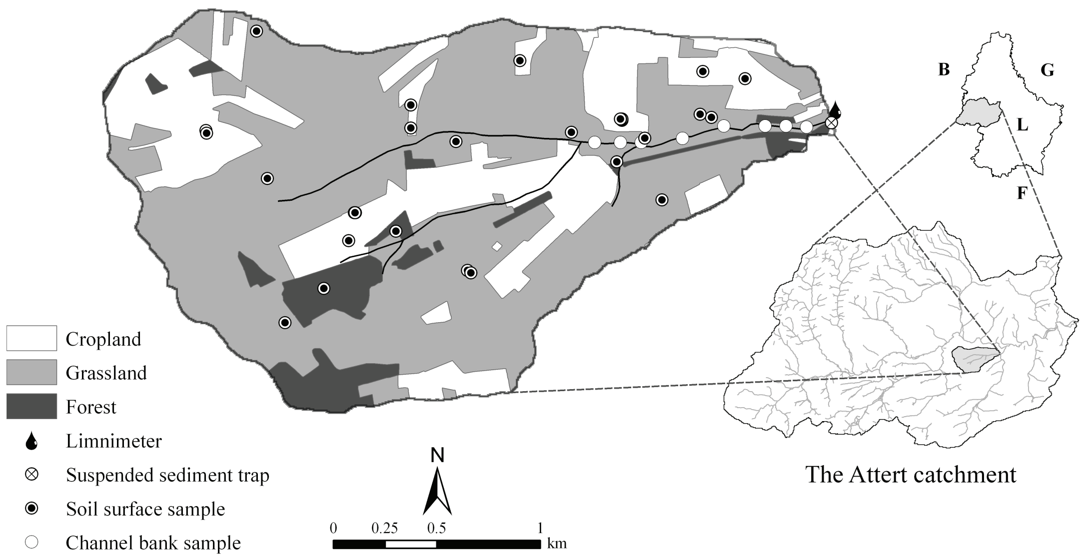

Fig. 1 The location of the Wollefsbach basin, the catchment land use and the location of suspended sediment, soil surface and channel bank sampling points within the catchment.

METHODS

Source material and suspended sediment sampling, preparation and analysis

Representative samples of source material were collected, ensuring that only material likely to be mobilised by erosion (top 2 cm) was sampled. Particular attention was directed to collecting surface material from large areas representative of each source type in different parts of the catchments that were considered to be connected with the stream network. At each sampling site, five grab samples were collected from a representative area of 25 m^2. This material was well mixed to provide a homogeneous sample. The number of samples collected was approximately proportional to the area occupied by each land use, resulting in the collection of 18 grassland topsoil samples, 12 cropland topsoil samples, 2 forest topsoil samples, and 8 channel bank samples. Suspended sediment (18 samples) was collected during rainfall–runoff events over the period October 2005 to February 2007, using time-integrated suspended sediment traps (Phillips *et al.*, 2000). The grain size composition of the suspended sediment particle size was predominantly <63 µm (mean 89% by weight). Following Walling & Woodward (1992), all suspended sediment and source material samples were sieved to <63 µm, to minimise contrasts in particle size composition between samples.

All samples were analysed using ICP-MS (ELAN Dynamic Reaction Cell–e, Perkin Elmer) after HCl/HNO_3 microwave digestion. This procedure provided information on the concentration of a range of trace elements (Li, Be, Mg, Al, Sc, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Sn, Sb, Cs, Ba, Pb), and rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb), as well as several actinides (Th, U). Total C and N were measured directly by pyrolysis using a CE Instruments automatic analyser. Total P was determined colorimetrically after digestion following the ascorbic acid method proposed by Murphy & Riley (1962) using a Beckmann Coulter spectrophotometer. ^{137}Cs and total ^{210}Pb activities were measured by gamma spectrometry (HPGe-detector (carbon-proxy), ε = 41%, t = 86 400).

Source ascription using multivariate mixing models

The Kruskal-Wallis H-Test was used to discard those tracer properties that were unable to discriminate between the different potential sources in the catchment. In addition, tracer properties that provided evidence of enrichment during the erosion process in more than 75% of the samples were also discarded from the analysis, since it is impossible to establish relative source contributions if the mixture (i.e. suspended sediment samples) is characterized by tracer property values which fall outside a convex polygon bounded by the equivalent values associated with the individual potential sediment sources (Phillips & Gregg, 2003). Discriminant function analysis (DFA) was used to assess the power of individual fingerprint properties to discriminate between the potential sources (e.g. Collins & Walling, 2002).

The relative contributions of the individual sources to the suspended sediment samples were calculated using a multivariate mixing model based on mass balance equations. The model seeks to solve the system of linear equations represented by:

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

while satisfying the following constraints:

$$\sum_{j=1}^{m} x_j = 1 \quad \text{with } x_j \geq 0 \qquad (2, 3)$$

where, b_i is the value of tracer property i (i = 1 to n) in the suspended sediment sample, $a_{i,j}$ is the value of tracer property i in source type j (j = 1 to m), x_j is the unknown relative contribution of source type j to the suspended sediment sample, m is the number of source types, and n is the number of tracer properties. In general, the relative contributions of m different sources can be uniquely determined by the use of m – 1 different tracers. However, the system has infinite solutions when the number of tracers is equal to, or higher than, the number of sources. The system is then mathematically over-determined, but the requirement for mass balance conservation can still be used to find multiple combinations of source proportions which are feasible solutions (Phillips & Gregg, 2003). The system is normally solved by optimisation, by minimising the errors between measured and estimated values. In this study we minimize the function $f(x_j)$ given by the sum of squares of relative errors (e.g. Collins *et al.*, 1997b). The tolerance criterion placed on constraint violations and parameter values (the maximum value by which parameter estimates can violate the constraints and still allow successful convergence) was set to $\pm 10^{-6}$. Following Motha *et al.* (2003), the initial values of x_j were set to 0.25, as providing the best starting point for optimisation.

Some workers have included particle size and organic carbon content correction factors in the mixing model formulation (e.g. Collins *et al.*, 1997a; Walling *et al.*, 1999; Gruszowski *et al.*, 2003). However, in this study no corrections were applied to take account of differences in organic matter content between sources and suspended sediment samples (cf. Collins *et al.*, 1997b; Walling *et al.*, 1999; Owens *et al.*, 2000) because the relationship between tracer concentration and organic matter content is complex and difficult to generalize (Walling *et al.*, 1999). In addition, simultaneous corrections of raw data for differences in both particle size and organic matter content may result in overcorrection of fingerprint parameter values (Collins *et al.*, 1997b).

Uncertainty evaluation

The uncertainty in the results obtained from the mixing model associated with the spatial variability of source tracer properties was explored using a Monte Carlo simulation technique. The sample mean and standard deviation for each tracer property associated with a particular source was estimated using a bootstrap procedure, and these values were assumed to approximate the population mean and standard deviation, in order to define the statistical distribution of the tracer property values for a particular source. The distribution is assumed to include the laboratory analytical error as well as the spatial variability of tracers. After undertaking a Normality test (Kolmogorov-Smirnov Normal distribution test, $\alpha = 0.05$), a cumulative Normal distribution function was produced for each tracer property for each source. From this function, tracer property values corresponding to a series of randomly generated cumulative frequency distributions were obtained for each source type. Negative trace property values were eliminated by repeating the above procedure until all the values were within the desired range. The system of linear equations was solved 5000 times. A pre-determined number of tracers and source tracer values were randomly selected from the available tracers and their distribution functions, respectively. The methodology is based on the GLUE approach, developed from an acceptance of the possible equifinality of models. The replicate random sampling permitted the calculation of confidence limits for the estimates of the relative contribution of each individual source type to each suspended sediment sample by directly weighting the likelihood of the 5000 mixing model iterations, which were subsequently used to derive the predictive probability of the output variables. The robustness of the source ascription solutions was assessed using a mean "goodness of fit" (GOF, modified from Motha *et al.*, 2003):

$$GOF = 1 - \left\{ \frac{1}{n} \times \sum_{i=1}^{n} \left| b_i - \sum_{j=1}^{m} \left(a_{i,j} \cdot x_j \right) \right| \Big/ b_i \right\} \tag{4}$$

Only sets of tracers that obtained a GOF higher than 0.8 (accepted sets) were used to assess model uncertainty. Since validation data were not available, this threshold was subjectively chosen after exploring several measures of model performance. Results were sorted from the smallest to the largest and an equal probability was assigned to each value that summed to unity, so the distribution function was obtained. 90% confidence intervals were assigned to the source contribution values for 5% and 95% probability. Figure 2 presents a simplified schematic representation of the procedure. Model uncertainty was assessed by comparing alternative models, by changing either the number or the type of tracers included in the mixing model. Hereafter "randomly selected tracers" refers to the case where for each iteration a pre-fixed number of tracers are randomly selected from all the available tracers (all tracers included in the assessment); whereas "fixed randomly selected tracers" refers to the case where a pre-fixed number of tracers are randomly selected at the start and are always used to solve the 5000 model iterations.

Additional model constraints

Tracer specific weightings (W_i) were used to ensure that the tracer property values for a particular source characterized by the smallest standard deviations exerted the greatest influence upon the optimised mixing model, since it was evident that as the standard deviation of the tracer property

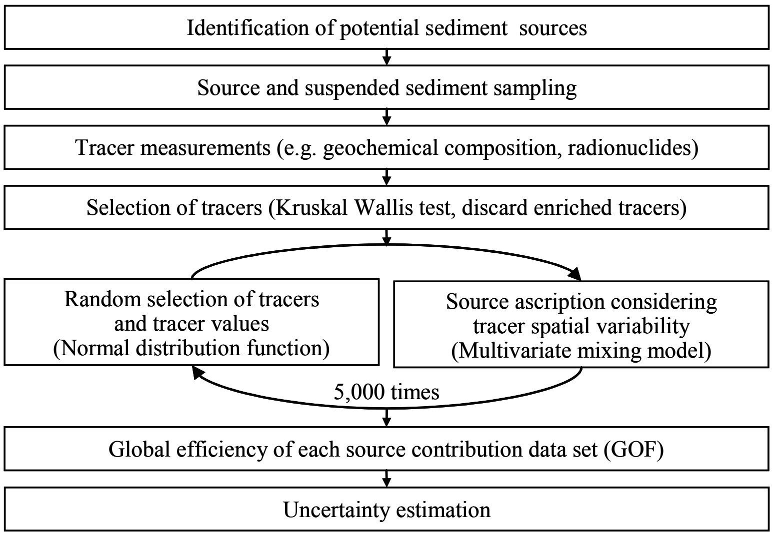

Fig. 2 A schematic representation of the procedure used to quantify the contribution from the individual source types to the suspended sediment using a multivariate mixing model. GOF: Goodness of fit.

values increased, the source ascription uncertainty also increased. The weighting value (W_i) was calculated using the inverse of the root of the variance associated with each source tracer. In the same way, the possibility of constraining the mixing model by incorporating existing understanding or knowledge of the process system was explored. For example, the relative contributions of some sources were limited to a particular numerical range (e.g. $x_j \leq 0.5$).

RESULTS AND DISCUSSION

Source and sediment tracer selection

Individual tracers were tested for their ability to discriminate the potential sediment sources in the Wollefsbach catchment using the Kruskal-Wallis H-Test. The results indicated that 32 tracers were able to discriminate the potential suspended sediment sources. Tracers unable to discriminate the sources were discarded (i.e. V, Mn, As, Sr, Be, Sn and Sb). In the same way, tracers enriched during the erosion and sediment mobilisation process were also discarded from the analysis and were not considered in the rest of the study (i.e. Co, Cu, Zn, Rb, Ba, Pb, Fe, Er and Yb).

The 23 tracers remaining were retained to estimate the contribution of the potential sediment sources to the suspended sediment output from the study catchment, using a multivariate mixing model. This set of tracers comprised trace elements (e.g. Al, Cr and Ni), rare earth elements (e.g. La, Ce and Pr), organic constituents (N, and P), and radionuclides (^{137}Cs and excess^{210}Pb). The advantages of using composite signatures have been previously demonstrated (Collins *et al.*, 1997b; Olley & Caitcheon, 2000; Walling, 2005). The mean and coefficient of variation of the tracer property values for the retained tracers, associated with the individual potential sediment sources, are given in Table 2. All tracer property values for the individual sources were normally distributed. Moreover, the DFA was used to assess the discriminating power of the individual fingerprint properties (Table 2). Th, ^{137}Cs, N, and Ni were the tracers with the highest discriminating power (67.5, 62.5, 62.5 and 60.0%, respectively), whereas Gd, Sm and Cs were the lowest (25.0, 27.5 and 27.5%, respectively).

Previous studies have used statistical tools to select the set of tracers that provides the best discrimination between the potential sediment sources, when a high number of possible tracers could be used. For instance, Collins *et al.* (1997a, 1997b, 2002, 2007a,b) used stepwise DFA. However, we have assumed that including all pre-selected tracers increases the likelihood that inappropriate tracers (e.g. those subject to geochemical transformation during fluvial erosion and

Table 2 Mean ($\bar{x}$) and coefficient of variation (CV) for the retained source tracing properties. Kruskal-Wallis H-Test significance levels for discriminating between the four potential suspended sediment sources in the Wollefsbach catchment. Percentage of samples correctly classified using discriminant function analysis (DFA).

Tracers	Cropland topsoil (n = 16)		Grassland topsoil (n = 18)		Forest topsoil (n = 2)		Channel banks (n = 8)		H-value[1]	% Samples correctly classified[2]
	$\bar{x}$	CV (%)	$\bar{x}$	CV (%)	$\bar{x}$	CV (%)	$\bar{x}$	CV (%)		
Al (µg/g)	27726	30.0	37841	27.8	27664	12.8	36699	9.6	10.30	37.5
Cr (µg/g)	42.55	32.6	67.28	36.1	48.46	14.6	48.31	12.8	11.58	52.5
Ni (µg/g)	21.03	34.9	36.60	36.1	26.89	21.9	30.59	15.9	13.77	60.0
U (µg/g)	1.49	14.5	1.76	26.2	1.56	8.3	2.02	12.2	13.68	42.5
Li (µg/g)	34.29	47.4	48.96	31.4	26.35	9.7	54.45	16.4	10.39	32.5
Mg (µg/g)	6576.2	77.4	12817.0	81.5	4338.7	3.5	9213.5	12.3	10.08	40.0
Ga (µg/g)	8.92	44.4	12.68	27.0	6.19	15.1	14.24	11.6	12.96	37.5
Sc (µg/g)	5.40	24.0	7.04	20.7	4.98	3.5	8.17	8.5	17.37	50.0
Cs (µg/g)	3.23	38.1	4.97	27.2	2.69	3.7	5.02	14.2	12.59	27.5
La (µg/g)	34.64	7.8	33.68	8.8	31.68	11.4	48.86	7.3	19.87	57.5
Ce (µg/g)	74.22	8.6	70.88	8.1	68.43	12.1	89.28	5.3	19.61	47.5
Pr (µg/g)	8.64	5.5	8.11	7.0	7.97	12.7	10.31	8.2	22.16	50.0
Nd (µg/g)	31.27	8.8	31.00	8.8	27.52	12.8	37.67	8.5	17.18	37.5
Sm (µg/g)	5.53	9.0	5.53	7.9	4.84	11.5	6.16	8.8	10.89	27.5
Eu (µg/g)	0.93	17.1	1.06	9.7	0.76	12.6	1.15	10.0	13.91	40.0
Gd (µg/g)	6.22	37.7	7.71	25.2	4.37	9.9	7.88	8.8	8.12	25.0
Dy (µg/g)	2.95	15.0	3.34	8.7	2.57	9.2	3.41	6.9	10.00	35.0
Th (µg/g)	9.55	6.5	8.77	8.2	9.10	5.8	12.61	3.0	24.09	67.5
C (%)	1.54	48.7	4.93	47.3	3.64	14.2	0.97	49.5	23.38	57.5
N (%)	0.18	37.6	0.47	34.7	0.28	12.7	0.15	34.0	22.05	62.5
P (mg/g)	0.51	36.1	0.84	36.0	0.32	8.8	0.36	26.4	21.57	42.5
^{137}Cs (Bq/kg)	9.28	45.7	18.97	57.3	29.40	23.5	2.41	71.7	27.66	62.5
^{210}Pb (Bq/kg)	48.85	23.5	53.50	14.9	66.20	15.0	53.69	25.1	9.27	35.0

[1] All significant at p = 0.05; [2] cross-validated grouped cases correctly classified.

transportation) will be represented in the model. There is a need to reduce the impact of properties that may be unreliable because of spurious source-sediment matches (e.g. Yu & Oldfield, 1989; Walling *et al.*, 1993).

Effect of the number and type of tracers included in the mixing model

The relative importance of the number of tracers included in the mixing model to the uncertainty of the output was assessed by solving the model whilst progressively increasing the number of tracers from 4 up to 22. The model was solved for each suspended sediment sample and the uncertainty ranges associated with the mean source contributions are shown in Fig. 3(a). The results indicate that the uncertainty ranges decrease when the number of tracers in the model is increased (for each number of tracers, the model seeks to solve the mixing model by randomly selecting tracers from the list of available tracers to make up this number). This is due to the fact that as the number of tracers included is increased, fewer tracer sets are able to achieve GOF higher than 0.8 (Fig. 3(a), number of runs with GOF > 0.8 decreases when the number of tracers is increased). As a consequence, a decrease in the uncertainty range was observed. A similar behaviour is observed in all individual samples, for the four potential sediment sources. Furthermore, it can be seen that as the relative contribution of a particular source increases, the mean uncertainty range also increases. For example, when using a 10 parameter mixing model, the estimated uncertainty range for the mean source contributions was 0–41% for the cultivated topsoil, 39–95% for the grassland topsoil, 1–36% for the forest topsoil, and 0–13% for the channel banks. However, the most certain source ascriptions (lower uncertainty ranges) are not expected to be obtained when contributions of the individual potential sources are similar, but rather when the

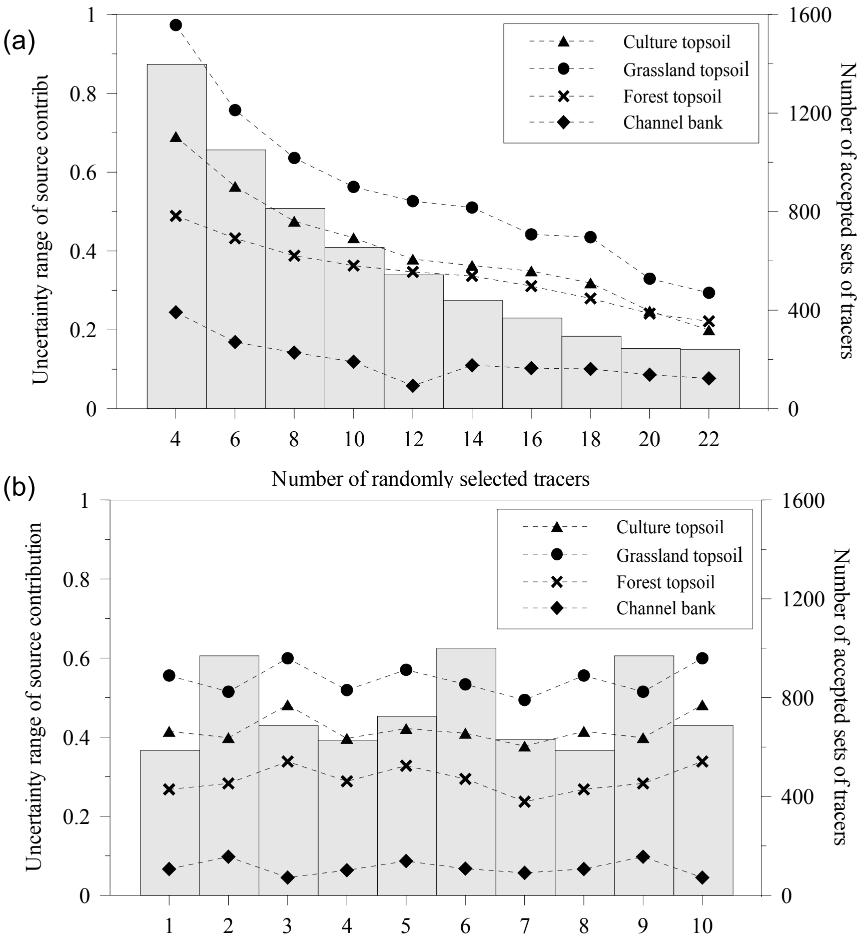

Fig. 3 (a) Mean source contribution uncertainty ranges obtained when solving the mixing model for the 18 suspended sediment samples collected at the Wollefsbach basin (2005–2007) using increasing number of randomly selected tracers to solve the model (GOF > 0.8), and number of accepted sets of tracers (GOF > 0.8); (b) Mean source contribution uncertainty ranges obtained when solving the mixing model for the 18 suspended sediment samples collected at the Wollefsbach basin (2005–2007) using 10 different combinations of 8 fixed randomly selected tracers to solve the model (GOF > 0.8), and number of accepted sets of tracers (GOF > 0.8).

suspended sediment tracer values are close to the values for one of the sources and that source dominates (e.g. Joerin *et al.*, 2002). As a result, source contribution uncertainty also depends on the tracer property values for the suspended sediment, since the geometry of the mixing diagrams and the location of the tracer values within this would also constrain the output uncertainty.

However, even though the uncertainty range decreased, the 50th percentile was seen to be stable. If the mean source contribution is equated with the mean 50th percentile result obtained (18 sample average) it would be possible to indicate that cultivated topsoil contributed 4±1.6%, grassland topsoil 75±2.7%, forest topsoil 8±1.2%, and channel banks 1±0.4% to the suspended sediment load.

The relative importance of the type of tracers included in the mixing model was studied by solving an eight-tracer mixing model using eight fixed randomly selected tracers (the mixing model is solved by always using the same tracers, randomly selected at the start). This exercise was repeated ten times (Fig. 3(b)). The results demonstrated that in the Wollefsbach basin the uncertainty was not dependent on the type of tracers included in the mixing model, since the 10 possible combinations of tracers tested provided similar uncertainty ranges.

All models present equifinality problems, because different combinations of source tracer values can achieve high efficiency values. This also indicates that a single optimisation solution is only one of a subset of statistically equivalent solutions, yet each of these may give very different model results in terms of the magnitude of the relative contributions assigned to the component source groups (Rowan *et al.*, 2000). The optimisation uncertainty is not considered in this study.

Spatial variability of the tracer signatures of individual sources

The relative contribution to the uncertainty of the output provided by the spatial variability of the tracer signatures associated with individual sources was investigated by solving the mixing model whilst increasing the coefficient of variation of the tracer property values associated with an individual source from 1% up to 40% of the mean measured values (Fig. 4). As might be expected, an increase in the spatial variability of the tracer property values was marked by an increase in the mean source uncertainty range (18 sample average). Thus, the establishment of source contributions becomes less certain as the tracer variability increases. When the model was solved without incorporating spatial variability (using mean values) the uncertainty associated with all source contributions was less than 10%. However, these uncertainty ranges were close to 40% when the spatial variability of all tracers reached 40% of their mean values.

It should be noted that the coefficients of variation of the source tracer properties measured in the Wollefsbach basin ranged from 3.0 up to 81.5%. Thus, the spatial variability of source tracer properties was considered to be a major source of uncertainty. However, further work is required to quantify the relative importance of the different sources of uncertainty.

Additional model constraints

Because the results outlined above show that the range of feasible contributions for each individual source can often be quite broad, attention has been directed to the possibility of constraining the model by: (1) incorporating weighting factors for individual tracers to take into account their spatial variability, and (2) constraining the model by using existing process understanding and knowledge of the study basin.

In this exercise, tracer specific weightings were used to ensure that the properties characterized by the smallest tracer standard deviations exerted the greatest influence upon the optimised mixing model. Furthermore, the model was constrained by limiting the maximum channel bank and forest topsoil contributions to 50%. It was assumed that eroding channel banks would be much more extensive if the contribution was higher than 50%. Equally, the forest areas are located near the margins of the catchment and are not well-connected with the stream network.

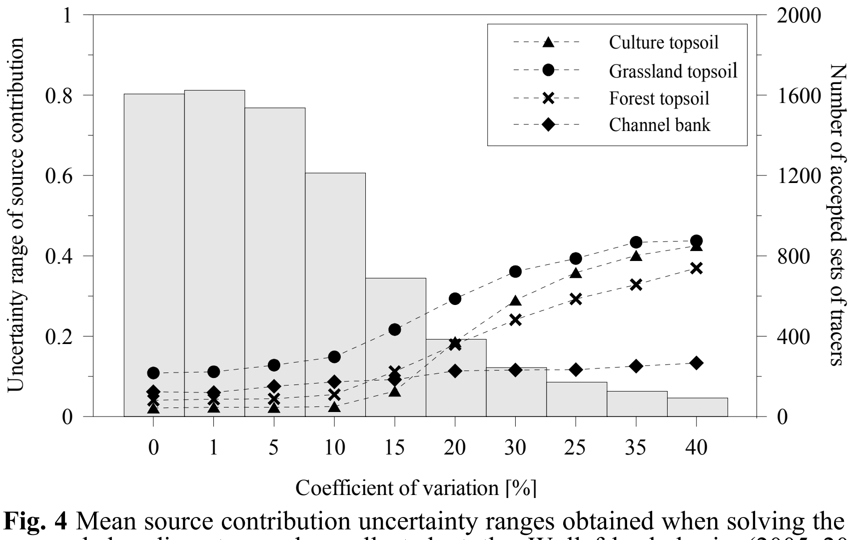

Fig. 4 Mean source contribution uncertainty ranges obtained when solving the mixing model for the 18 suspended sediment samples collected at the Wollefsbach basin (2005–2007) using 16 randomly selected tracers and increasing the coefficient of variation from 0 up to 40% (GOF > 0.8); and number of accepted sets of tracers (GOF > 0.8).

The results of introducing these weighting factors and constraints demonstrate that the mean uncertainty range (for 18 samples) of the sediment source ascription was reduced by up to 8%. The mean uncertainty ranges for the source contributions were estimated to be 0–33% for cultivated topsoil, 57–98% for grassland topsoil, 1–21% for forest topsoil, and 0–4% for the channel banks.

However, high inter-storm variability was observed in these uncertainty estimates. Table 3 shows the estimated uncertainty range of source contributions obtained when applying the multivariate mixing model with constraints to the 18 suspended sediment samples collected in the Wollefsbach basin (2005–2007). It is possible that the uncertainty of suspended sediment fingerprinting is specific to each sediment sample studied, and, consequently, it is specific to each rainfall–runoff event. These differences in uncertainty ranges are linked to different locations of the suspended sediment tracer values on the different mixing diagrams.

Table 3 Results of the fingerprinting analysis for the 18 suspended sediment samples collected in the Wollefsbach basin.

Storm event	Cropland topsoil (%)	Grassland topsoil (%)	Forest topsoil (%)	Channel banks (%)
17/11/05	0–36.5	17.8–67.7	18.9–67.3	0–4.5
06/12/05	0–51.7	44.4–100	0–19.2	0–6.5
16/01/06	0–29.7	64.4–100	0–14.0	0–4.6
26/01/06	0–56.7	41.7–100	0–26.2	0–6.4
22/02/06	0–81.8	18.2–100	0–35.2	0–5.5
07/04/06	0–68.2	29.2–100	0–29.3	0–6.2
11/05/06	0–29.7	34.8–100	0–65.2	0–0.0
18/05/06	0–20.3	53.5–100	0–37.2	0–2.6
24/05/06	0–17.3	75.7–100	0–7.4	0–4.0
30/05/06	0–25.3	70.1–100	0–5.4	0–3.3
05/07/06	0–9.7	83.9–100	0–0.0	0–1.8
03/08/06	0–20.3	69.2–100	0–18.7	0–2.2
11/09/06	0–0.0	90.9–100	0	0–1.4
10/10/06	0–9.0	81.6–100	0–3.6	0–1.3
25/10/06	0–7.4	85.2–100	0	0–1.0
21/11/06	0–14.8	79.7–100	0	0–3.1
13/12/06	0–45.9	52.3–100	0–15.2	0–4.6
25/01/07	0–66.2	31.3–100	0–26.2	0–5.5

In general, under the assumptions made, grassland topsoil was shown to be the dominant suspended sediment source in all rainfall events, followed by cropland topsoil, while forest topsoil and channel banks are shown to provide a smaller contribution. Since part of the basin is drained, and the forest and cropland areas are poorly connected with the stream network, the contribution of these sources to the overall suspended sediment yield from the basin is reduced. However, channel banks provided a higher contribution during the winter season, possibly as a consequence of instability caused by freezing processes and the absence of vegetation cover.

CONCLUSIONS

The main goal of this study was to assess model uncertainty by considering the spatial variability of source tracer properties using the GLUE approach. The method recognizes the equivalence or near-equivalence of different sets of parameters (equifinality). Monte-Carlo procedure and likelihood measures were employed to obtain the distribution functions of the different sediment sources used to subsequently derive the confidence intervals. Moreover, it was assumed that by including all the pre-selected tracers (i.e. those passing the Kruskall-Wallis test and not subject to transformation during erosion and transport) the likelihood that inappropriate tracers could be incorporated into the mixing model is increased.

A primary objective of this study was to understand better the relative importance to the final uncertainty of the output of: (1) the number and type of tracers included in the mixing model, and (2) the spatial variability of the tracer signatures of individual sources. The results obtained indicate that, for the Wollefsbach basin, under the assumptions made, the main sources of uncertainty were associated with the number of tracers included in the mixing model, and the spatial variability of the tracer signatures used to represent an individual source. The type of tracer included was shown to be of lesser importance. In some cases, the final estimates of source contributions were well constrained and informative, but in other cases, the ranges were so broad as to provide little information regarding the relative importance of the potential sources. The study demonstrates that uncertainty assessment should always be carried out when using the fingerprinting approach, even though any uncertainty assessment will always be conditional on the possibilities considered and the assumptions made (Beven, 2007).

A range of solutions up to 8% narrower were obtained when incorporating tracer weightings to reflect the spatial variability of source signatures, and constraining the mixing model to reflect current process understanding. The mean source contribution uncertainty ranges estimated for the 18 suspended sediment samples collected in the Wollefsbach basin (2005–2007) were 0–33% for the cultivated topsoil, 57–98% for the grassland topsoil, 1–21% for the forest topsoil, and 0–4% for the channel banks. However, high inter-storm variability of these uncertainty ranges was observed, since the uncertainty of suspended sediment fingerprinting is specific to each sediment sample studied. These differences were linked to the fact that source contribution uncertainty also depends on the tracer property values obtained for the suspended sediment, since the geometry of the mixing diagrams and the location of the tracer values within these will also influence the output uncertainty.

Despite the uncertainties involved, the proposed methodology provides a formalized procedure by which sediment source contributions, qualified by their uncertainty ranges, can be readily established using tracer mixing models.

Acknowledgements This study was supported by the "Ministère Luxembourgeois de la Culture, de l'Enseignement Supérieur et de la Recherche". The authors would like to thank Dr A. Kies and Z. Tosheva from the Radiation Physics Laboratory at the University of Luxembourg for radionuclide analysis, the "Administration des Services Techniques de l'Agriculture" in Ettelbruck (Luxembourg) for C and N analysis, as well as J. Ziebel, C. Guignard and F. Barnich at the CRP-Gabriel Lippmann for their help with ICP-MS measurements.

REFERENCES

Beven, K. J. (2007) Towards integrated environmental models of everywhere: uncertainty, data and modelling as a learning process. *Hydrol. Earth System Sci.* **11**(1), 460–467.

Beven, K. J. & Binley, A. M. (1992) The future of distributed models: calibration and predictive uncertainty. *Hydrol. Processes* **6**, 279–298.

Collins, A. L. & Walling, D. E. (2002) Selecting fingerprint properties for discriminant potential suspended sediment sources in river basins. *J. Hydrol.* **261**, 218–244.

Collins, A. L. & Walling, D. E. (2004) Documenting catchment suspended sediment sources: problems, approaches and prospects. *Prog. Phys. Geogr.* **28**(2), 159–196.

Collins, A. L. & Walling, D. E. (2007a) The storage and provenance of fine sediment on the channel bed of two contrasting lowland permeable catchments, UK. *River Res. Appl.* **23**, 429–450.

Collins, A. L. & Walling, D. E. (2007b) Sources of fine sediment recovered from the channel bed of lowland groundwater-fed catchments in the UK. *Geomorphology* **88**, 120–138.

Collins, A. L., Walling, D. E. & Leeks, G. J. L. (1997a) Source type ascription for fluvial sediment based on quantitative composite fingerprinting technique. *Catena* **29**, 1–27.

Collins, A. L., Walling, D. E. & Leeks, G. J. L. (1997b) Source type ascription for fluvial suspended sediment based on a quantitative composite fingerprinting technique. *Catena* **29**, 1–27.

Foster, I. D. L. & Walling, D. E. (1994) Using reservoir deposits to reconstruct changing sediment yields and sources in the catchment of the Old Mill Reservoir, South Devon, UK, over the past 50 years. *Hydrol. Sci. J.* **39**, 347–368.

Gruszowski, K. E., Foster, I. D. L., Lees, J. A. & Charesworth, S. M. (2003) Sediment sources and transport pathways in a rural catchment, Herefordshire, UK. *Hydrol. Processes* **17**, 2665–2681.

Joerin, C., Beven, K. J., Iorgulescu, I. & Musy, A. (2002) Uncertainty in hydrograph separation based on geochemical mixing models. *J. Hydrol.* **255**, 90–106.

Lees, J. A. (1997) Mineral magnetic properties of mixtures of environmental and synthetic materials: linear additivity and interaction effects. *Geophys. J. Int.* **131**, 335–346.

Motha, J. A., Wallbrink, P. J., Hairsine, P. B. & Grayson, R. B. (2003) Determining the sources of suspended sediment in a forested catchment in southeastern Australia. *Water Resour. Res.* **39**(3), Art. no. 1056.

Motha, J. A., Wallbrink, P. J., Hairsine, P. B. & Grayson, R. B. (2004) Unsealed roads as suspended sediment sources in an agricultural catchment in south-eastern Australia. *J. Hydrol.* **286**(1–4), 1–18.

Murphy J. & Riley J.-P. (1962) A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.* **27**, 31–36.

Olley, J. & Caitcheon, G. (2000) Major element chemistry of sediment from the Darling-Barwon River and its tributaries: implications for sediment and phosphorous sources. *Hydrol. Processes* **14**, 1159–1175.

Owens, P. N., Walling, D. E. & Leeks, G. J. L. (2000) Tracing fluvial suspended sediment sources in the catchment of the River Tweed, Scotland, using composite fingerprints and a numerical mixing model. In: *Tracers in Geomorphology* (ed. by I. D. L Foster), 291–307. John Wiley & Sons Ltd, Chichester, UK.

Pfister, L., Humbert, J. & Hoffmann, L. (2000) Recent trends in rainfall-runoff characteristics in the Alzette River basin, Luxembourg. *Climatic Change* **45**, 323–337.

Pfister, L., Barnich, F., Bouchet, A., El Idrissi, A., Hoffmann, L., Iffly, J. F., Matgen, P., Salvia-Castellví, M., Taillez, C., Van-den-Bos, R., Hofmann, H., Kies, A., Stellato, L. & Tosheva, Z. (2006) Cycleau project final report. National Research Fund - Program 'Eau'. Centre de Recherche Public – Gabriel Lippmann, Département Environnement et Biotechnologies and Uniersité du Luxembourg, Laboratoire de Physique des Radiations.

Phillips, D. L. & Gregg, J. W. (2003) Source partitioning using stable isotopes: coping with too many sources. *Oecologia* **136**, 261–269.

Phillips, J. M., Russell, M. A. & Walling, D. E. (2000) Time-integrated sampling of fluvial suspended sediment: a simple methodology for small catchments. *Hydrol. Processes* **14**, 2589–2602.

Rowan, J. S., Goodwill, P. & Franks, S. W. (2000) Uncertainty estimation in fingerprinting suspended sediment sources. In: *Tracers in Geomorphology* (ed. by I. D. L Foster), 279–290. John Wiley & Sons Ltd, Chichester, UK.

Salvia-Castellví, M., Iffly, J. F., Borght, P. V. & Hoffmann, L. (2005) Dissolved and particulate nutrient export from rural catchments: A case study from Luxembourg. *Sci. Total Environ*. **344**(1–3), 51–65.

Van den Bos, R., Hoffmann, L., Juilleret, J., Matgen, P. & Pfister, L. (2006) Conceptual modelling of individual HRU's as a trade-off between bottom-up and top-down modelling, a case study. In: *Conf. Environmental Modelling and Software. Proc. 3rd Biennal meeting of the international Environmental Modelling and Software Society* (Vermont, USA).

Walling, D. E. (2005) Tracing suspended sediment sources in catchments and river systems*. Sci. Total Environ.* **344**, 159–184.

Walling, D. E. & Woodward, J. C. (1992) Use of radiometric fingerprints to derive information on suspended sediment sources. In: *Erosion and Sediment Transport Monitoring Programmes in river Basins* (ed. by D. E. Walling & T. Day) (Proc. Oslo Symp. August, 1992), 153–164. IAHS Publ. 210. IAHS Press, Wallingford, UK.

Walling, D. E., Woodward, J. C. & Nicholas, A. P. (1993) A multi-parameter approach to fingerprinting suspended sediment sources. In: *Tracers in Hydrology* (ed. by N. E. Peters, E. Hoehn, Ch. Leibundgut, N. Tase & D. E. Walling), 329–337. IAHS Publ. 215. IAHS Press, Wallingford, UK.

Walling, D. E., Owens, P. N. & Leeks, G. J. L. (1999) Fingerprinting suspended sediment sources in the catchment of the River Ouse, Yorkshire, UK. *Hydrol. Processes* **13**, 955–975.

Yu, L. & Oldfield, A. (1989) A multivariate mixing model for identifying sediment source from magnetic measurements. *Quatern. Res*. **32**, 168-181.