

The use of visible and near-infrared reflectance measurements for identifying the source of suspended sediment in rivers and comparison with geochemical fingerprinting

Dries Verheyen · Jan Diels · Endalkachew Kissi ·
Jean Poesen

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Abstract

Purpose Visible and near-infrared (Vis-NIR) reflectance measurements may be an alternative technique to identify suspended sediment sources in streams of headwater catchments. In this study, we examined if Vis-NIR reflectance measurements are capable of estimating sediment source contributions to sediment yield and compared this technique with a more conventional (i.e. geochemical) technique.

Materials and methods Two headwater catchments in Ethiopia, Unta (2,052 ha) and Desera (1,657 ha), were analysed with the same techniques in order to find similarities and differences in the results obtained. The first technique used Vis-NIR spectral analysis as a fingerprint, using a partial least squares regression model. The second technique was a quantitative composite fingerprinting technique using geochemical analysis of source materials and suspended sediment samples. As a comparison, the partial least squares model was also used on the geochemical data. In August and September 2009, 30 soil samples of three different land uses (landslides, croplands, and grazing lands) and 21 suspended sediment samples at the catchment outlet were collected. Source samples were sieved to <63 µm. Geochemical analyses consisted of total element concentrations, percentage carbon, percentage nitrogen, and atom percentage ^{15}N and $\delta^{13}\text{C}$. Reflectance measurements were taken on dried source samples with a spectrometer.

Results and discussion Neither technique was able to predict the contributions of the three land use types; they could only distinguish between landslide and topsoil material. The agreement between the results of both techniques was significant for the Unta catchment ($R^2=0.80$) but not for the Desera catchment ($R^2=0.39$). The uncertainty of the technique using Vis-NIR reflectance measurements was slightly higher than with the geochemical approach. Both techniques revealed that topsoil erosion played an important role during storm runoff discharges. Using the partial least squares model for the geochemical data revealed that uncertainty can differ greatly when using other statistical techniques.

Conclusions The quantitative composite fingerprinting technique using spectral signatures from both source and suspended sediment samples was able to quantify the contribution of two source materials (landslides and topsoil). It provided a faster and more cost effective alternative to the conventional geochemical procedure.

Keywords Fingerprinting · Landslides · Sediment yield · Suspended sediments · Vis-NIR

1 Introduction

Transport of sediments in rivers may lead to a series of problems such as flooding, siltation of reservoirs and channels, pollution by sediment-fixed contaminants and degradation of aquatic habitats. Therefore, there is a need for reliable techniques that allow workers to determine the source (origin) of that sediment so that target measures can be taken to reduce sediment production. However, the complex interactions of sediment mobilization and delivery, in addition to spatial and temporal variations, make these processes difficult to assess. Furthermore, there are large costs associated with the long-term monitoring of large-scale river basins (Collins and

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D. Verheyen (✉) · J. Diels · J. Poesen
Department of Earth and Environmental Sciences, KU Leuven,
Celestijnenlaan 200 E, 3001 Leuven, Belgium
e-mail: dries.verheyen@ees.kuleuven.be

E. Kissi
Department of Natural Resource Management, School of
Agriculture, Jimma University, POB 378, Jimma, Ethiopia

Walling 2004). Traditionally, information on sediment sources has been collected using direct techniques aimed at quantifying sediment losses at the source location. However, spatial and temporal sampling constraints, as well as many operational difficulties, hamper the reliability of these techniques (Peart and Walling 1986). In this respect, the fingerprinting technique is an indirect technique known to be valuable and effective for sediment source determination in river catchments (Collins et al. 1998, 2001). The technique is based on two main assumptions: first, the potential sources of the river sediment can be discriminated on the basis of their physical or biogeochemical properties; and secondly, that the measured properties of source and sediment samples allow for the determination of the relative importance of the sources. Several studies have used various geochemical and physical sediment properties for fingerprinting sediment sources. A composite fingerprint in combination with a multivariate mixing model is able to determine the quantitative contribution of the sources, and this procedure has been successfully applied to a range of environments (e.g. Collins et al. 1997, 1998, 2001; Walling et al. 1999; Minella et al. 2008; Motha et al. 2003; Guzman et al. 2013). However, the application of this technique faces some methodological constraints. Labour and costs for the analysis of potential sediment sources and suspended sediment samples for a range of properties can be very high. Also the statistical procedure does not take into account the inherent variability of the different sediment source properties (Collins and Walling 2002). Another constraint is that the degree of uncertainty associated with the numerical solutions of the mixing model cannot be calculated (Phillips and Gregg 2001, 2003). Recent studies have begun to deal with these problems by using a Monte Carlo approach that incorporates source variability (e.g. Franks and Rowan 2000; Small et al. 2002; Motha et al. 2003; Martinez-Carreras et al. 2010a, b, c; Collins et al. 2010a, b).

Fingerprinting using visible and near-infrared (Vis-NIR) reflectance measurements may be an alternative method for determining sediment sources in river catchments (e.g. Poulenard et al. 2009; Martinez-Carreras et al. 2010a, b; Evrard et al. 2013; Legout et al. 2013). A requirement for using a mixing model to estimate sediment source properties from reflectance measurements is that these reflectance values show linear additive behaviour (Lees 1997). Multiple scattering on different components of a mixture may lead to non-linear behaviour (Keshava and Mustard 2002). Martinez-Carreras et al. (2010b) tested the linearly additive behaviour of three colour parameters calculated from reflectance parameters of artificial mixtures in the visible wavelength range (350–700 nm) and observed linearly additive behaviour. A similar testing by Poulenard et al. (2012) showed good linear additive behaviour for Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) in the mid-infrared range. Further testing of this important requirement for other

sediment types and wavelengths (e.g. NIR) would be desirable before the method can be applied more widely.

Fingerprinting sediment sources using reflectance measurements are often coupled with advanced multivariate statistical methods like partial least squares regression (PLSR) analysis (Wold et al. 2001; Viscarra Rossel et al. 2006b). The PLSR analysis allows a confidence interval of the predicted sediment contributions to be calculated. Several recent studies have used reflectance measurements to estimate sediment contributions. The spectral measurements can be used to calculate colour indices (Martinez-Carreras et al. 2010b) or geochemical properties (Martinez-Carreras et al. 2010a) to use in a multivariate mixing model. Several studies used the spectral measurements directly to estimate sediment source contributions using a PLSR approach (e.g. Poulenard et al. 2009, 2012; Evrard et al. 2013; Legout et al. 2013). It is also possible to use the spectral measurements directly in a mixing model using linear spectral mixture analysis (Somers et al. 2010); however, this technique is not yet implemented in fingerprinting suspended sediment sources. The study of Evrard et al. (2013) is one of the first attempts to compare the geochemical fingerprinting method with the spectroscopic approach using mid-infrared (MIR) spectra. The present study provides an early attempt of comparing the technique using the geochemical method and spectra in the Vis-NIR range. An unresolved question is how uncertainty related to estimates of sediment source contributions is influenced when reflectance measurements using PLSR estimates are used instead of conventional sediment fingerprinting using mixing model analyses (Martinez-Carreras et al. 2010a).

2 Study area

The study area is located in the Gilgel Gibe catchment in Kefa province, Oromiya region, Ethiopia, ca. 260 km southwest of Addis Abeba (Fig. 1). The Gilgel Gibe catchment is situated on the south-western Ethiopian plateau. The area is strongly influenced by past volcanic activity. It is characterised by a series of basic and subsilicic effusive volcanic rocks, frequently inter-layered with reddish paleosols of Tertiary age (Ministry of Mines and Energy 1997). The rocks found in this area are trachytic or basaltic. The volcanic layers have a gradient of a few degrees in a south-western direction and are crossed with fractures and faults. These are related to the main tectonic alignment of the region, the Ethiopian Rift Valley (Ministry of Mines and Energy 1997). The elevation of the Gilgel Gibe catchment is between 1,000 and 3,300 m above sea level. It consists of a series of gentle sloping low hills and broad plains surrounded by mountains. The area has a sub-humid climate with an average air temperature of 19.2 °C and an average annual rainfall of 1,535 mm (Ministry of Mines and Energy 1997). The rainy season

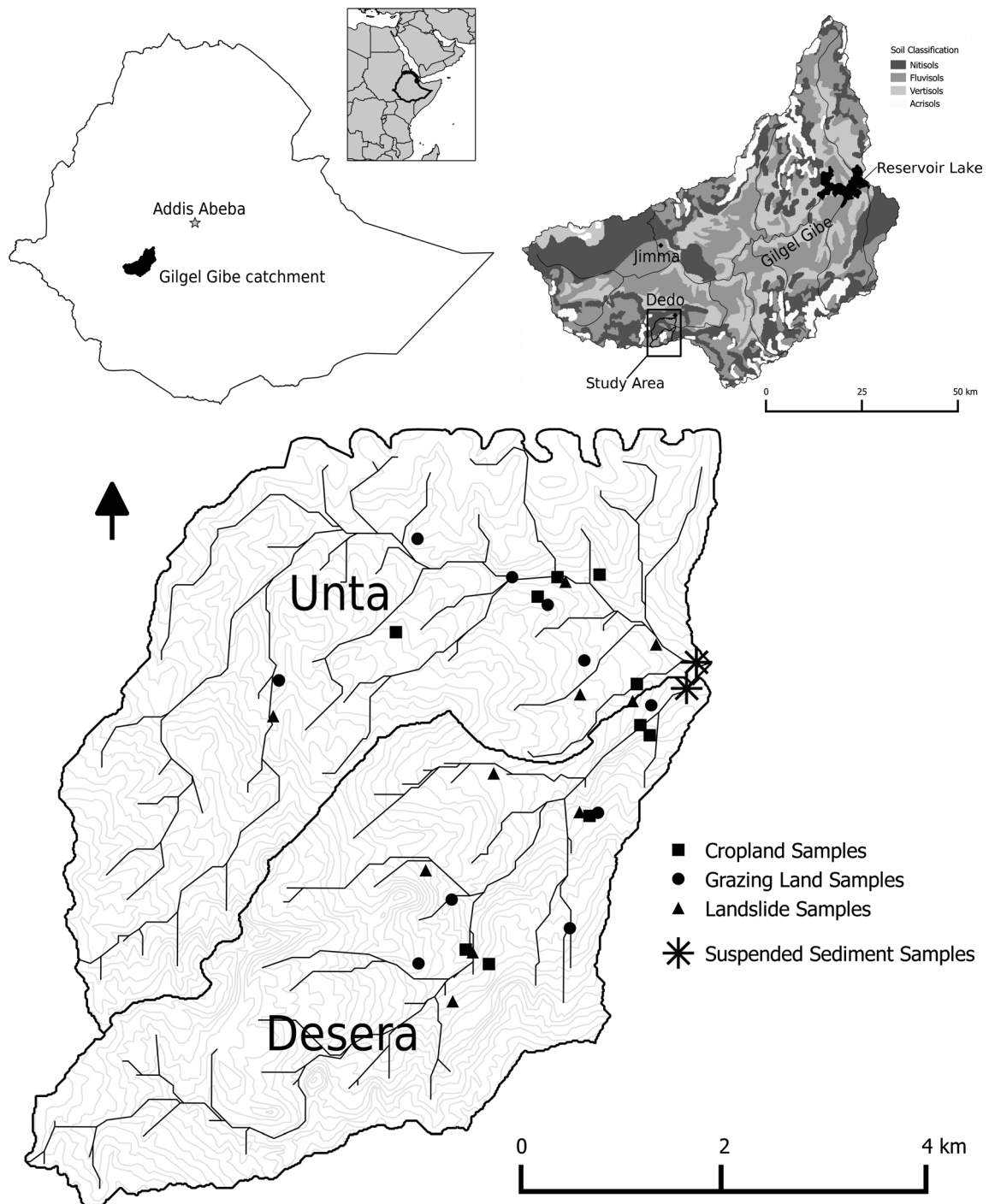


Fig. 1 Location of the Gilgel Gibe catchment, Ethiopia, and the headwater Unta and Desera subcatchments. The suspended sediment monitoring stations, and topsoil and landslide sample sites are indicated on the map

covers the months June until October. The two headwater catchments, Unta (2,052 ha) and Desera (1,657 ha), are situated about 22 km south of Jimma, near the town of Dedo. The major soil types of the area are Nitisols, Acrisols and Vertisols (FAO-UNESCO 1974). Vertisols in the area are limited to flat valley bottoms, mostly situated in the lower areas, and did not occur in the two studied catchments. A study of a soil

toposequence in the upland area near Dedo town revealed that the upland soils were quite similar in their morphological, physical, chemical and mineralogical characteristics (Tolossa et al. 2009). Land use consists mainly of cropland. Some plots are kept as grazing land by the farmers, but such plots are mostly small and surrounded by hedges or tree rows. Forest is only found in the highest regions in the catchment. Total forest

cover is only 11 %, of which most is exploited by the farmers (Broothaerts et al. 2012). The region is threatened by landslides which affect the siltation of the Gilgel Gibe dam (Broothaerts et al. 2012). An exploratory study predicted that the dam will be totally filled with sediment within 20 years if the siltation continues at the current rate, even though the dam was planned to serve for 70 years (Devi et al. 2008).

3 Materials and methods

3.1 Sample collection

Samples from sediment source types were taken from representative areas of different land use. Surface soil samples were taken from grazing land, cropland (maize (*Zea mays* L.), barley (*Hordeum vulgare* L.), teff (*Eragrostis tef* (Zucc.) Trotter), sorghum (*Sorghum bicolor* (L.) Moench) and wheat (*Triticum aestivum* L.)), actively eroding channel banks and landslides using an auger. Care was taken that only material likely to be eroded was sampled: the top 2 cm of grazing lands and croplands, and active landslides exhibiting erosion. For each catchment (Unta and Desera), 15 soil samples were collected, i.e. five from each land use type. This number of samples is rather limited, mainly due to practical reasons, but care was taken to get representative samples from every land use class. Therefore, soil sampling was spread as much as possible over the catchments to capture the variation in sediment sources. For the surface soils of cropland and grazing land, a soil sample consisted of 10 individual samples of the top 2 cm of the soil taken at ca. 10 m intervals on a randomly selected transect to form a composite sample. For the landslides, the samples consisted of material that was situated close (<5 m) to the river. Depth-integrated suspended sediment samples from the rivers were manually taken with a 1.5 l bottle at four equidistant positions within the cross-section of the river; each sediment sample used for further analysis was a composite sample from the four 1.5 l samples collected. The samples were taken at the monitoring stations at the outlet of the catchments. An effort was made to collect suspended sediment samples at different water heights and on as many times as possible. However, no samples were taken at the lowest flows because sampling at low flow would provide an amount of sediment that was insufficient for fingerprinting analysis, as the sampling was not time integrated. Sediment samples were taken during the rainy season at times when an event occurred. The sampling program ran from 1 August until 30 September 2009. A total of 21 sediment samples were collected.

3.2 Laboratory analysis

All source material samples were wet-sieved through a 63- μm mesh, oven-dried at 105 °C and manually disaggregated using a

pestle and a mortar. Sediment samples were not sieved prior to drying and disaggregation because particle-size analysis of the sediment samples taken during the highest flow rates (and with highest sediment load) indicated they contained little or no sand. The reflectance of the suspended sediment and source samples in the Vis-NIR light were determined with an ASD LabSpec[®] Pro spectrometer (Analytical Spectral Devices Inc., Boulder, CO, USA). This mobile instrument has one Si array (350–1,000 nm) and two Peltier-cooled InGaAs detectors (1,000–1,800 nm and 1,800–2,500 nm). The sampling interval is 1.4 nm at 350–1,000 nm and 2 nm at 1,000–2,500 nm. The light source is a quartz-halogen bulb of 3,000 K build into the high intensity probe. Every three samples, a white reference was measured to calibrate the sensor. The spectral properties of the sieved and dried source material and suspended sediment samples were recorded as follows: ± 20 g of soil/sediment was transferred into a small disposable petri dish of 1.0 cm height and 3.6 cm diameter. The filled cup was gently tapped on the table, hereafter the surface was carefully levelled with a spatula to obtain maximum reflection. The cup was placed under the sensor as close as possible (3 mm). The diameter of the sensor was 2 cm, resulting in a field of view of 3.14 cm². Four separate reflectance readings were taken from each soil/sediment specimen by rotating the cups by 90° after each reading. The final spectrum was the average of the four reflectance readings.

The geochemical analysis of both the source material and suspended sediment samples consisted of a range of potential fingerprint properties. Total element concentrations were analysed using a digestion with LiBO₂ in graphite crucibles (002380-000 crucible, CML YU40 grade, SCP Science, Quebec, Canada). After the digestion of the soil sample at 1,000 °C in a muffle furnace, the melt was dissolved in 50 ml of a 0.42 M HNO₃-solution. A 1/10 dilution of this solution was analysed with an ICP-OES (Varian 720ES, Agilent Technologies Inc., Palo Alto, CA, USA) analyser for macro elements (Suhr and Ingamell 1966). In addition to total element concentrations, percentage carbon (C), percentage nitrogen (N), atom percentage ¹⁵N and $\delta^{13}\text{C}$ were also analysed on the ground samples with an isotope ratio mass spectrometer (ANCA-GSL 20-20, Sercon Limited, Cheshire, UK).

3.3 Discriminating catchment sediment sources

For all statistical analysis, R software was used (R Core Team 2013). For both of the methods (colour and geochemical), the range of concentrations of different properties and wavelengths was tested between the source samples and the suspended sediment samples according to Walden et al. (1997). If properties or wavelengths of the suspended sediment fell out of the range of the source samples, these were discarded for further analysis.

In order to discriminate sediment sources using Vis-NIR spectral measurements, multivariate techniques described by Lees (1997) and Poulénard et al. (2009, 2012) were employed.

First, principal component analysis (PCA) was used to determine the natural clustering of samples. This natural clustering was used to investigate if the data were capable of determining sediment source samples by use of the principal components. The PCA scores were then used as input into a discriminant analysis.

For the geochemical method, the two-stage statistical selection procedure described by Collins and Walling (2002) was used to identify the sediment source. In stage one, all individual fingerprint properties were tested for their ability to distinguish between individual source types, using the Kruskal-Wallis H test. Next, discriminant function analysis (DFA) was used to identify an optimum composite fingerprint from the fingerprint properties that passed the H test. Because variables predicting group membership can be strongly correlated, a stepwise selection algorithm was used to select a subset of parameters to predict group membership. The method used was the minimization of Wilk's lambda. If all the group means were the same, a lambda of 1 occurs. A low lambda value means that the variability within the groups is small compared to the total variability (Collins et al. 1998). The stepwise forward variable selection starts with an initial model defined by the fingerprint property which best separates the groups (lowest lambda). The model is then extended by including extra properties. The selection stops if the p value of including another property is not statistically significant ($p > 0.05$).

3.4 Mixing model

The prediction of source type contributions to the sediment samples based on Vis-NIR spectra was assessed using a partial least squares regression (PLSR) model using the package pls (Mevik and Wehrens 2007). Partial least squares regression is a modelling technique usually used for quantitative predictions of sample properties. It is used especially when there are many predictor variables that are strongly correlated. Unlike principal component regression (PCR), it searches for orthogonal factors that maximize the covariance between predictor (X , spectra) and response variables (y , source type contribution). In order to calibrate the PLSR model and to test the linearly additive behaviour of the reflection properties, mixtures of source material samples were made depending on the outcome of the PCA. First, mixtures of pure sources (i.e. landslide, grazing land, cropland) were made, i.e. only soil samples of one source were mixed in the same ratio. Then, mixtures of these 'pure' mixtures were made to obtain a range of different source material ratios. These mixtures were then measured with a Vis-NIR spectrophotometer in order to calibrate the model. Model calibration was assessed on individual soil samples, pure mixtures and ratio mixtures as a whole, so that the total variability of soil samples was included in the model. Different pretreatments of the Vis-NIR data were applied to investigate if they could improve the performance

of the model. The pretreatments that were used were multiplicative scatter correction and standardisation (Stenberg et al. 2010). The first step when selecting a PLSR model is to determine the number of components to include in the model. The optimal number of components gives the best compromise between the description of the calibration set and the model's prediction ability. The PRESS statistic was used to decide which model to use, and the optimum number of components is the one with the lowest PRESS statistic. For comparison, the adjusted coefficient of determination (R^2_{adj}) and the root mean square error of prediction (RMSEP) were calculated. In order to calculate the PRESS value, a cross validation was performed, using at random four or five samples as a test set. The model was cross validated 10 times, and the ultimate PRESS value was the mean PRESS value of the 10 cross-validated models.

In order to test the linearly additive behaviour of the spectra, the reflectance spectra of artificial linear mixture samples of source types were computed. The reflectance spectrum of such an artificial sample was calculated as a weighted average of the source samples that were mixed. The spectra of these artificial mixtures were used to calibrate a PLSR model that predicts source type contribution. This model was then applied to the measured (real) mixture samples. If the model predicts the contribution of the source in the mixed samples well, then this reveals the linearly additive behaviour of Vis-NIR spectra.

For the quantification of source contributions to sediment yield using the geochemical method, a modified numerical mixing model based on that of Collins et al. (2010a, b) was used. The basic assumption is that a mixing model relates the fingerprint properties of the suspended sediment samples to the properties of the three possible source samples (landslide, cropland, grazing land):

$$\hat{C}_i = \sum_{j=1}^m P_j S_{i,j} \quad (1)$$

With \hat{C}_i being the predicted concentration (e.g. mg kg^{-1}) of the i th fingerprinting property in the suspended sediment sample, S_{ij} the mean concentration of the i th fingerprint property in the source type j (ls = landslide, g = grazing land, c = cropland), and P_j is the mass fraction of the suspended sediment sample originating from source j . The proportions sum up to one and must have a value between 0 and 1:

$$0 \leq P_j \leq 1 \quad (2)$$

$$\sum_{j=1}^n P_j = 1 \quad (3)$$

For each suspended sediment sample, the proportion was determined by minimizing the sums of squares error (SSE)

between the fingerprint property concentrations measured on the suspended sediment sample and those predicted with the mixing model:

$$SSE = \sum_{i=1}^n \left\{ \left(C_i - \left(\sum_{j=1}^m P_j S_{i,j} SV_{i,j} \right) \right) / C_i \right\}^2 W_i \quad (4)$$

where C_i = the measured value of the i th property of the sediment samples (mg/kg or g/kg), P_j = the optimised fraction of sediment contribution, $S_{i,j}$ = the mean concentration of a fingerprint property (mg/kg or g/kg), W_i = a correction factor weighting for the discriminatory power of a certain property, calculated from the scaled H values of the Kruskal-Wallis test of that property, n = number of fingerprint properties, m = number of sediment sources, and $SV_{i,j}$ = a correction factor taking into account the within-source variability of a property (i) in the samples of a source category (j) calculated as the inverse of the scaled standard deviation of each property in each source category. This was done using an algorithm proposed by Haskell and Hanson (1981) that is implemented in R (Soetaert et al. 2009). In this calculation, no corrections have been made for particle size and organic matter. This is because little is known about the potential errors associated with the use of correction factors for particle-size composition and organic matter content (Koiter et al. 2013). The difference in particle size was minimized by sieving the soil samples to the <63 μ m fraction.

When using geochemical properties for fingerprinting, there are different types of uncertainties that need to be taken care of when calculating the sediment source contributions. The most important type of uncertainty comes from the use of the mean property values for each sediment source to predict the proportions in the sediment. This mean value is based on a number of samples taken for a given sediment source, and hence subject to sampling error and natural source variability. Therefore, a Monte Carlo approach according to Collins et al. (2010b) was used to translate sampling errors and source variability into uncertainty on the estimated sediment source contribution P_j . Distributions of each fingerprint property for each sediment source were calculated using the median and robust scale estimator (Q_n) (Rousseeuw and Croux 1993). A total of 5,000 numbers ($S_{i,j}$) were picked out of this distribution using a random number generator with a non-negative constraint. These values were then used to solve the mixing model equation 5,000 times to create a 95 % confidence interval of the sediment contributions.

In order to better compare the results—because different fingerprint properties were used, as well as different statistical procedures—PLSR was also performed on the data of the geochemical analysis. All data were included that passed the range test, because the PLSR will decide on the weighting of the parameters that best predict topsoil contribution. A PLSR was performed on the geochemical dataset predicting source

type contribution, using only the data from the pure samples. Here, no mixtures of source samples were analysed geochemically. To truly compare the spectra and geochemical tracers under the same conditions, the PLSR model of the spectral data was also performed on pure samples; the mixture samples were discarded from the analysis.

4 Results and discussion

4.1 Vis-NIR fingerprinting

4.1.1 Vis-NIR reflectance spectra of soil samples

Figure 2 shows typical Vis-NIR reflectance spectra for the three types of potential source materials and suspended sediment samples. The spectra of all the samples contain absorption features corresponding to the bending and stretching of OH-bonds of free water. These peaks occur in the NIR (700–2,500 nm) region, at a wavelength of 1,400 and 1,950 nm. The absorption features at around 2,200 nm are characteristic of the AL–OH bend plus O–H stretch of clay minerals like kaolinite and gibbsite. In the visible (400–700 nm) range, reflectance is related to electronic transitions (Viscarra Rossel et al. 2006b) and with minerals containing iron like haematite and goethite (Stenberg et al. 2010). Soil organic matter can also produce broad absorptions in the visible region, due to humic acid. The visible region was different for the landslides compared to that for the grazing and cropland. Landslides were more lightly coloured, because they contain less organic C. Figure 3 plots the mean spectra for each source type. The differences in albedo of the spectra can reflect a difference in the grain sizes of the soil samples (Stenberg and Viscarra Rossel 2010). Although source material was sieved through a 63- μ m mesh, landslide samples still contained relatively more silt than grazing land and cropland samples. Also the difference in mineralogy between the top soil (grazing land and cropland) and subsoil (landslides) can have an influence on the albedo (Viscarra Rossel et al. 2006a). Soil organic C is also known to decrease reflectance in the VIS and near-to-shortwave infrared range (Bayer et al. 2012).

4.1.2 Principal component and discriminant analysis of source materials

Principal component analysis was used as an exploratory technique to determine the natural clustering of samples, in order to evaluate overall variability and to find out if sediment sources can be distinguished. Ten principal components explain more than 99 % of the variance. The two first principal components of the data, explaining 98.2 % of the variability, represent the axes in which the data have the most variability

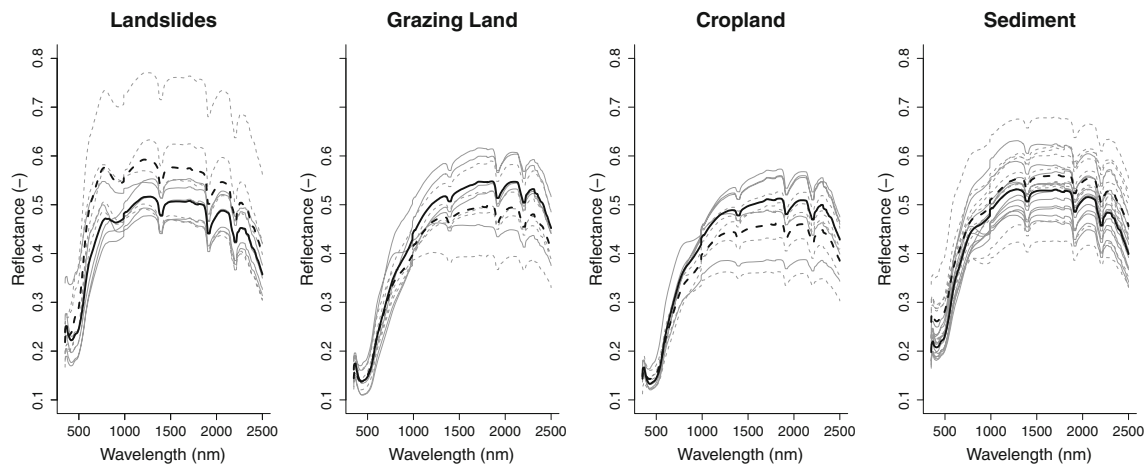


Fig. 2 Typical spectra from different types of source materials and suspended sediment samples in the Unta (*full line*) and Desera (*dashed line*) catchment. Individual samples are plotted in *grayscale*, mean spectra are *black*

(Fig. 4). From the plot, it is clear that landslides can be separated from grazing lands and croplands. A large overlap between grazing lands and croplands exists; even the mean values (centroids) are plotted close to each other. When the scores of the first 10 principle components of the PCA were used as input for a discriminant analysis, the separation between the groups was greater (Fig. 5). Although the separation of the three source categories is better after discriminant analysis, there is still a large overlap between the grazing lands and the croplands. All the landslide samples were placed in the right category, but only 7 out of the 10 cropland samples and 8 out of the 10 grazing land samples were correctly classified. In total, 83.3 % of the samples were predicted to be in the right category. Even after a maximal separation of the groups, a distinction between grazing lands and croplands is

difficult to make based on reflectance readings. These results indicate that Vis-NIR spectra can be used to determine two types of sediment sources: landslides (i.e. subsoil material); and topsoils.

4.1.3 Partial least squares regression model using mixtures

From the PCA analysis, it could be concluded that it was not possible to differentiate between topsoils from grazing lands and croplands using the Vis-NIR spectra of soils. Therefore, a PLSR model was created that considered all topsoils (from grazing lands and croplands) as one group and predicted the topsoil contribution to the suspended sediment. Table 1 represents the mixing scheme per catchment. In total, 23 mixtures were made per catchment (Unta and Desera). Mixtures were

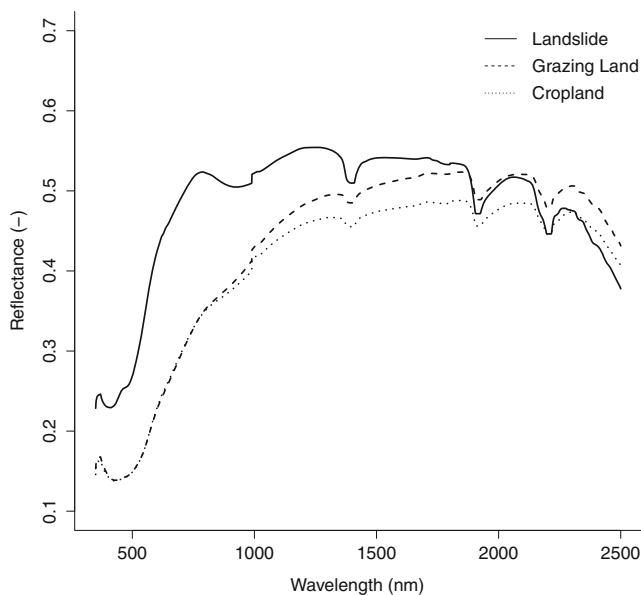


Fig. 3 Mean spectrum from different types of source materials in the Unta and Desera catchments

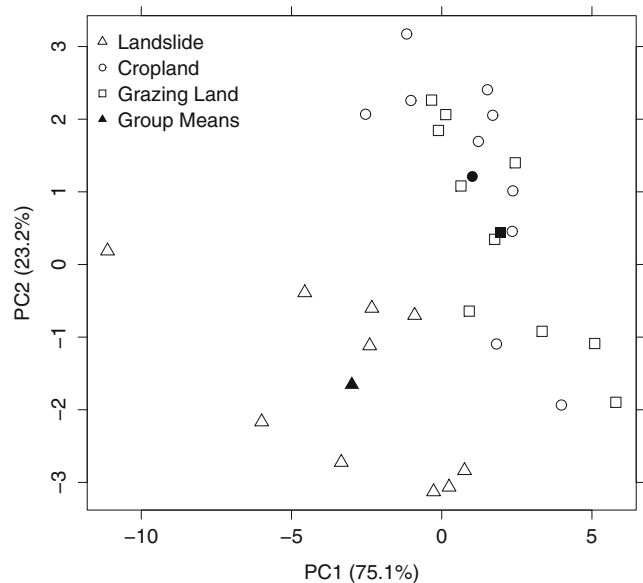


Fig. 4 Plot of the first two principal components from the principal components analysis (PCA) of the VIS-NIR spectra of the source samples (Unta and Desera samples)

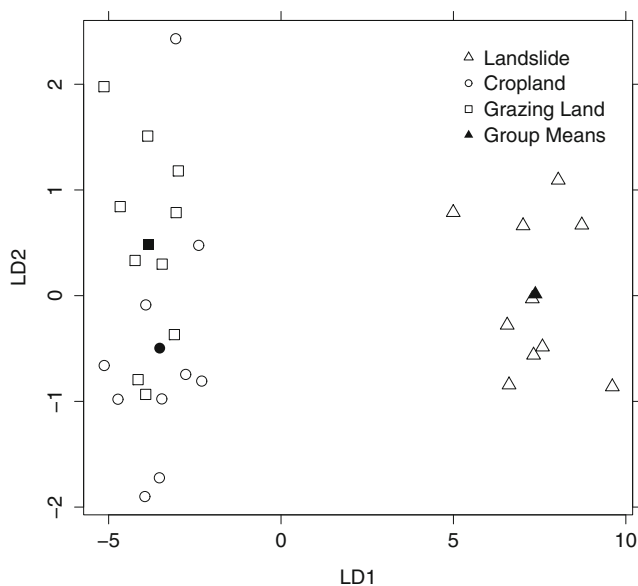


Fig. 5 Plot of the first two linear discriminants from the linear discriminant analysis (LDA) using the principal components analysis (PCA) scores as input (Unta and Desera samples)

made to obtain a range of different topsoil:landslide ratios, because the PLSR model was mainly intended to predict the topsoil contribution in the sediment samples. The model with

the lowest PRESS value was chosen as the optimal model. The best model was the model with no pretreatment and eight components, and had a PRESS value of 0.652. If no pretreatment is used, no correction is made for the albedo differences or scatter of the Vis-NIR spectrum. This means that the albedo difference can be a good predictor of the topsoil contribution to suspended sediment. The R^2_{adj} value was 0.947 and the RMSE of prediction was 0.091. This means that the error of the model is 18 %, which is an acceptable error (Fig. 6). This confidence interval is in agreement with Poulenard et al. (2009).

Chemometric methods usually are used in chemical analysis to determine the concentration of various chemical compounds. In this study, this approach was used to predict the fractions of topsoil occurring in suspended sediment samples. Hereby, the linear additive behaviour of the spectra was tested by making artificial linear mixtures of topsoil and landslide samples and calibrating a PLSR model on those linearly computed mixtures. When the reflectance readings of the mixtures were applied to that model, the fit had a R^2 of 0.97. The good fit shows that the reflectance measurements of the mixtures show linear additive behaviour according to the topsoil contribution. It shows that the spectrum of a mixed sample is a linear combination of the spectra of pure landslide

Table 1 Composition of the source sample mixtures used to calibrate the partial least squares regression (PLSR) model. This table represents the mixing scheme for one catchment. Identical mixtures were produced for both the Unta and the Desera catchments (LS = landslide, CL = cropland and GL = grazing land)

Sample label	Weight percentage of the classes of source material				
	Landslide material	Cropland top soil	Grazing land top soil	Total top soil	Total landslide
Pure mixtures					
LS	100			0	100
GL			100	100	0
CL		100		100	0
Ratio mixtures					
LS CL 10 90	10	90		90	10
LS CL 25 75	25	75		75	25
LS CL 50 50	50	50		50	50
LS CL 75 25	75	25		75	25
LS CL 90 10	90	10		10	90
LS GL 10 90	10		90	90	10
LS GL 25 75	25		75	75	25
LS GL 50 50	50		50	50	50
LS GL 75 25	75		25	75	25
LS GL 90 10	90		10	10	90
LS CL GL 10 10 80	10	10	80	90	10
LS CL GL 10 80 10	10	80	10	90	10
LS CL GL 25 25 50	25	25	50	75	25
LS CL GL 25 50 25	25	50	25	75	25
LS CL GL 33 33 33	33	33	33	67	33
LS CL GL 80 10 10	80	10	10	20	80
LS CL GL 50 25 25	50	25	25	50	50

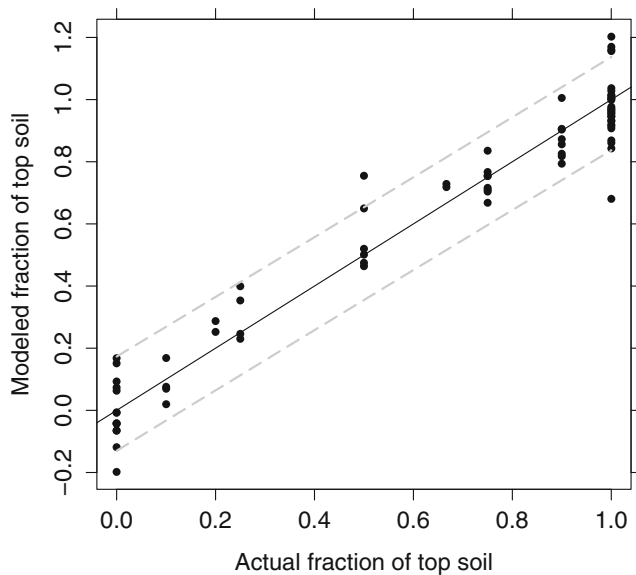


Fig. 6 Calibration plot of the partial least squares regression (PLSR) modelling for topsoil contribution of the mixed samples. The grey dashed line is the 95 % prediction interval

and pure topsoil samples. The PLSR model predicted a range of 15.8–70.2 % for topsoil contribution for the Unta catchment and 19.8–70.0 % topsoil contribution for the Desera catchment, with an 18.2 % error. These measurements indicate that topsoil erosion plays an important role in both catchments. The PLSR model enabled the calculation of a confidence interval for the predictions of sediment sources. Despite its importance, this information is often missing in conventional fingerprinting procedures (e.g. Collins et al. 1997, 2001; Collins and Walling 2002, 2004). Only recently, uncertainty associated with sediment source type ascription was assessed using the Monte Carlo approach (e.g. Motha et al. 2003; Collins et al. 2010b; Martinez-Carreras et al. 2010a, b) or a likelihood function approach (Minella et al. 2008).

4.1.4 Partial least squares regression model using pure samples

When only pure samples and no mixtures were used to calibrate the PLSR model, almost the same model performance was acquired. The model with the lowest PRESS value of 0.545 used seven components and had an R^2_{adj} of 0.92. The correlation between the predicted contribution of topsoil to the suspended sediment with the model using mixtures was 0.98 for Unta and 0.99 for Desera. The main difference is that the RMSEP value of the model using pure samples was 0.13. This means that the uncertainty of the prediction rises by 7.8 % if only pure samples are used to calibrate the model instead of pure samples and mixtures. It could be argued that with using mixtures the uncertainty is only reduced artificially by adding extra data points in the middle of the regression line. The model based on pure samples only, therefore, better reflects

the uncertainty involved in fingerprinting using spectral measurements.

4.2 Geochemical fingerprinting

4.2.1 Geochemical analysis of soil samples

The mean concentrations of a range of fingerprint properties measured in the source samples from the Unta and Desera catchment and the results of the Kruskal-Wallis H test are presented in Table 2. In total, eight properties passed the test with a critical H value of 7.38. The results in Table 2 show that a number of selected properties provide powerful source discrimination. For example, C was able to successfully classify 93.3 % of all the source samples, followed by N (83.33 %), manganese (Mn; 80.0 %), aluminium (Al; 66.7 %), zinc (Zn; 66.7 %), zirconium (Zr, 60.0 %), ^{15}N (56.7 %) and $\delta^{13}\text{C}$ (50 %).

There was a small difference in C for grazing lands (3.67 %), which was a little higher than that for croplands (2.94 %), but was highly different from that for landslides (0.65 %). This is because landslide material consists mainly of subsoil (weathered rock), which contains little or no C from vegetation. The small difference in C between grasslands and croplands is explained by the fact that grasslands in this area are overgrazed, and therefore cannot sequester much C. Also, grazing lands are situated on lands that can no longer be used for crop production. Therefore there is a rotation of alternating land use between cropland and grazing land, so that differences between these two land use types will become less distinct (Smith and Blake 2014). Percentage N follows the same trend as C.

There were also no differences in $\delta^{13}\text{C}$ measurements for the soils under grazing land and croplands. The dominant crops of the cropland are maize, teff and sorghum, which are C_4 -type plants. Also most tropical grasses have a C_4 -type metabolism. The ranges of the $\delta^{13}\text{C}$ values of C_4 -type plants are between -6 and -19‰ , whereas for C_3 -type they are between -24 and -34‰ (Smith and Epstein 1971). The lower value of the landslide samples could be explained by the presence of forest (tree) vegetation, 50 to 100 years ago. Tree species are C_3 -type species, and the roots of the trees could have provided a lower $\delta^{13}\text{C}$ value to the subsoil compared to the topsoil of grazing land and cropland.

There was a large difference in concentration of Mn between landslide and topsoil samples. Mn has two oxidation states, +II which is more mobile and +IV. The solubility of Mn in soils is mainly affected by pH and redox potential. This normally leads to higher Mn bioavailability in flooded soils. The saturated subsoil of landslides reduces the Mn and makes it more mobile and hence more easily leached. In the topsoil of grazing land and cropland Mn retention by cation exchange

Table 2 The ability of individual fingerprint properties to distinguish sediment source type, assessing the Kruskal-Wallis H test and discriminant function analysis (DFA)

Fingerprint property	Mean concentration				Kruskal-Wallis				DFA	
	Landslides mean	CV (%)	Cropland mean	CV (%)	Grazing land mean	CV (%)	H value ^a	P value	Significance	Correctly classified samples (%)
Al (g kg ⁻¹)	117	10	90	13	87	14	19.38	<0.001	***	67
As (mg kg ⁻¹)	26	27	29	36	29	56	0.20	0.904		
Ba (mg kg ⁻¹)	392	36	385	12	380	23	0.28	0.869		
Ca (g kg ⁻¹)	6.19	85	3.80	33	3.41	31	1.44	0.486		
Cr (mg kg ⁻¹)	142	71	117	37	138	57	0.07	0.965		
Cu (mg kg ⁻¹)	35	46	35	22	34	22	0.29	0.865		
Fe (g kg ⁻¹)	85.2	21	92.9	18	86.3	18	2.39	0.303		
K (g kg ⁻¹)	8.14	79	8.33	24	7.78	33	0.64	0.727		
Mg (g kg ⁻¹)	7.19	56	5.12	37	4.41	28	4.66	0.097		
Mn (g kg ⁻¹)	1.13	31	3.24	20	3.20	20	19.40	<0.001	***	80
Na (g kg ⁻¹)	6.86	111	3.85	26	3.87	35	0.06	0.968		
Ni (mg kg ⁻¹)	89	63	71	32	80	41	0.84	0.658		
P (g kg ⁻¹)	1.43	62	1.17	14	1.16	18	0.01	0.995		
Sc (mg kg ⁻¹)	22	27	18	28	17	35	5.27	0.072		
Si (g kg ⁻¹)	198	10	201	9	202	11	0.26	0.879		
Sr (mg kg ⁻¹)	112	67	67	28	66	36	4.86	0.088		
Ti (g kg ⁻¹)	14.6	28	15.9	30	13.8	36	1.56	0.459		
V (mg kg ⁻¹)	214	35	238	33	199	37	2.52	0.284		
Zn (mg kg ⁻¹)	146	18	224	14	214	15	16.85	<0.001	***	67
Zr (mg kg ⁻¹)	485	38	1054	24	1083	23	16.85	<0.001	***	60
%N	0.05	59	0.28	12	0.35	15	22.43	<0.001	***	83
atom% ¹⁵ N	0.38	0	0.38	0	0.38	0	12.16	0.002	**	57
%C	0.65	56	2.94	10	3.67	14	23.08	<0.001	***	93
δ ¹³ C ‰	-22.38	9	-19.27	7	-19.11	6	12.31	0.002	**	50

DFA discriminant function analysis, Al aluminium, As arsenic, Ba barium, Ca calcium, Cr chromium, Cu copper, Fe iron, K kalium, Mg magnesium, Mn manganese, Na sodium, Ni nickel, P phosphorus, Sc scandium, Si silicium, Sr strontium, Ti titanium, V vanadium, Zn zinc, Zr zirconium

* $P < 0.05$; ** $P < 0.01$; *** $P < 0.001$

^a Critical H value=7.38

capacity and ligand exchange reactions will reduce leaching of Mn to the subsoil (Patrick and Turner 1968).

Table 3 gives the geochemical and organic matter properties of the suspended sediment samples. The range of organic C (0.41–3.13 %) is situated between that of the source samples, but most sediment samples have values that are quite high. This is possibly due to an enrichment effect of the organic matter associated with the clay content that is related to sediment transport. Another possible explanation could be that there was another source with a high C content.

4.2.2 Discriminant function analysis of source materials

The optimum composite fingerprint, given in Table 4, is capable of classifying 93.3 % of the source samples. The fingerprinting properties are not capable of classifying all sediment

sources in the right category. This is because there is an overlap between the grazing lands and the croplands. No single property for both sediment source types was different enough to differentiate between the two sources. On the other hand, the difference in fingerprinting properties of landslides with those of the grasslands and croplands was very clear. Because of this, it is better to merge grazing lands and croplands in the same category, i.e. topsoils. Now, the source ascription of the sediment is only distinguishing between two main sediment source types, i.e. landslides and topsoils. This also makes the source ascription more reliable. There would be too much uncertainty in the prediction if three source types would have been used. The Kruskal-Wallis H test is performed again, now for topsoil and landslide as sediment sources. The same composite fingerprint was calculated, now classifying 100 % of source samples in the correct category.

Table 3 Mean geochemical and organic matter properties of the suspended sediment samples. See Table 2 for elements and units

Date (d/m/y)	Catchment	Al	Ba	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Sc	Si	Sr	Ti	V	Zn	Zr	%N	atom% ¹⁵ N	%C	δ ¹³ C ‰
14/08/09	Unta	107	523	11.3	181	40.2	92.3	10.19	8.08	2.93	7.58	95.5	1.76	20.1	217	136	11.8	171	276	799	0.23	0.3683	2.16	-20.99
20/08/09	Unta	98	419	7.8	116	35.3	77.5	10.80	6.21	2.28	6.37	70.7	1.72	15.1	225	101	9.7	141	273	949	0.42	0.3686	3.13	-22.01
22/08/09	Unta	113	554	14.0	206	35.2	98.7	8.29	9.80	2.25	8.04	110.7	1.74	25.2	206	166	13.3	186	216	549	0.15	0.3691	0.79	-22.38
30/08/09	Unta	112	413	11.3	141	45.4	79.8	8.87	8.68	1.64	8.00	100.8	1.57	25.2	208	136	10.3	146	368	675	0.36	0.3691	2.08	-22.09
31/08/09	Unta	112	429	10.5	141	35.3	82.8	9.24	7.98	1.84	7.09	85.8	1.54	20.2	211	136	11.1	162	379	803	0.27	0.3694	2.04	-21.74
02/09/09	Unta	111	434	8.4	172	40.4	87.0	8.69	8.84	2.12	5.69	101.0	1.47	25.3	217	116	13.3	177	187	697	0.15	0.3695	1.36	-19.93
02/09/09P	Unta	105	443	8.7	171	35.3	84.7	8.92	7.60	2.10	6.43	90.7	1.72	20.2	217	111	11.2	166	212	655	0.23	0.3689	2.04	-22.62
05/09/09	Unta	110	501	10.8	248	40.5	106.0	8.19	10.67	2.57	7.17	126.6	1.70	25.3	210	137	14.1	198	208	593	0.12	0.3696	0.96	-21.80
07/09/09	Unta	108	440	11.0	142	40.4	84.4	10.04	8.40	2.09	7.48	96.0	1.61	20.2	209	131	10.4	162	329	824	0.28	0.3698	2.16	-21.40
08/09/09	Unta	112	455	8.7	157	40.4	85.4	8.94	7.36	1.94	5.97	85.9	1.75	20.2	215	116	11.3	167	242	743	0.24	0.3690	1.95	-22.14
10/09/09	Unta	108	471	9.2	172	35.4	90.9	10.17	7.74	2.27	7.64	91.1	1.51	20.2	219	127	12.4	177	197	744	0.17	0.3689	1.54	-20.78
14/08/09	Desera	97	397	10.6	65	20.1	80.4	18.06	7.42	1.91	16.10	40.3	1.51	20.1	233	126	9.8	156	201	553	0.19	0.3687	1.70	-22.57
15/08/09	Desera	114	545	10.6	35	20.2	96.0	9.55	9.64	1.66	7.55	30.3	2.44	25.2	201	156	18.3	247	192	429	0.08	0.3694	0.41	-21.98
20/08/09	Desera	93	252	6.1	40	10.1	56.3	25.61	3.91	1.38	23.07	25.2	1.06	15.1	256	66	7.1	86	197	611	0.21	0.3686	1.82	-23.37
22/08/09	Desera	98	349	11.4	56	10.1	67.5	22.65	6.82	1.22	22.38	30.4	1.33	15.2	245	132	8.9	111	192	465	0.14	0.3692	0.82	-23.48
02/09/09P	Desera	101	411	8.3	76	25.3	80.6	16.34	6.94	1.84	13.45	50.7	1.44	20.3	230	117	11.6	152	162	563	0.14	0.3693	1.33	-21.67
02/09/09	Desera	97	217	9.7	40	10.1	51.5	25.95	4.92	0.92	25.12	25.3	0.81	15.2	249	91	5.7	61	243	667	0.13	0.3695	1.05	-23.11
05/09/09	Desera	101	303	7.8	56	15.2	64.3	23.51	5.13	1.23	22.09	90.9	1.22	15.2	251	91	7.8	101	177	540	0.27	0.3693	1.38	-23.97
07/09/09	Desera	96	358	8.2	96	20.1	76.0	16.22	6.56	1.51	13.47	60.4	1.23	20.1	230	106	10.9	151	176	589	0.12	0.3686	1.22	-25.65
08/09/09	Desera	100	232	5.1	35	5.0	53.8	25.50	3.38	1.13	22.56	20.2	0.96	15.1	251	60	6.1	65	146	579	0.14	0.3697	1.27	-22.71
10/09/09	Desera	104	272	7.2	55	15.1	58.1	23.57	4.90	1.07	21.26	40.3	0.96	15.1	247	81	7.2	91	217	564	0.14	0.3684	1.44	-24.37

Table 4 Results of the stepwise discriminant function analysis for identifying an optimum composite fingerprint for discriminating source types (landslide, grazing land, cropland)

Step	Fingerprint property	Wilks lambda	Samples classified correctly (%)
1	%C	0.07676	93.3
2	%C + Mn	0.06058	90.0
3	%C + Mn + Zr	0.05066	93.3

4.2.3 Mixing model

Figures 7 and 8 show the probability density functions (pdf) of the median contributions from topsoils and landslides for the Unta and the Desera catchment as obtained with the geochemical fingerprinting technique. The uncertainty because of variation in concentration of properties of the source samples ranged between 5.4 and 10.7 % for the Unta and 4.0 and 9.4 % for the Desera catchment. Topsoil erosion plays a significant role in the Unta catchment; the contribution of topsoil material to the sediment yield ranged between 3.6 and 59.3 %. For the Desera catchment, landslide processes

are the dominant processes that contribute sediment to the river. Here, the topsoil contribution ranged between 0.8 and 18.4 %.

A hypothesis is that at low flows, the contribution of landslides is the highest. Table 5 gives an overview of the sediment samples taken with the corresponding stage height, sediment load and predicted topsoil contribution for both methods (Vis-NIR using PLSR modelling of mixtures and geochemical using the mixing model). The lowest flow measured (52 cm flow depth at the Desera catchment on 15/08/09) corresponds to a landslides contribution of 99.1 ± 1.9 %. This low flow almost corresponds to the base flow in the rainy

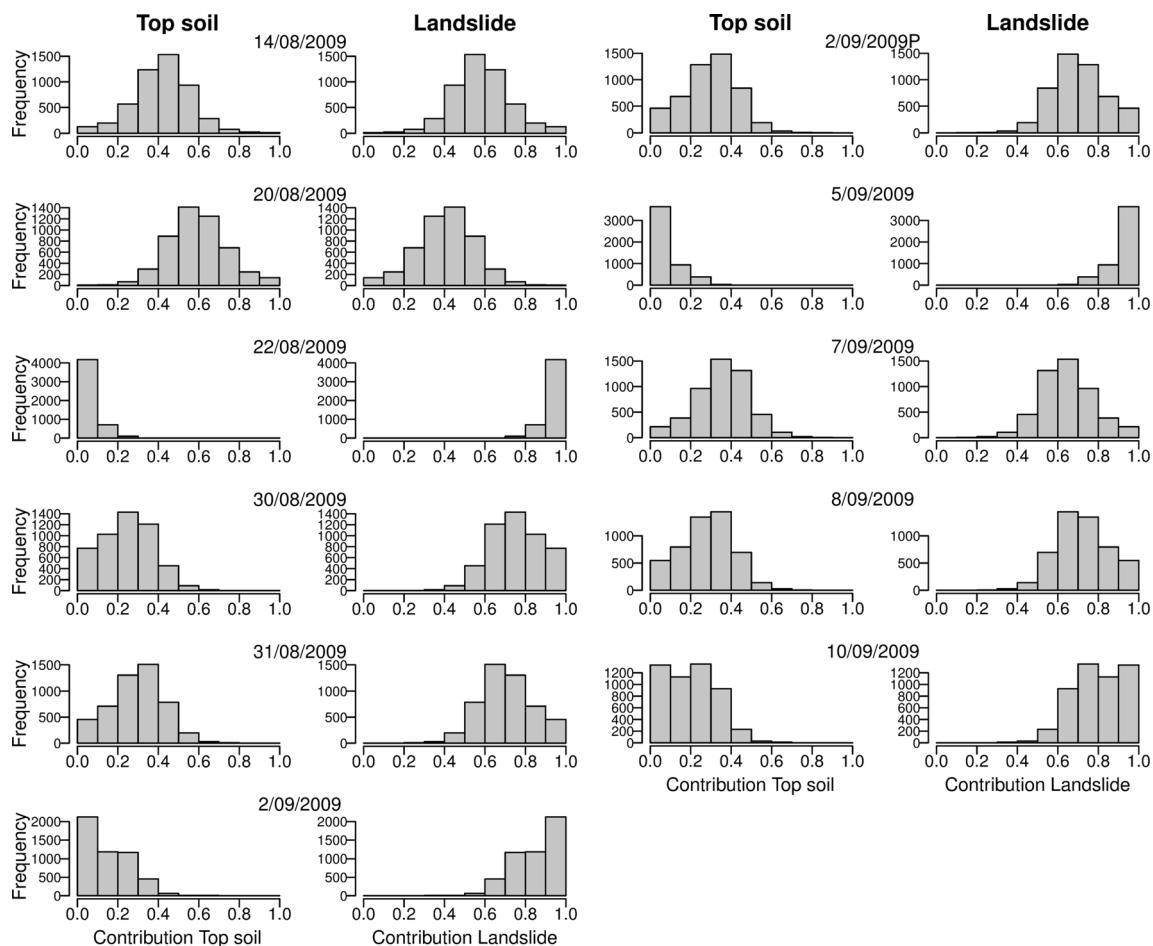


Fig. 7 Probability density functions for the predicted median contributions from each source type to sediment yield in the Unta catchment using the geochemical technique. Results are given for suspended sediment

samples collected on different dates. P in one day (02/09/2009) indicates sediment sample was taken during peak flow

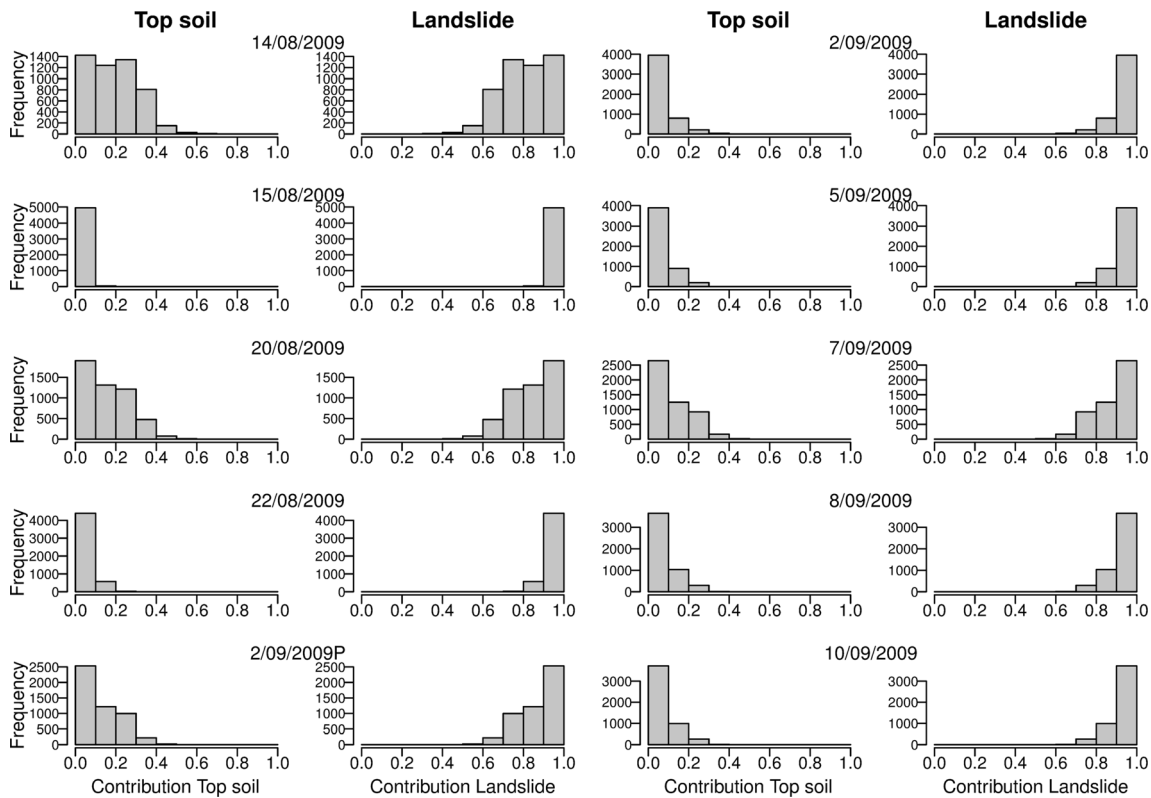


Fig. 8 Probability density functions for the predicted median contributions from each source type to sediment yield in the Desera catchment using the geochemical technique. Results are given for suspended

sediment samples collected on different dates. P in one day (02/09/2009) indicates sediment sample was taken during peak flow

season. These flows occur between the rain showers. In this period, no soil erosion on cropland or grassland occurs. The only sediment that reaches the river is landslide material,

which is directly connected to the river. Landslides can contribute to river sediment for a long time after the rain event, because the landslides are still active (Broothaerts et al. 2012).

Table 5 Stage height, sediment concentration and predicted topsoil contribution of the suspended sediment samples taken. Two samples were taken on 02/09/2009, and the record marked with ‘P’ after the date

indicates the sediment sample was taken during peak flow. Stage height readings were recorded at a bridge further downstream where the Unta and Desera Rivers have merged

Date (d/m/y)	Unta				Desera			
	Stage height (cm)	Sediment conc.(g/l)	Topsoil contribution (%)		Stage height (cm)	Sediment conc. (g/l)	Topsoil contribution (%)	
			Vis-NIR	Geochemical			Vis-NIR	Geochemical
14/08/09	85	4.59	54.9	41.7	85	4.63	70.0	18.4
15/08/09					52	4.89	43.	0.9
20/08/09	62	1.49	70.2	59.3	62	2.95	41.8	15.2
22/08/09	62	3.11	17.6	3.7	62	3.49	64.7	2.7
30/08/09	58	0.64	15.8	24.5				
31/08/09	60	0.70	33.8	29.2				
02/09/09	98	4.27	23.0	14.2	80	13.36	37.5	4.7
02/09/09P	80	5.52	48.5	29.4	98	49.39	49.9	11.4
05/09/09	70	2.91	22.2	6.1	70	2.09	19.8	4.8
07/09/09	64	0.74	32.2	35.5	64	0.74	44.1	10.6
08/09/09	65	2.31	53.9	27.8	65	4.04	43.8	5.7
10/09/09	80	5.17	44.0	19.8	80	4.06	44.0	5.4

At peak flows, more erosion of topsoils occurs. Most of the samples were taken directly after or during the rainfall event, mainly on the falling limb of the hydrograph. At these moments, a significant contribution from topsoils can be observed. The difference between the Unta and the Desera catchment is that in the Desera catchment the landslides contribute relatively more to the sediment load of the rivers (Broothaerts et al. 2012). The Unta and Desera Rivers are very responsive, because the catchments are small, and the topography is undulating. Therefore, the Unta and Desera Rivers are narrow and incised and all the sediment that erodes into the stream will be transported directly through the river system. No storage of fine sediment will take place in the riverbed. Further downstream, in the broader valleys, storage of fine sediments will take place.

4.2.4 Partial least squares modelling of geochemical fingerprints

The PLSR modelling based on the geochemical fingerprints of the source samples contains six components that explain 25.4 % of the variance. The value of the PRESS statistic was 0.778, the R^2_{adj} was 0.88 and the RMSEP was 0.156. The elements with the highest loadings on the first component are Al, Mn, Zn, Zr, N, ^{15}N , %C and $\delta^{13}\text{C}$ ‰. These high loadings correspond to the elements that passed the Kruskal-Wallis test in the mixing model. The first component explains 9.4 % of the variance. In the other components, elements that did not pass the Kruskal-Wallis test like Fe, Ti, V, Cr, Na and Ni have also a high loading. The model predicts a range of topsoil contributions for the Unta catchment of 14.7–67.9 % and 11.6–46.1 % for the Desera catchment. The correlation between both solutions of the mixing model and the PLS model for the geochemical fingerprints are 96.1 % for the Unta and 90.8 % for the Desera catchment. Overall, the PLSR model predicts somewhat higher contributions than the mixing model. The main difference is the higher amount of uncertainty for the PLSR model, which is 30.2 %.

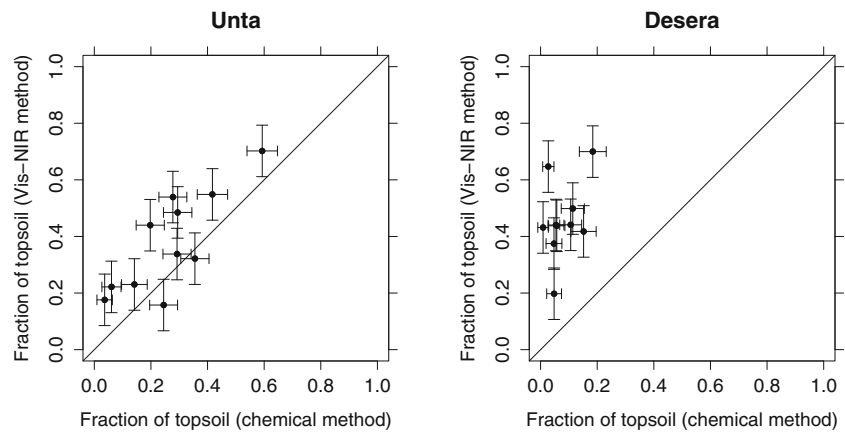
4.3 Comparison of the models

Figure 9 shows the correlation plots of the results from the two fingerprinting techniques used to assess sediment source ascription in the two catchments. The comparison is made for the PLS model based on reflectance readings using mixtures and for the mixing model based on geochemical analysis of the data. For the Unta catchment, a correlation coefficient of 0.80 between the two methods is obtained. This means that almost the same results have been achieved using Vis-NIR spectra of sediment samples as compared to the conventional technique. For the Desera catchment, the correlation coefficient is only 0.39.

The results achieved by the Vis-NIR method seem to overestimate the contributions of topsoil to sediment yield as compared to the conventional technique in both catchments. As a control, PLS modelling for landslide contributions to the suspended sediment showed that landslide contributions were underestimated compared to the geochemical technique (data not shown here); thus providing the same results. For the Desera catchment, the overall estimates of topsoil contributions are low (Fig. 9). The range of topsoil contributions using the geochemical method (0.01–0.18) is smaller compared to the Vis-NIR method (0.23–0.73). The mixing model of the geochemical technique constrains the contributions between 0 and 1 (Eq 2). This constraining of the data is needed, because otherwise no useful data would be calculated. Further constraining the contributions with a priori information may reduce uncertainty even more (Collins et al. 2010a), although this constraining can only be applied if a clear explanation of the basis for such constraints is given. If these constraints are to be applied with confidence, catchment-specific data have to be used. It could be that due to the constraining, the uncertainty of the solution is estimated as being lower. This constraining can have an influence on the estimation of the uncertainty of the sediment contribution if the contribution is close to 0 or 1. In the plot of the Desera catchment, the uncertainty ranges get smaller with lower topsoil contributions. Normally, in linear models, prediction uncertainty will be higher at the extreme values of the regression. Uncertainty of the PLS model is higher because the model was not constrained.

In order to know the influence of the statistical technique used, PLSR modelling for topsoil contributions was also performed on the geochemical data. Figure 10 shows the correlation plot when using the same statistical technique on the different data sets (geochemical and spectroscopic). Here, the comparison is made between the PLSR model based on reflectance readings using pure samples only and for the PLSR model based on geochemical fingerprints. For the Unta catchment, the correlation coefficient is 0.66 and for Desera it is 0.52. Overall, there is less overestimation for the Unta catchment, but in the Desera catchment the topsoil contribution is still overestimated relative to the PLS regression based on the spectroscopic data. The range of topsoil contributions is higher for the Desera catchment using a PLSR model with geochemical fingerprints (12–46 %) compared to the mixing model (1–18 %). Also, the two models used different weightings (i.e. correction factors) for all parameters. Note the high uncertainty (31 %) related to PLSR modelling for the geochemical data. The main reason for this is that in the calibration procedure only the data from the pure source samples were used. Here, the total variability of the source samples is used to calibrate the model. In the Monte Carlo approach (e.g. Motha et al. 2003; Collins et al. 2010b), the robust scale estimator (Q_n) is used to reflect the uncertainty of the source samples in calculating the

Fig. 9 Correlation between results from the geochemical method using a mixing model and the Vis-NIR method using mixtures in both catchments (Unta and Desera) used for fingerprinting. Bars indicate the uncertainty related to each technique



contribution. Q_n provides a lower range of values than the total variability. Also, if the PLSR model had been constrained, this would lead to a lower uncertainty value.

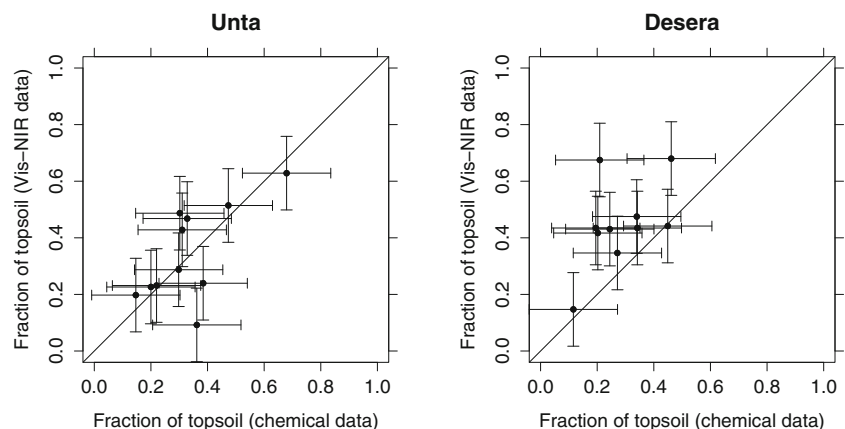
The mean spectrum of the suspended sediment samples for the Desera catchment (Fig. 2) has a higher albedo than that from the Unta catchment. In the visible region, they are positioned closer together than in the NIR region. The only small difference in the visible region can explain the agreements in percentage topsoil contribution from the two catchments, calculated with the Vis-NIR model. This is because a lot of weight is given to the loadings in the visible region of the spectrum of the first component of the PLSR (data not shown here). However, the conventional method shows a large difference between the two catchments. The value of mean %C in the suspended sediment is lower in the Desera (1.24 %) than in the Unta catchment (1.84 %). This can explain the lower topsoil contribution in the Desera catchment using the geochemical method. The difference in %C is not reflected in the reflectance measurements of the suspended sediment in both of the catchments, only a little in the NIR region of the spectrum. Validation of the fingerprinting results by erosion measurements can give information on which processes contribute the most sediment to a river. Using

different property sets to calculate sediment source ascription will probably always produce somewhat different results. Field observations revealed that a larger area in the Desera catchment is affected by landslides (Broothaerts et al. 2012), supporting the conventional analysis. These findings suggest that the Vis-NIR technique overestimated the contribution of topsoil erosion in the Desera catchment. However, a good agreement between the results for both methods in the Unta catchment was achieved. This suggests that Vis-NIR spectroscopy could be a good alternative technique to predict source type contributions of suspended sediment samples.

5 Conclusions

This study aimed to compare fingerprint procedures based on two different techniques: one using geochemical analysis of both source and sediment samples, and the other using spectroscopic (Vis-NIR) measurements of those samples. In comparing the spectral measurements with the conventional geochemical technique using a mixing model, a good agreement between both techniques was found in one of the study

Fig. 10 Correlation between results from the partial least squares regression (PLSR) model using the geochemical data and the Vis-NIR data only using pure samples for both catchments (Unta and Desera) used for fingerprinting. Bars indicate the uncertainty related to each technique



catchments. In the other catchment, there was little agreement, and the spectroscopic technique systematically overestimated the topsoil contribution. We found that Vis-NIR reflectance spectra exhibit linear additive behaviour, which is a requirement when using a PLSR model to estimate sediment source contributions.

Predictions of sediment source contributions based on the spectroscopic technique combined with PLSR had wider confidence intervals than predictions based on the geochemical technique with a mixing model (and Monte Carlo sampling to derive confidence intervals). But this difference in uncertainty was related to the difference in statistical technique used (PLS regression vs. mixing model), and not to the type of data it was based on (Vis-NIR spectra vs. geochemical data). When PLSR was used to estimate sediment source contributions from both types of data, the uncertainty was similar.

Fingerprinting procedures based on spectral reflectance signatures are attractive because of their simplicity in laboratory analysis. Moreover, the costs in both time and equipment compared with the geochemical fingerprinting approach are small. Therefore, it provides a good means of assessing suspended sediment source ascription in small river basins, and in particular for situations where many suspended sediment samples need to be analysed (i.e. when variations in sediment sources during rainfall events are to be examined). Our results confirm that fingerprinting based on Vis-NIR spectra offers great potential and the values obtained are comparable to more established techniques such as those based on geochemical fingerprints.

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