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# Using source-specific models to test the impact of sediment source classification on sediment fingerprinting

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## Abstract

Sediment fingerprinting estimates sediment source contributions directly from river sediment. Despite being fundamental to the interpretation of sediment fingerprinting results, the classification of sediment sources and its impact on the accuracy of source apportionment remain underinvestigated. This study assessed the impact of source classification on sediment fingerprinting based on diffuse reflectance infrared Fourier transform spectrometry (DRIFTS), using individual, source-specific partial least-squares regression (PLSR) models. The objectives were to (a) perform a model sensitivity analysis through systematically omitting sediment sources and (b) investigate how sediment source-group discrimination and the importance of the groups as actual sources relate to variations in results. Within the Aire catchment (United Kingdom), five sediment sources were classified and sampled ($n$ = 117): grassland topsoil in three lithological areas (limestone, millstone grit, and coal measures); riverbanks; and street dust. Experimental mixtures ($n$ = 54) of the sources were used to develop PLSR models between known quantities of a single source and DRIFTS spectra of the mixtures, which were applied to estimate source contributions from DRIFTS spectra of suspended ($n$ = 200) and bed ($n$ = 5) sediment samples. Dominant sediment sources were limestone topsoil (45 ± 12%) and street dust (43 ± 10%). Millstone and coals topsoil contributed on average 19 ± 13% and 14 ± 10%, and riverbanks 16 ± 18%. Due to the use of individual PLSR models, the sum of all contributions can deviate from 100%; thus, a model sensitivity analysis assessed the impact and accuracy of source classification. Omitting less important sources (e.g., coals topsoil) did not change the contributions of other sources, whereas omitting important, poorly-discriminated sources (e.g., riverbank) increased the contributions of all sources. In other words, variation in source classification substantially alters source apportionment depending on source discrimination and source importance. These results will guide development of procedures for evaluating the appropriate type and number of sediment sources in DRIFTS-PLSR sediment fingerprinting.

KEYWORDS

discrimination, DRIFTS, fine sediment, partial least-squares regression, sediment tracing, sensitivity analysis, source apportionment, source identification

## 1 | INTRODUCTION

Sediment occurs naturally in rivers across the world. Yet excessive sediment is damaging to the ecological and biochemical state of river systems and causes increased water treatment and infrastructural maintenance costs (Béjar, Gibbins, Vericat, & Batalla, 2017; Grove, Bilotta, Woockman, & Schwartz, 2015; Jones et al., 2012; Kemp, Sear, Collins, Naden, & Jones, 2011; Selbig, Bannerman, & Corsi, 2013; Taylor & Owens, 2009). Sediment in a river generally originates from the upstream channel and catchment through processes of soil erosion (Rickson, 2014); geomorphic processes (e.g., bank erosion and landslides; Vanmaercke, Ardizzone, Rossi, & Guzzetti, 2016); and other landscape disturbances (e.g., cattle trampling, vehicle combustion, road construction; Bilotta, Brazier, & Haygarth, 2007; Rossi et al., 2013; Vercruysse, Grabowski, & Rickson, 2017). Therefore, identification and quantification of the different "origins" of river sediment (i.e., sediment sources) are essential to improve scientific understanding of sediment transport processes (Fryirs & Brierley, 2013; Grabowski & Gurnell, 2016) and develop targeted sediment management solutions (Collins et al., 2017).

One approach to investigate sediment sources is sediment fingerprinting, which estimates sediment source contributions directly from the river sediment (Collins et al., 2017; Collins & Walling, 2004; Davis & Fox, 2009; Mukundan, Walling, Gellis, Slattery, & Radcliffe, 2012; Owens et al., 2016; Walling, 2013). Sediment fingerprinting requires classifying potential sediment sources within the catchment (based on attributes such as land cover and geology) and selecting source-specific sediment properties (i.e., the fingerprint) to develop statistical models that describe the relationship between sediment properties of river sediment and sediment source contributions (Davis & Fox, 2009; Walling, 2013).

Therefore, classification of potential sediment sources within the studied area is the foundation on which the statistical approach to sediment fingerprinting is based (Pulley, Foster, & Collins, 2017). The results of sediment fingerprinting are only useful if the sediment source classification is a good representation of the actual river sediment, that is, if all dominant sediment sources are correctly identified and included into the statistical modelling (Collins & Walling, 2004; Davis & Fox, 2009; Haddadchi, Ryder, Evrard, & Olley, 2013; Koiter, Owens, Petticrew, & Lobb, 2013). Yet although uncertainty in many aspects of the analytical process of sediment fingerprinting has been more explicitly quantified in recent research (Collins, Walling, Webb, & King, 2010; Cooper, Krueger, Hiscock, & Rawlins, 2014; Koiter et al., 2013; Laceby et al., 2017), for example, by using Bayesian uncertainty estimation frameworks (e.g. Cooper, Krueger, et al., 2014; Moore & Semmens, 2008; Nosrati, Govers, Semmens, & Ward, 2014) or Markov Chain Monte Carlo algorithms (e.g., Collins et al., 2010; Palazón, Gaspar, Latorre, Blake, & Navas, 2015; Wilkinson, Olley, Furuichi, Burton, & Kinsey-Henderson, 2015), important uncertainties remain concerning the impact of source classification on sediment fingerprinting results (Collins et al., 2017; Davis & Fox, 2009; Haddadchi et al., 2013; Laceby & Olley, 2015; Mukundan et al., 2012; Owens et al., 2016).

To this end, research has investigated the possibility of classifying potential sediment sources more objectively using cluster analysis to distinguish statistically significant source groups (Walling & Woodward, 1995; Walling, Woodward, & Nicholas, 1993); select source groups based on the similarity between source material and river sediment (Pulley, Foster, & Collins, 2017); and test the effect of multiple source-group configurations and different composite fingerprint properties (Pulley & Collins, 2018). However, this type of research is mainly focussed on traditional sediment fingerprinting techniques based on a single mass balance equation combining all classified sources (Carter, Owens, Walling, & Leeks, 2003; Collins & Walling, 2004; Walling & Woodward, 1995). Approaches based on a mass balance equation are constrained by the boundary condition that the sum of all source contributions must add up to 100%, even if there might be a source missing in the classification. Contrarily, sediment fingerprinting using individual, source-specific statistical models can theoretically be used to assess whether all important sediment sources are indeed identified (i.e., if all individually estimated source contributions sum up to approximately 100%). For example, experimental mixtures of sediment sources (i.e., mixtures of known quantities of the classified sources) can be used to calibrate source-specific regression models (i.e., regression between known quantities of a source in the mixtures and sediment properties of suspended sediment, SS), so that each regression model individually estimates the relative contribution (%) of one source. A sum of the estimated source contributions close to 100% can then be interpreted as an indication that all dominant sediment sources were correctly identified (Legout et al., 2013; Poulenard et al., 2009; Poulenard et al., 2012). However, different model uncertainties are associated with the regression models, so that it remains uncertain to what extent the deviation from 100% is caused by these model uncertainties or to the initial classification of sediment sources (i.e., whether a source might be missing or redundant).

To the authors' knowledge, no study has explicitly tested the impact of source classification on source apportionment using individual, source-specific regression models and thus tested the hypothesis that individual models produce representative source apportionments. Therefore, this study assesses the impact of source classification on sediment fingerprinting, based on diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) using individual, source-specific partial least-squares regression (PLSR) models. To this end, the specific objectives are to (a) perform a model sensitivity analysis by systematically omitting sediment sources from the classification and (b) investigate how sediment source-group discrimination and the importance of the groups as actual sources relate to variations in results.

## 2 | METHODS

### 2.1 | Study area

The study was applied to the River Aire catchment, upstream of the City of Leeds (United Kingdom). The River Aire has a total catchment area of 879 $km^2$ (690 $km^2$ upstream of Leeds), with a mean annual water discharge of 15 $m^3\ s^{-1}$ entering the city and a mean rainfall of 1,018 mm $year^{-1}$ (1961–2017). The geology of the catchment is

Carboniferous with the lower reaches defined by the coal measures (31%; siltstone, mudstone, and sandstone) and an area in the middle with millstone grit (46%; sandstone), and the higher part of the catchment is mainly characterised by limestone and shale formations (23%; British Geological Survey, 2016; Figure 1). The soils in the Aire catchment are predominantly poorly draining loamy and clayey soils. The upper part is characterised by raw oligo-fibrous peats and stagnohumic and stagnogley soils, and the lower and middle part by brown earths and pelo-stagnogley soils (Carter et al., 2003). Land cover in the catchment is predominantly grassland (59%) and urbanised area (25%), and the rest of the catchment is covered with moorland (12%) and scattered arable land (4%; Morton et al., 2011).

## 2.2 | Sediment data

### 2.2.1 | Sediment source classification and sampling

In a previous sediment fingerprinting study in the upper reaches of the River Aire, sediment sources were classified in two separate classifications: one based on land cover (arable land, grassland and woodland, and urban) and another based on geology (limestone, millstone grit, and coal measures; Carter et al., 2003). The study showed that the contribution of arable and woodland upstream of Leeds were negligible. Therefore, both classifications were merged into five potential sediment sources in this study: uncultivated grassland topsoil from the limestone and shale area ("limestone," L); millstone grit area ("millstone," M) and coal measures area ("coals," C); eroding riverbanks ("riverbank," R); and urban street dust ("urban," U; Figure 1).

Locations for source material sampling were identified based on accessibility and guided by areas most prone to erosion based on the revised universal soil loss equation (Renard, Foster, Weesies, & Porter, 1991). A total of 117 source samples were taken, which included three subsamples taken within 1 $m^2$ at each soil sampling location. Samples from grassland topsoils (21 locations × 3) and subsoil samples from eroding riverbanks (12 locations × 3) were collected using a nonmetallic trowel (Figure 1). For riverbank sampling, locations were selected with public access to the river, and only visibly eroding areas were sampled. For the topsoil samples, the surface (top 5 cm) of the topsoil was sampled to ensure that only the material likely to be eroded and transported to the river was collected (Carter et al., 2003; Cooper, Krueger, et al., 2014; Martínez-Carreras et al., 2010; Pulley, Foster, & Antunes, 2015). Street dust samples (18 samples) were collected along road drains using a dustpan and brush (or trowel when wet; Cooper, Krueger, et al., 2014; Pulley et al., 2015).

### 2.2.2 | Fine river sediment sampling

Between June 2015 and March 2017, SS samples ($n$ = 200) were collected with a depth-integrating SS sampler during individual precipitation events at a single location in the river within the city centre of Leeds (Figure 1). The median particle size of SS in the River Aire ranges between 5.2 and 13.3 μm (Carter, Walling, Owens, & Leeks, 2006; Walling et al., 2003). Additionally, to investigate the contribution of sediment sources to the fine, mobile sediment along

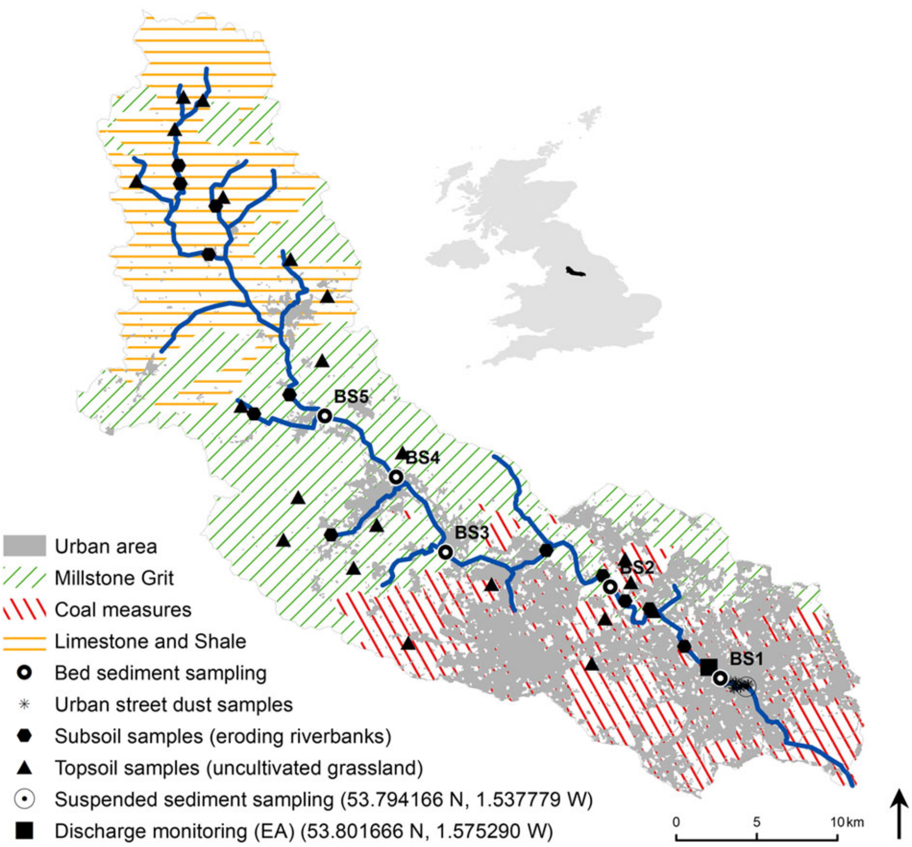


**FIGURE 1** Aire Catchment (United Kingdom; WWF, 2017), including locations for suspended sediment, channel bed sediment, and sediment source sampling (land cover data: LCM2007, Morton et al., 2011)

the profile of the river, five grab (i.e., bed sediment, BS) samples were taken by removing surficial fine sediment off the channel bed using a metal bucket that was scraped along the surface of the bed in the middle of the river (between June 16 and 18, 2016; Figure 1).

## 2.3 | Sediment fingerprinting

The sediment fingerprinting technique applied in this study is based on the approach developed by Poulenard et al. (2009), which uses DRIFTS to identify sediment source fingerprints. The approach consists of three steps: (a) analysis of sediment samples with DRIFTS; (b) sediment source discrimination; and (c) development of statistical regression models to estimate source contributions to the SS. Furthermore, an additional fourth step was added in this study to test the sensitivity of the regression models to source classification.

### 2.3.1 | DRIFTS analysis of sediment samples

BS and sediment source samples were wet sieved to retain the <63 μm fraction to reduce the effect of particle size variations on source attribution and spectral distortion (Laceby et al., 2017; Poulenard et al., 2009). All sediment and soil samples (SS, BS, and sources) were then filtered on quartz fibre filters and oven-dried for 2 hr at 105°C (Cooper, Krueger, et al., 2014; Pulley et al., 2015). The filters containing sediment were scanned with DRIFTS using a Bruker Vector 22 and a Perkin Elmer Spectrum Spotlight 200 spectrometer at a 4 $cm^{-1}$ resolution across the 4,000–400 $cm^{-1}$ spectrum with 32 co-added scans per spectrum. The data were processed using the software provided by the manufacturer of the spectrometers. A minimum of 20 mg of sediment was required on the filters to prevent interference from the filter substrate.

The average spectra of the three subsamples of the soil material were used for further analysis (Brosinsky, Foerster, Segl, & Kaufmann, 2014; Evrard et al., 2013; Poulenard et al., 2009; Poulenard et al., 2012). Preprocessing techniques were applied to the DRIFTS spectra to reduce additional noise. Mean-centring and filtering using a Savitzky–Golay algorithm were applied, as a combination of those techniques has been shown to improve results in similar studies (Cooper, Rawlins, Lézé, Krueger, & Hiscock, 2014; Martínez-Carreras et al., 2010). To avoid $CO_2$ interference in the area between 2,400 and 2,300 $cm^{-1}$, only the ranges 3,800–2,400 $cm^{-1}$ and 2,300–650 $cm^{-1}$ were used for further statistical analysis (Poulenard et al., 2009).

### 2.3.2 | Sediment source discrimination

A general step in sediment fingerprinting is to compare the sediment characteristics of the source material with the river sediment to test whether sources can be discriminated between each other and the river sediment and whether the sediment properties behave conservatively (Collins et al., 2017). Poulenard et al. (2012) tested the conservative behaviour of DRIFTS properties by placing microporous bags with source material in the river and found that the properties did not change significantly after 2 weeks. Conservatism was not further tested, but source material and river sediment were compared through visual inspection of the DRIFTS spectra. Furthermore, a discriminant analysis (DA) was performed on the source material.

#### Visual interpretation

The DRIFTS spectra were examined visually to assess any major differences between the source samples as a geochemical indication for discrimination. DRIFTS spectra of soils are controlled by the differential reflectance and absorbance characteristics of sediment properties and especially characterised by absorption peaks caused by inorganic fractions such as clays, silica, and carbonates in combination with organic matter (Reeves III, 2012). Due to spectral distortions and overlapping of absorption peaks, DRIFTS spectra cannot be used to directly quantify the sediment composition without calibration with quantitative reference. Therefore, inspection of the spectra was done to provide semiquantitative information on differences in sediment composition between sediment sources (Poulenard et al., 2012; Reeves III, 2010). If calibration would be performed, source variability ratios can be calculated to quantify the differences between property concentrations between source groups (Pulley et al., 2015).

#### Discriminant analysis

Statistical techniques were then applied to test whether the source samples can be statistically discriminated based on their respective DRIFTS spectra. First, a principal component analysis (PCA) was performed on the preprocessed DRIFTS spectra. Second, a DA based on Mahalanobis distances was performed using the PCA scores as input data (Poulenard et al., 2009; Stevens & Lopez, 2015). Mahalanobis distances are expressed in standard deviations and therefore provide a statistical measure to assess whether the DRIFTS spectra of source samples are significantly different from each other. Based on the results of the DA, sediment sources with sufficient discriminatory power based on their respective DRIFTS spectra are retained for analysis.

### 2.3.3 | Unmixing model development

To estimate sediment source contributions directly from the DRIFTS spectra of SS and BS samples, statistical unmixing models were calibrated with experimental mixtures. A total of 54 experimental mixtures were prepared containing variable, known quantities of soil from the sediment sources (Table 1). To do this, a reference sample of each of the sources was created by mixing equal quantities of all individual source samples, which was then used to create mixtures containing different sources. The design of experimental mixtures results in a multivariate regression problem between the (preprocessed) DRIFTS spectra ($X$ predictors) of the experimental mixtures and the weight contributions of the sediment sources (dependent $Y$ variables). Spectral data are highly correlated and noisy, containing much more variables than samples; hence, a simple multivariate regression is not suitable. Therefore, PLSR was used because it is better able to handle this type of data (Karaman et al., 2013; Martens & Martens, 2000; Wold, Sjostrom, & Eriksson, 2001).

Five separate PLSR models were developed (i.e., one for each source): $PLSR_L$ (limestone), $PLSR_M$ (millstone), $PLSR_C$ (coals), $PLSR_R$ (riverbank), and $PLSR_U$ (urban street dust; Figure 2a). PLSR works by maximising the covariance between two datasets based on the respective scores (Stevens & Lopez, 2015). X-scores (***U***) are computed as linear combinations of the original X variables with a set of weights

**TABLE 1** Set of experimental mixtures for PLSR-model calibration

| | Topsoil | | | | |
|---|---|---|---|---|---|
| | Limestone | Millstone | Coals | Riverbank | Street dust |
| Mix1 | 25% | 25% | 25% | 25% | |
| Mix2 | 25% | 25% | 25% | | 25% |
| Mix3 | 33% | 33% | 33% | | |
| Mix4 | 10% | 20% | 40% | 30% | |
| Mix5 | 40% | 10% | 20% | 30% | |
| Mix6 | 20% | 40% | 25% | | 15% |
| Mix7 | 10% | 40% | 20% | | 30% |
| Mix8 | 40% | 10% | 20% | | 30% |
| Mix9 | 20% | 40% | 25% | | 15% |
| Mix10 | 25% | 25% | | 25% | 25% |
| Mix11 | | 25% | 25% | 25% | 25% |
| Mix12 | 25% | | 25% | 25% | 25% |
| Mix13 | 20% | 30% | | 30% | 20% |
| Mix14 | | 20% | 30% | 30% | 20% |
| Mix15 | | 60% | | 20% | 20% |
| Mix16 | | 30% | 30% | 40% | |
| Mix17 | 50% | 25% | | 25% | |
| Mix18 | 20% | 20% | | | 60% |
| Mix19 | | 20% | 40% | 40% | |
| Mix20 | | 40% | 50% | | 10% |
| Mix21 | | 80% | 20% | | |
| Mix22 | 80% | 20% | | | |
| Mix23 | 10% | 90% | | | |
| Mix24 | | 10% | 90% | | |
| Mix25 | | | | 75% | 25% |
| Mix26 | | | | 25% | 75% |
| Mix27 | 100% | | | | |
| Mix28 | 10% | | | 50% | 40% |
| Mix29 | 80% | | | 15% | 5% |
| Mix30 | 60% | | | 10% | 30% |
| Mix31 | 10% | | | 90% | |
| Mix32 | 90% | | | 10% | |
| Mix33 | 10% | | | | 90% |
| Mix34 | 90% | | | | 10% |
| Mix35 | | 100% | | | |
| Mix36 | | 10% | | 50% | 40% |
| Mix37 | | 85% | | 15% | |
| Mix38 | | 60% | | 15% | 25% |
| Mix39 | | 10% | | 90% | |
| Mix40 | | 90% | | 10% | |
| Mix41 | | 10% | | | 90% |
| Mix42 | | 90% | | | 10% |
| Mix43 | | 100% | | | |
| Mix44 | | 50% | | 40% | 10% |
| Mix45 | | 80% | | 10% | 10% |
| Mix46 | | 30% | | 40% | 30% |
| Mix47 | | | 100% | | |
| Mix48 | | | 10% | 50% | 40% |
| Mix49 | | | 80% | 10% | 10% |
| Mix50 | | | 60% | 10% | 30% |

(Continues)

**TABLE 1** (Continued)

| | Topsoil | | | | |
|---|---|---|---|---|---|
| | Limestone | Millstone | Coals | Riverbank | Street dust |
| Mix51 | | | 10% | 90% | |
| Mix52 | | | 90% | 10% | |
| Mix53 | | | 10% | | 90% |
| Mix54 | | | 90% | | |

*Note*. PLSR: partial least squares regression.

***W*** so that ***X*** can be expressed in terms of scores, loadings, and residuals. The Y dataset is also decomposed in scores (***T***) and loadings (***F***), but in such a way that the covariance between the X-scores ***U*** and the Y-scores ***T*** is maximised. As a result, X-scores can serve as good predictors of Y, so that a multivariate regression can be approached with **W** * **F** as regression coefficients (Wold et al., 2001).

The mixture dataset was divided into two parts: 75% for calibration and 25% for validation. To randomly select the calibration set, a Kennard–Stone sampling algorithm was used (Poulenard et al., 2009). To avoid underfitting or overfitting of the model, the best compromise between the description of the calibration set and the model predictive power was determined by identifying the appropriate number of PLSR components based on leave-one-out cross validation in the calibration phase (Evrard et al., 2013; Poulenard et al., 2009; Poulenard et al., 2012; Wold et al., 2001). The optimal number of components is the number with the lowest root mean squared error (RMSE) of cross validation (Martens & Martens, 2000; Poulenard et al., 2009; Wold et al., 2001). Standard errors of prediction (RMSEP) associated with the model estimates were calculated and expressed as 95% confidence intervals (CIs; Legout et al., 2013; Martínez-Carreras, Krein, et al., 2010; Poulenard et al., 2012).

### 2.3.4 | Model sensitivity to source classification

The model RMSEP can be considered as an estimate of the final uncertainty on the model output if measurement errors and the intrasource variability of the DRIFTS spectra are minimal. However, as stated in the introduction, this is only valid when the experimental mixtures are a good representation of the actual river sediment samples (Collins & Walling, 2004; Davis & Fox, 2009; Haddadchi et al., 2013; Koiter et al., 2013; Pulley, Foster, & Collins, 2017).

The contributions estimated with the individual, source-specific PLSR models can be totalled: ( $(L\% + M\% + C\% + R\% + U\%) \pm \sqrt{(CI_L)^2 + (CI_M)^2 + (CI_C)^2 + (CI_R)^2 + (CI_U)^2}$). In theory, a sum of 100% should indicate that all dominant sources were identified. Yet due to the propagated uncertainty associated with the individual PLSR models, it is impossible to use this sum to confirm this hypothesis. Therefore, to test the impact of the sediment source classification on the final model estimates, sets of PLSR “test-models” were developed, whereby individual sources were systematically omitted from the classification (i.e., mixtures containing a certain source were omitted from model calibration; Table 2, Figure 2b). Subsequently, the outputs of the “reference PLSR models” (i.e., models where all sources are included in classification) were compared with the outputs of the PLSR test models by calculating the average RMSE between

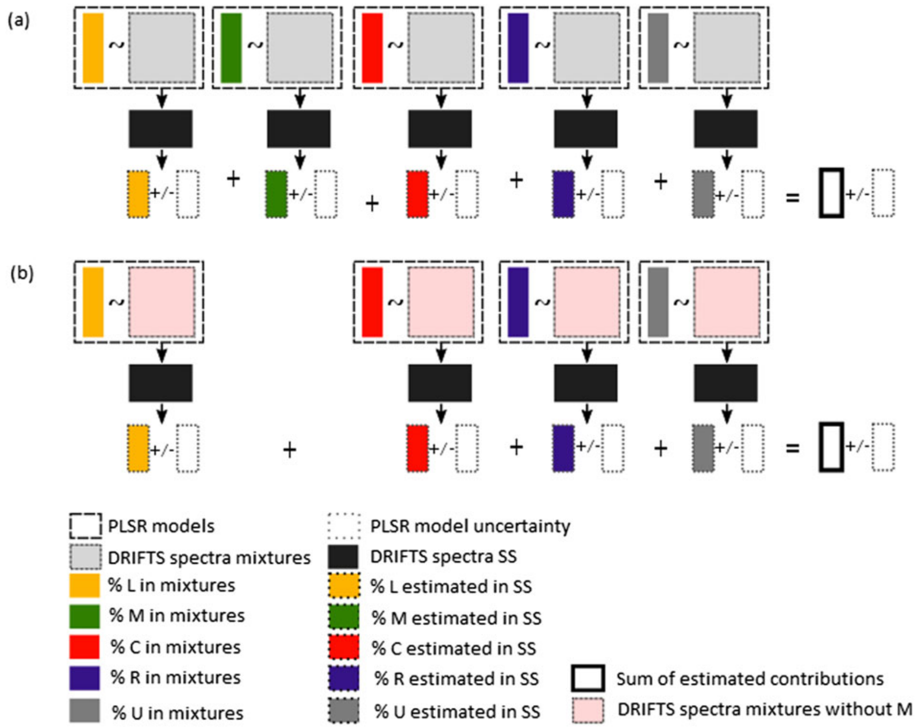


**FIGURE 2** Illustration of partial least squares regression (PLSR) model development and application: (a) five individual, source-specific PLSR models are calibrated between the diffuse reflectance infrared Fourier transform spectrometry (DRIFTS) spectra of the experimental mixtures and the corresponding known quantities of a single source in the mixtures. The PLSR models are then applied to the DRIFTS spectra of the suspended sediment (SS) to estimate its source contributions. Estimated source contributions are each characterised by a different PLSR model uncertainty. (b) Example of partial model test, whereby one source (here M) is omitted as a source (i.e., experimental mixtures containing M are removed)

**TABLE 2** PLSR models

| Model set | Source omitted | *n* mixtures | PLSR models developed |
|---|---|---|---|
| Reference | / | 54 | $PLSR_L$, $PLSR_M$, $PLSR_C$, $PLSR_R$, $PLSR_U$ |
| NL | Limestone | 24 | $PLSR_M$, $PLSR_C$, $PLSR_R$, $PLSR_U$ |
| NM | Millstone | 35 | $PLSR_L$, $PLSR_C$, $PLSR_R$, $PLSR_U$ |
| NC | Coals | 29 | $PLSR_L$, $PLSR_M$, $PLSR_R$, $PLSR_U$ |
| NR | Riverbank | 21 | $PLSR_L$, $PLSR_M$, $PLSR_C$, $PLSR_U$ |
| NU | Urban | 31 | $PLSR_L$, $PLSR_M$, $PLSR_C$, $PLSR_R$ |

*Note*. Reference: all sources included in classification; NC: coals excluded; NL: limestone excluded; NM: millstone excluded; NR: riverbank excluded; NU: urban excluded; PLSR: partial least squares regression; /: reference model set, no sources omitted.

both: $RMSE = \sqrt{\sum_{i=1}^{n}(X_{Refi} - X_{NYi})^2/n}$, with $X_{Refi}$ the contribution of source X with the reference model, $X_{NYi}$ the contribution of source X with the model without source Y, *i* the observation, and *n* the amount of observations.

## 3 | RESULTS

### 3.1 | Sediment source discrimination

#### 3.1.1 | Visual interpretation

Based on the DRIFTS spectra of the sediment source samples, 17 characteristic absorption peaks were identified that are typical for soil samples (Figure 3; Tiecher et al., 2016). The 3,695 and 3,620 cm$^{-1}$ peaks are characteristic for aluminosilicates (kaolinite and micas), which are typically present in clays (Parikh, Goyne, Margenot, Mukome, & Calderón, 2014; Poulenard et al., 2012; Tiecher et al., 2016; Yang & Mouazen, 2012). The peaks around 2,920 and 2,850 cm$^{-1}$ are generally attributed to organic matter (Poulenard et al., 2009; Reeves III, 2012; Tiecher et al., 2016), whereas the peak at 2,505 cm$^{-1}$ is attributed to carbonates (inorganic carbon; Poulenard et al., 2012; Reeves III, Mccarty, & Reeves, 2001; Viscarra Rossel et al., 2016). The 1,990; 1,870; and 1,785 cm$^{-1}$ peaks are generally related to quartz (Qz), and 1,630 cm$^{-1}$ to Qz and clay minerals. The peaks around 1,530 and 1,360 cm$^{-1}$ are attributed to Qz and organic matter, whereas 1,160 cm$^{-1}$ relates to clay minerals and organic matter (Tiecher et al., 2016). Finally, the 1,115 to 698 cm$^{-1}$ peaks are attributed to the combination of clay minerals and Qz (Ge, Thomasson, & Morgan, 2014; Parikh et al., 2014; Reeves III, 2012; Viscarra Rossel, Walvoort, McBratney, Janik, & Skjemstad, 2006).

In general, the spectra of SS and BS are comparable with the spectra of the source material and the experimental mixtures, especially for wavelengths >2,000 cm$^{-1}$. The spectra of BS had a more pronounced trough at 1,020 cm$^{-1}$ compared with the SS, and the peak at 1,160 cm$^{-1}$ (clay + OM) in the spectra of SS and BS is not as pronounced in the spectra of the source material. Furthermore, the grassland and riverbank sources appeared to have a higher clay content compared with urban street dust, whereas urban street dust had a relatively higher OM and Qz content (Figure 3b,c). The urban street dust also appeared to be enriched in Qz and inorganic carbon. Topsoil from the coals area had the highest clay content and relatively

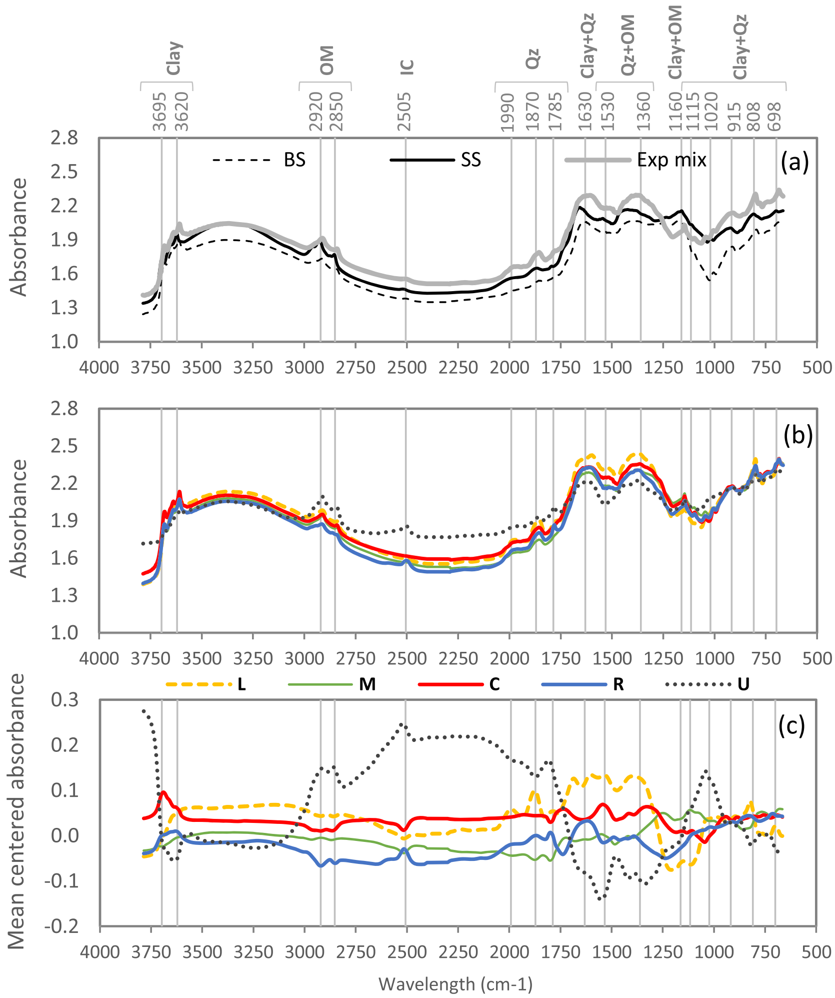


**FIGURE 3** Mean diffuse reflectance infrared Fourier transform spectrometry spectra of (a) suspended sediment (SS), bed sediment (BS), and experimental mixtures (Exp. mix); (b) unprocessed and (c) preprocessed (i.e., smoothened and mean centred) sediment source samples. Vertical lines represent absorption peaks ascribed to clay minerals, organic matter (OM), inorganic carbon (IC), and quartz (Qz)

high Qz peaks, whereas topsoil from the millstone area appeared to be characterised by the lowest clay content.

### 3.1.2 | Discriminant analysis

The (preprocessed) DRIFTS spectra (Figure 3c) were used as input for the PCA. The results of the PCA indicated that nine components describe 99% of the variation in the data. Therefore, the first nine components were retained for the DA. Most samples were consistently closer (standard deviations <3) to the mean of their own group compared with the other group (Figure 4). Urban street dust samples are most strongly discriminated from the other sources (standard deviations up to 40), whereas the samples from riverbanks were less strongly defined by their DRIFTS spectra (i.e., high intrasource variability). Despite the relatively weak discriminative power of riverbank sources, it was decided to take into account all classes as potential sediment sources to evaluate the effect of the discriminative power on the final sediment source estimates.

## 3.2 | Sediment unmixing

Five reference PLSR models were developed to estimate sediment contributions from each source (i.e., all mixtures in Table 1 were used for model calibration). Model calibration indicated that eight components minimises the RMSE in all models and thus is the optimal number of components. The PLSR models had a RMSEP ranging between 4% and 6%, with exception of the riverbank model (9%), resulting in 95% CIs between ±10% and ± 18% (Table 3). The PLSR models were applied on the DRIFTS spectra of the SS to estimate average sediment source contributions. During the sampled period, the dominant fine sediment sources in the River Aire appeared to be topsoil from the limestone area (45 ± 12%) and urban street dust (43 ± 10%). Topsoil from the millstone and coals area contributed on average 19 ± 13% and 14 ± 10%, respectively, and eroding riverbanks 16 ± 18% (Figure 5).

The mean sum of the source contributions estimated based on the individual, reference PLSR models is 137 ± 28% ($(45+43+19+14+16) \pm \sqrt{(12)^2+(10)^2+(13)^2+(10)^2+(18)^2}$). It is therefore impossible to make conclusions about the validity of the source classification and whether all actual sediment sources are correctly represented by the source groups (i.e., the sum is as close to 100% as it is to 170%). The effect of source classification on source apportionment is further examined in the next section.

## 3.3 | Model sensitivity to source classification

To test how the models vary when omitting specific sediment sources, PLSR test models were developed and again applied on the SS samples (Figure 5). With the test models without coals (NC in Figure 5), the sediment source contributions were very similar to the reference model

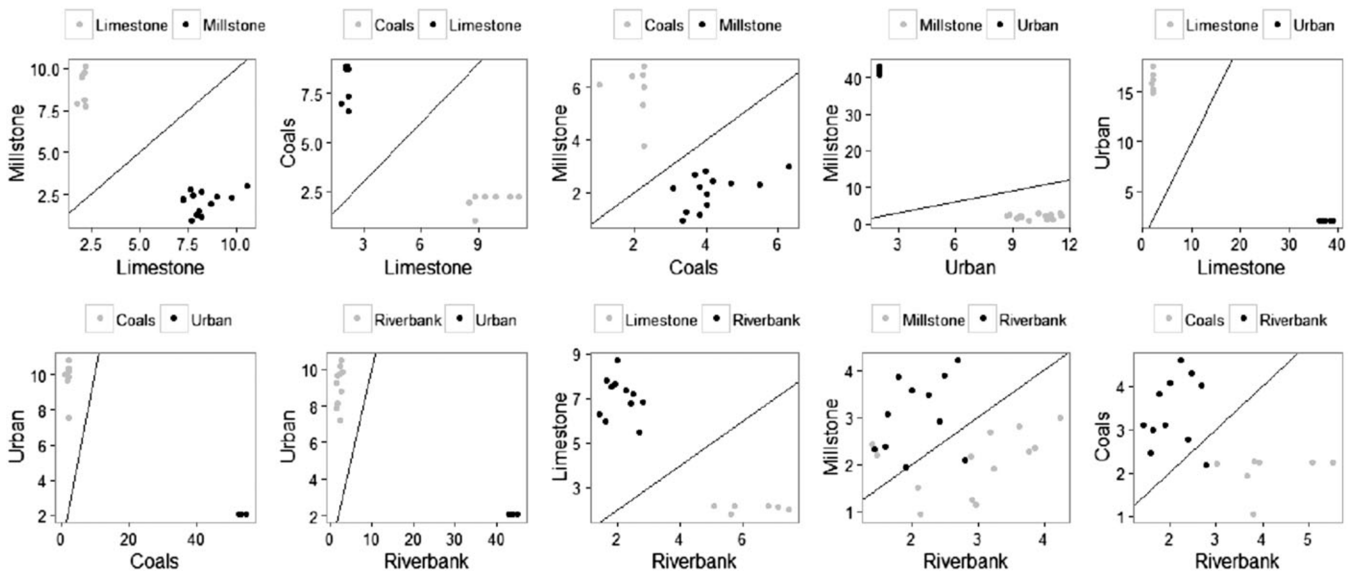


**FIGURE 4** Pairwise comparison of Mahalanobis distances between sediment source classes

**TABLE 3** Reference PLSR model statistics (i.e., all sources are included)

| Model | $R^2$ | RMSEC | RMSEP | 95% CI | Explained variance |
|---|---|---|---|---|---|
| PLSR$_{\mathrm{L}}$ | 0.884 | 0.053 | 0.059 | ±12 | 99.09 |
| PLSR$_{\mathrm{M}}$ | 0.877 | 0.148 | 0.065 | ±13 | 93.78 |
| PLSR$_{\mathrm{C}}$ | 0.929 | 0.151 | 0.053 | ±10 | 85.57 |
| PLSR$_{\mathrm{R}}$ | 0.790 | 0.156 | 0.092 | ±18 | 88.92 |
| PLSR$_{\mathrm{U}}$ | 0.772 | 0.091 | 0.045 | ±10 | 96.19 |

*Note*. CI: confidence interval; PLSR: partial least squares regression.

estimations, whereby limestone and urban street dust are the dominant sediment sources. Contrarily, when limestone (NL), millstone (NM), or urban (NU) were excluded as sources, the riverbank contributions became very high (80% to 180%), and when riverbank was excluded as a source, most of the sediment was attributed to millstone (140%). Furthermore, the sum of the average contributions per model set varied between 108% (NC) and 233% (NL). Based on these numbers, it is difficult, if not impossible, to evaluate how well the source classification accurately represents the actual sediment sources.

The variation in the source estimates between model sets was further quantified by calculating the RMSE between the estimations of the reference models and the test models (Table 4). Source contributions from the coals area varied the least between model sets (14% on average), whereas estimations for riverbank contributions varied considerably (up to 155%). Furthermore, when coals was removed as a source (NC), the deviations from the reference models

**TABLE 4** RMSE between source estimates of the reference and test models

| | | RMSE between | | | | |
|---|---|---|---|---|---|---|
| Model | Contribution | Ref-NL | Ref-NM | Ref-NC | Ref-NU | Ref-NR |
| PLSR$_{\mathrm{L}}$ | Limestone | / | 28% | 15% | 29% | 32% |
| PLSR$_{\mathrm{M}}$ | Millstone | 15% | / | 11% | 11% | 112% |
| PLSR$_{\mathrm{C}}$ | Coals | 11% | 9% | / | 10% | 25% |
| PLSR$_{\mathrm{U}}$ | Urban | 22% | 37% | 5% | / | 36% |
| PLSR$_{\mathrm{R}}$ | Riverbank | 155% | 74% | 17% | 133% | / |

*Note*. Reference: all sources included in classification; NC: coals excluded; NL: limestone excluded; NM: millstone excluded; NR: riverbank excluded; NU: urban excluded; /: no data.

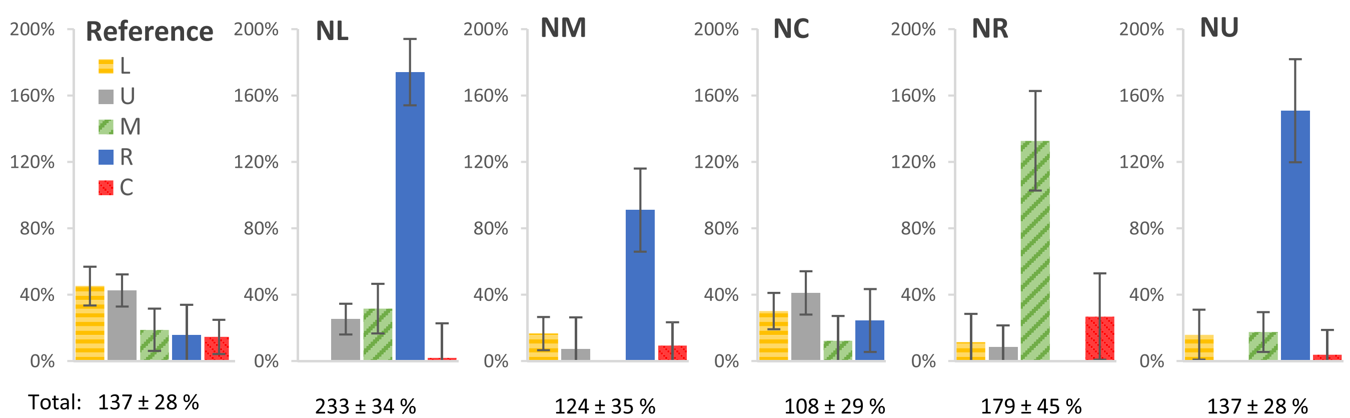


**FIGURE 5** Average source contributions to the suspended sediment in the River Aire based on different model calibrations (Reference: all sources included in classification; NC: coals excluded; NL: limestone excluded; NM: millstone excluded; NR: riverbank excluded; NU: urban excluded)

were within the CIs associated to the reference models (Table 3). However, when other sources were removed, the effect was more pronounced: removing limestone and urban (NL and NU) most strongly influenced the riverbank contribution (155% and 133%, respectively), whereas removing millstone (NM) both influenced the urban (37%) and riverbank (74%) contribution. Finally, when riverbank was removed as a source (NR), the estimated millstone contribution changed most significantly (112%).

The above observations are also illustrated with two examples (Figure 6). First, based on the reference model (i.e., all sources included in classification), there was no coals contribution to the BS (Figure 6a). Given that the first three locations of BS samples (BS5 to 3) are located in the millstone area, no contribution of the coals area is indeed expected. However, with the test models, high coals contributions (up to 80%) were estimated even where it was geographically not possible (Figure 6a). Furthermore, when coals was removed as a source (NC), the other source contributions did not change significantly compared with the reference model, while removing riverbank (NR) had a pronounced effect on the millstone contribution.

Second, similar observations were made for the estimated SS source contributions during an individual high-flow event in September 2016 (Figure 6b): coals appeared to be an important sediment source during the peak in Suspended Sediment Concentration (SSC), but when coals was removed as a source, the other source contributions remain relatively constant compared with the reference model. Furthermore, millstone became more important when riverbank was removed as a source, whereas the riverbank contributions increased with removal of limestone.

## 4 | DISCUSSION

Individual, source-specific regression models (based on PLSR) were developed to estimate sediment source contributions to SS and BS samples from the River Aire. The dominant sediment sources were topsoil from the limestone area (45 ± 12%) and urban street dust (43 ± 10%). Topsoil from the millstone and coals area contributed on average 19 ± 13% and 14 ± 10%, respectively, and eroding riverbanks 16 ± 18%.

The estimated sediment source contributions generally correspond well with field evidence and a previous sediment fingerprinting study in the River Aire catchment (Carter et al., 2003). The dominant contribution from the limestone area reflects the steeper topography and connectivity of this area to the river system compared with the scattered, less connected patches of topsoil in the coals area (Figure 1). The high urban street dust contributions to the SS and downstream BS (BS1, Figures 1 and 6) and the lower riverbank contributions reflect the urban environment of the sampling locations.

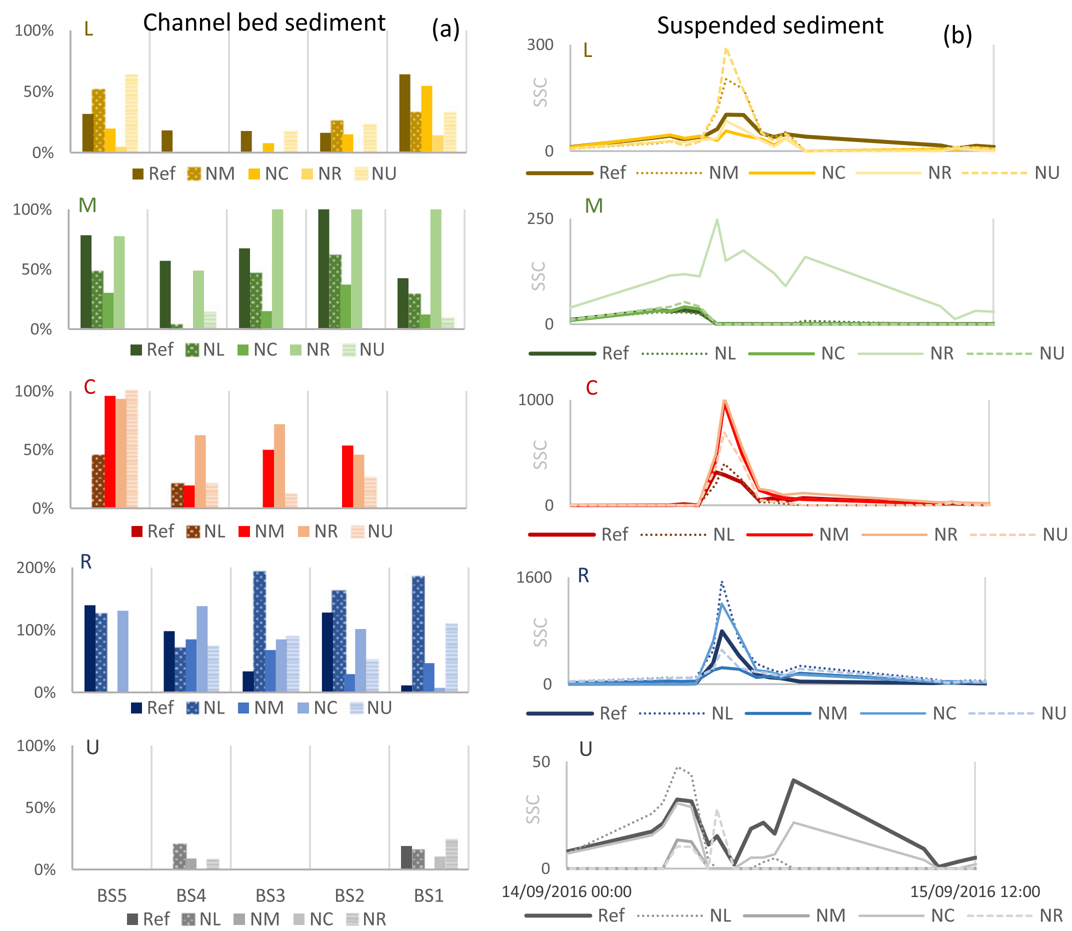


**FIGURE 6** Examples of sediment source contributions estimated by different model sets for (a) bed sediment samples and (b) suspended sediment (SSC, mg $L^{-1}$) during a high-flow event in September 2016 (reference: all sources included in classification; NC: coals excluded; NL: limestone excluded; NM: millstone excluded; NR: riverbank excluded; NU: urban excluded)

Furthermore, model testing showed that when sources are omitted, the sum of source contributions does not provide a clear indication about the representativeness of the source groups as actual sediment sources (i.e., sum does not decrease to less than 100% when a source is omitted). In what follows, the geochemical basis for discrimination between source classes is discussed further to evaluate how the combination of source group discrimination and their importance as actual sediment sources affects model outputs and uncertainties.

## 4.1 | Sediment source discrimination

The sediment sources are not equally well discriminated from each other, which has implications for developing regression models that are statistically comparable. Riverbank sources are the least well discriminated of all sources, whereas urban street dust is most strongly discriminated (Figure 4; Table 3). This variability in discrimination can be linked back to the primary origin of the source material (Koiter et al., 2013).

First, urban street dust is the best defined class because of its distinctly different sediment composition (Figure 4), which is in line with previous observations that street dust is characterised by the least within-source variability and highest discrimination based on geochemistry (Pulley et al., 2015). The mean DRIFTS spectrum of street dust suggests that street dust samples were depleted in clay minerals and enriched in OM and quartz, which reflects the primary origin of street dust as a mixture of particles from urban run-off, sewage and atmospheric deposition, and soils and sand from construction works (Franz, Makeschin, Weiß, & Lorz, 2014; Shilton et al., 2005; Taylor & Owens, 2009).

Second, the grassland samples are also generally characterised by a low intrasource variability, making them relatively well-defined classes (Figure 4). The difference between the grassland sources is mainly defined by the parent mineral material of the lithological areas. Grassland topsoil from the limestone area was defined by a combination of peak areas corresponding to clay, OM, carbonates, and quartz (Figure 3), which is linked to the limestone (carbonates) and shale (quartz) bed rock of the area (British Geological Survey, 2016). Topsoil from the coals area had the highest clay content and was mainly defined by quartz peaks, which is also in agreement with the main lithology (mixture of siltstone, mudstone, and sandstone; British Geological Survey, 2016). Contrarily, topsoil from the millstone area (sandstone) appeared to be characterised by the lowest clay content of the topsoils and an average mineral content compared to the other sources (Figure 3).

Finally, the within-source variability of riverbank samples was higher compared with the other sources, and the discrimination from especially millstone and coals samples was less pronounced (Figure 4). This observation is in agreement with the fact that riverbank material generally represents a mixture of floodplain deposits consisting of various primary sediment sources (Vale, Fuller, Procter, Basher, & Smith, 2016), so that its discrimination from topsoil sources is strongly influenced by different degrees of weathering since deposition (Pulley et al., 2015; Vale et al., 2016). These findings illustrate the challenge of including riverbank material as a separate source using DRIFTS. In further research, it would potentially be useful to combine DRIFTS with other techniques (e.g., 137C; Omengo, Alleman, Geeraert, Bouillon, & Govers, 2016; Smith & Blake, 2014) to further test the importance of riverbank material as an actual sediment source.

## 4.2 | Sediment source importance

The findings suggest that the degree of discrimination between the source classes, in combination with the importance of the source classes as actual sediment sources, determines the sensitivity of the model to the exclusion of a particular source. These observations are synthesised in five scenarios (Figure 7):

1. All a priori classified sediment sources are included in the classification (reference).
2. An important, well-discriminated sediment source is omitted from classification.

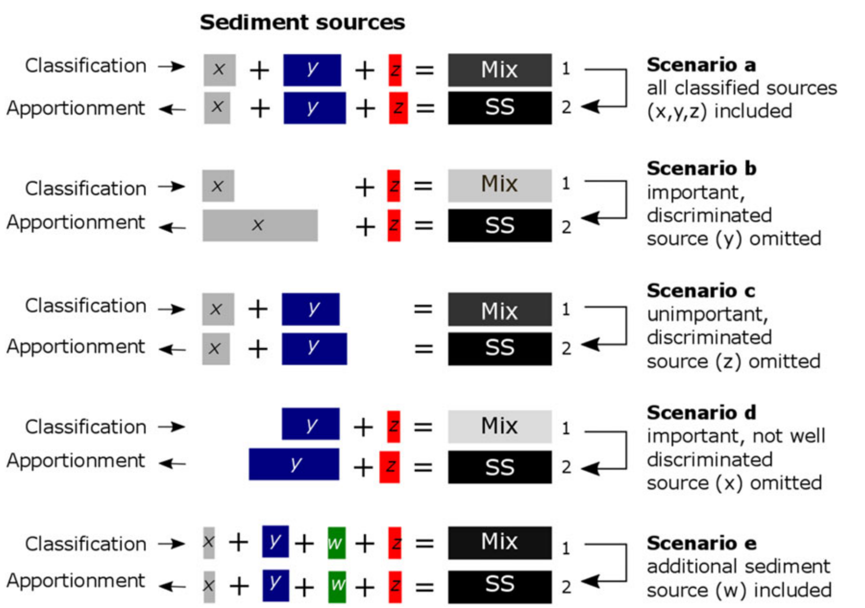


**FIGURE 7** Scenario's in sediment source classification: (1) calibration of partial least squares regression models with experimental mixtures of a set of classified sources and (2) application of the models on a suspended sediment (SS) sample to estimate sediment source contributions

3. An unimportant, well-discriminated sediment source is omitted from classification.
4. An important, poorly discriminated sediment source is omitted from classification.
5. An additional sediment source was added to classification.

The first scenario (1) represents the reference model set in this study where all classified sources are included in the model calibration. It is assumed that all important sediment sources were identified and thus that the mixtures used to calibrate the models are a close representation of the SS. Therefore, omission of a dominant, well-defined sediment source has a pronounced impact on the apportionment of other sources (Scenario 2). For example, limestone-grassland and urban street dust are well-discriminated and also dominant sources to the SS (Figure 5). Removing these sources results in mixtures that are not comparable with the SS, so that part of the SS remains unclassified. Consequently, when applying this model to the actual SS, a higher contribution is attributed to the least well-discriminated source (i.e., riverbank) to compensate for the unclassified part.

Contrarily, when a well-discriminated, though unimportant, source is omitted from the classification, the mixture does not differ substantially from the SS (Scenario 3). For example, when topsoil from the coals area is excluded as a source, the estimated contributions of the other sources do not change significantly compared with the reference estimations. The apparent insensitivity of the models to the exclusion of coals as a source suggests that topsoil from the coals area may not be a significant sediment source. In other words, without coals as a source, there is little of the SS sample that remains unidentified and is being attributed to other sources. This corresponds well to what would be expected based on land use in the Aire catchment. The amount of grassland in the coal area upstream of the point of SS sampling is limited; most of the area is strongly urbanised with scattered patches of grassland that are poorly connected to the river system. However, during the event in September 2016 (Figure 6b), the coals contribution reaches high levels and becomes the second largest sediment source during the peak SSC. For this reason, it can be argued that coals may generally not be a dominant sediment source, but its importance varies over time, which can be driven by changes in the connectivity of the catchment to transfer sediment to the river system (e.g., as a result of precipitation; Bracken, Turnbull, Wainwright, & Bogaart, 2015; Wethered, Ralph, Smith, Fryirs, & Heijnis, 2015).

Furthermore, omitting an important, but poorly discriminated source from the classification can cause a significant difference between the experimental mixture and the SS (Scenario 4). For example, although riverbank appears to be an important sediment source (especially to the BS; Figure 6b), it is also the least well-discriminated source based on DRIFTS. Consequently, removing riverbank as a source results in a significant impact on the other source contributions (e.g., coals contribution where no is expected; Figure 6a).

Finally, these observations suggest that in the River Aire case study, important sediment sources may have been missed and their contribution was attributed to the most poorly defined source in the model (i.e., riverbank; Scenario 5). This hypothesis is supported by the small differences between the DRIFTS spectra of BS, SS, and the source material, especially at 1,160 and 1,020 $cm^{-1}$ (Figure 3). A possibly additional source could be solids from sewage treatment works, which was estimated to contribute 14–18% of the SS in the fingerprinting study by Carter et al. (2003).

### 4.3 | Methodological implications and recommendations

The model testing results demonstrate that source group classification can substantially alter sediment fingerprinting results and confirm that using source-specific PLSR models is not sufficient to test the representativeness of the source groups as actual sediment sources. Specifically, omitting less important sources (coals topsoil) does not change the contributions of other sources, whereas omitting important (in terms of contribution), but poorly-discriminated, sources (riverbank) increases contributions of all other sources. Therefore, there is a need for standardised techniques to assess the impact of alternative source groupings when using DRIFTS-PLSR sediment fingerprinting.

However, DRIFTS-PLSR sediment fingerprinting based on experimental mixtures (Poulenard et al., 2009) is different in methodological design compared with more traditional techniques based on a composite fingerprint and a mass balance equation (Collins, Walling, & Leeks, 1997; Pulley & Collins, 2018). This difference in methodology implies that standardised techniques to assess the impact of source groupings (e.g., testing alternative source groups based on cluster analyses; Pulley & Collins, 2018; Pulley, Van Der Waal, Collins, Foster, & Rowntree, 2017) are not directly transferable to DRIFTS-PLSR sediment fingerprinting. Similarly, standard techniques used in traditional sediment fingerprinting to test the effect of particle size differences and nonconservativeness (e.g., pairwise comparisons of fingerprinting properties; Pulley & Collins, 2018) are also less appropriate with the DRIFTS-PLSR approach. Although the conservative behaviour of the DRIFTS spectra and the effect of particle size were not explicitly tested due to the experimental focus of the research, these remain important steps in producing reliable sediment fingerprinting results. Therefore, to fully make use of the potential advantages of DRIFTS-PLSR sediment fingerprinting (i.e., faster analysis and less sediment material required; Cooper, Rawlins, et al., 2014), the model testing presented here should be further developed alongside the comparison of existing and alternative methods to test the impact of variations in source groupings, as well as particle size effects and conservativeness of DRIFTS spectra.

Finally, source sampling in this study was guided by erosion-prone areas within the catchment. Yet the sediment fingerprinting results indicate that differences in connectivity control sediment source contributions to the SS in the River Aire, which illustrates that material coming from erosion-prone areas is not necessarily the same material that is most likely to reach the river. Therefore, it is recommended for future studies to combine erosion information with sediment routing (e.g., SCIMAP; Perks et al., 2017) to guide sediment source sampling.

## 5 | CONCLUSION

DRIFTS-based sediment fingerprinting using individual, source-specific PLSR models was applied to assess the impact of sediment source classification on sediment fingerprinting results. Although the associated model uncertainties are statistically acceptable, sensitivity analysis showed that source apportionment is strongly influenced by the specific source classification considered, driven by the effect of source discrimination and importance of source groups as actual sediment sources.

The study illustrates the critical importance of initial source classification in DRIFTS-PLSR sediment fingerprinting and the need for standard methods to assess the impact of source classification on source apportionment. The presented model sensitivity testing will guide the development of standard methodological procedures to evaluate the appropriate number and type of sediment sources specifically targeted to DRIFTS-PLSR sediment fingerprinting. Better understanding of the uncertainties related to source classification in sediment fingerprinting and methods to evaluate these uncertainties will push forward the development of future sediment-related studies and help target management decisions related to ecology, geomorphology, and water quality.

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