**Tracing sediment sources during floods using Diffuse Reflectance Infrared
Fourier Transform Spectrometry (DRIFTS): A case study in a highly erosive
mountainous catchment (Southern French Alps)**

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Abstract

In mountainous catchments, large quantities of sediment are exported within very short periods leading to numerous environmental problems (e.g. reservoir siltation). The origin of suspended sediment during two distinct floods was determined by conducting an original fingerprinting method coupling Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and a chemometric technique (i.e. Partial Least Squares – PLS – analysis). Samples of the potential sediment sources were collected in badland areas developed on various substrates (i.e. molasse, marly limestones, black marls and gypsum) in the Galabre 20 km²-catchment located in the French Southern Alps. DRIFTS spectra provided a way to discriminate between the different potential sediment sources. Furthermore, the use of mid-infrared spectra allowed the direct quantification of the gypsum proportion in sediment. This contribution was systematically null at the catchment outlet because of the rapid dissolution of gypsum in the river. A PLS model was then constructed to estimate the contribution of the three other potential sources to the sediment flux during the floods. This model was developed and validated using a set of 45 "experimental" samples that were prepared in the laboratory in order to contain various proportions of the three remaining sources. By introducing DRIFTS spectra into the PLS model, we could predict the proportions of those sources in the mixed 'experimental' samples with a confidence interval of ca. $\pm 10\%$. The model was then applied to the sediment collected during the two selected floods in order to outline their origin. Black marls provided the highest contribution of sediment during both events, but the analysis also revealed a significant contribution of molasse. Results also showed the remobilisation of sediment originated from molassic substrates that deposited on the riverbed during a preceding event. Opportunities for improvement and further use of

64 this method as an alternative or rapid complementary sediment fingerprinting
65 technique are finally discussed.

66

67 **Keywords:** Sediment sources; Partial Least Squares, Suspended Sediment,
68 Fingerprinting,

1. Introduction

Sediment export from mountainous catchments occurs within very short periods, which exacerbates several environmental problems (e.g. reservoir siltation, increase in water turbidity and transport of contaminants; Vörösmarty et al., 2003; Meybeck et al., 2003). Information on the spatial origin of sediment within mountainous catchments is therefore crucial to guide river management and to outline areas where erosion control should be implemented in priority (Förstner & Salomons 2008). During the last decades, important research efforts were conducted to identify and to quantify the contribution of different sources delivering suspended sediment to the rivers (e.g. Collins and Walling, 2004). This knowledge also proved to be essential to provide estimations of catchment sediment budgets (Walling and Collins, 2008). The type of sources (i.e. soil types, rock types and land uses) to discriminate depends on the local catchment context. In the current context of land use and climate change, information regarding spatial patterns of erosion is required to develop, calibrate and validate spatially-distributed erosion models operating at the catchment scale (Boardman, 2006).

Furthermore, in addition to those spatial aspects, previous research showed that the origin of sediment can change throughout a flood (e.g. Walling and Woodward, 1995), consequently to the combination of several factors, like (i) the distance between the different potential sources and the catchment outlet, (ii) the different erodibility of soils within the catchment, (iii) the spatial pattern of rainfall and (iv) storm characteristics. Gaining knowledge on sediment source variation during a flood therefore provides important insights to understand the hydrological and sedimentary dynamics in catchments (e.g. Collins and Walling, 2004; Walling and Collins, 2008; Walling, 2005).

One of the strategies that dominated to assess the origin of sediment during floods consisted in analysing hysteresis relationships between the river discharge and Suspended Sediment Concentrations (SSC) (Asselman, 2000). Given that flow velocity – correlated with discharge – controls suspended sediment transport (Klein, 1984; Seeger et al., 2004), variations of the relationship between SSC and discharge are traditionally attributed to variations in the quantity of material that is available for transport by the river (Williams, 1989). This suspended material can then either originate from recent hillslope erosion or from the resuspension of sediment stored temporarily in the river bed (Bronsdon and Naden, 2000). Different hysteresis patterns are thus traditionally interpreted by drawing hypotheses on the type and the location of erosion areas involved (Lefrançois et al., 2007; Lenzi and Marchi, 2000; Duvert et al., 2010).

To decrease the uncertainties associated with this ‘classical’ monitoring approach, sediment fingerprinting methods were developed in the 1980s to identify unambiguously the sources of sediment (see Walling, 2005, for a review of fingerprinting studies). During the last decades, this approach has been increasingly applied to identify and ‘trace’ several distinctive characteristics of the source material that can be compared to the same characteristics measured on river suspended sediment samples (see Collins and Walling, 2004 and references therein; Foster et al., 2007; Minella et al., 2008). The choice of potential fingerprinting properties is generally guided by the availability of analytical facilities at the laboratory. The most frequently used tracers are radionuclides (^{137}Cs , unsupported ^{210}Pb , ^7Be), and various chemical elements (Stutter et al., 2009). Measurement of those properties was greatly facilitated during the last years, e.g. by the development of Inductively Coupled Plasma – Mass Spectrometry (ICP-MS). However, certain methods, and

119 particularly ICP-MS, still require a time-consuming and critical preliminary sample
120 preparation (i.e. total sediment digestion). Reliability of the results derived from those
121 chemical measurements strongly depends on the quality of this sediment total
122 digestion step (Chen and Ma, 2001).

123 Enlarging the spectra of potential fingerprinting properties with characteristics that
124 can be measured in a rapid and cheap way on samples and that require a minimal
125 sample preparation could therefore be explored. Measurement of this kind of
126 alternative properties would facilitate the analysis of a larger number of samples and
127 enlarge the application field of the method. For instance, Walling et al. (1979)
128 demonstrated the potential use of mineral magnetic measurements to discriminate
129 sediment sources during floods. Other attempts focused on the measurement of
130 diffuse spectroscopy properties in the visible and the near-infrared parts of the
131 spectrum. The technique of diffuse reflectance spectroscopy is commonly used to
132 assess various soil physical, chemical and biological properties. However, Mid-
133 infrared (MIR) (4000 to 400 cm^{-1} or 2500 to 25000 nm) Fourier Transform Diffuse
134 Reflectance spectroscopy (DRIFTS) recently appeared to provide two major
135 advantages compared to NIR spectroscopy (Reeves et al., 2001 ; Reeves, 2010). It
136 provides a larger statistical and functional selectivity, and the MIR part of the spectra
137 contains useful information on the organic and mineral fractions of the soil. Potential
138 “soil fingerprints” can then be derived from this part of the spectra and be used for
139 sediment source tracing. Unfortunately, this region of the spectra can be affected by
140 specular distortions due to differences of concentration in organic (humic acid) and
141 inorganic fractions (carbonate, silica) (Reeves et al., 2005). However, this problem
142 can now be overcome when using modern chemometrics methods, such as PLS
143 (Reeves, 2010).

Overall, source fingerprinting studies used those reflectance measurements in three different ways. Martínez-Carreras et al. (2010a) used directly colour indices in an optimised mixing model as fingerprint properties. Alternatively, Martínez-Carreras et al. (2010b) combined reflectance measurements with PLS models to predict the concentrations of specific geochemical fingerprints which were then used in an optimised mixing model. A third method consists in using directly infrared signatures to estimate the proportion of the different sources in a sediment sample after conducting an original calibration procedure.

It is based on the coupling of the DRIFTS method with the modern PLS chemometrics techniques to outline the origin of sediment in a catchment. Poulenard et al. (2009) demonstrated in a preliminary study that the origin of sediment from different land uses (i.e. grassland, cropland) or river location (i.e., river banks and riverbed) can be derived from the DRIFTS spectra, that those properties remain at least temporarily (i.e. min. one month) conservative in the river, and that the use of chemometric multivariate analysis methods provided a way to quantify the contribution of different sources to river sediment.

This paper aims at evaluating the potential of the DRIFTS method to distinguish directly the contributions of different lithological sources to river sediment. This technique will also be used to quantify the evolution of the source contributions during different flood types. To this end, a statistical model calibrated on experimental soil samples prepared in laboratory will be constructed in order to quantify the contribution of the potential sources of sediment. The conservative behaviour of those alternative fingerprint properties will also be tested. Opportunities for improvement and further use of this method as an alternative sediment fingerprinting technique will finally be discussed.

2. Materials and methods

2.1. Study Site

This study was conducted in the 22-km² Galabre catchment, which drains into the larger Bléone River basin and the Rhône River district, in the French Southern Alps (Figure 1). In this region, climate is transitional and undergoes continental and Mediterranean influences. Rainfall is characterised by important seasonal variations, with a maximum in spring and autumn, mainly in the form of heavy storms (Mano et al., 2009). Major floods are mostly observed during those periods. The Galabre catchment is underlain by highly erodible rocks, such as marly limestones (54%), molasses (31%), black marls (9%), gypsum (4%) and conglomerates (2%) (Haccard et al., 1989). Main land uses in the catchment are grassland (67%), sparse vegetation areas (19%) and forests (11%). Pressure exerted by human activities remains very low. The occurrence of heavy storms on highly erodible soils led to the development of extensive badland areas characterised by steep slopes and the absence of vegetation cover (e.g. Mathys et al., 2005), which developed on different types of sedimentary materials (Fig. 1). In the Galabre catchment, badland areas cover 8% of the surface (Evrard et al., 2011).

2.2. Monitoring and Sampling

A monitoring station was installed at the outlet of the catchment (22 km²) in October 2007. It measured water level with a high frequency (10 minutes) using the radar technique (24GHz, Paratronic Crusoe). A rating curve was constructed to calculate discharges based on the 10 min. frequency water level measurements. Suspended Sediment Concentrations (SSC) were also recorded continuously using a turbidity sensor (WTW, Visolid 700 IQ sensor, time step 10 min). An automatic sampler was coupled and triggered by the turbidity sensor. The automatic sampler was

195 programmed to collect routinely a sample every week. During floods, a sample was
196 collected every 30 min. SSC were thus determined by filtration of the water samples
197 through pre-weighed Durieux fibreglass filters (pore size diameter of 0.7 μm) dried at
198 105 °C during two hours. Filters were kept for further spectrometric analysis. A
199 calibration curve was then used to convert the SSC estimated by the turbidity sensor
200 into SSC in g L^{-1} . The uncertainties associated with both relationships (water level-
201 discharge and SSC turbidity-SSC) were estimated at less than 10 % and 20 %
202 respectively for this specific station (Navratil et al. (2011) and Némery et al. (2010)).

203 Figure 2 presents Q and SSC records at this station between October 2007
204 and October 2008. Floods characterised by very high sediment loads (maximum SSC
205 of about 140 g L^{-1}) were recorded late in summer (August and September 2008).
206 Such events were generally triggered by very short and intense storms. More
207 frequent hydrological events were recorded the rest of the year in response to long-
208 lasting and low intensity precipitation. In normal conditions, very low SSC ($< 0.5 \text{ g L}^{-1}$)
209 were measured in the Galabre River. Navratil et al. (2011) estimated that 90 % of the
210 annual Suspended Sediment Yield ($\text{SSY} = 805 \text{ t km}^{-2} \text{ yr}^{-1}$) was exported by the river
211 in less than 2% of the annual time (i.e., 7 days). The bulk of the sediment yield from
212 this catchment was then exported during massive and episodic floods.

213 To trace the origin of sediment, a set of 30 soil samples were collected in the
214 Galabre catchment (Figure 1) during winter in 2008. The sampling strategy was
215 prepared using lithological maps and aerial photographs of the study site. Location of
216 sampling points was defined by overlaying those information layers in a GIS, and by
217 paying attention to collect samples from all the major lithological substrate types
218 observed within the catchment. For each pre-defined sampling point, 2-3 soil
219 subsamples were collected within a perimeter of 3–5 meters and mixed in the

laboratory. The collected material was representative of the topmost 5 centimetres. Finally, samples representative of the different lithologies were prepared as follows: 6 samples on undefined Quaternary materials, 6 on gypsum, 3 on molasse, 4 on marly limestone and 11 on black marls. These samples were then dried at 105°C and stored before spectrometric analysis.

These soil samples were compared to suspended sediment samples collected at the monitoring station during two contrasted heavily loaded floods (Figure 2a and 2b) identified on the records available in order to determine the proportion of each source to the SS flux at the outlet.

The first selected flood lasted six days (21/11/2007 - 27/11/2007). Two flood peaks resulted from low intensity long-lasting winter precipitation (total rainfall depth of 125 mm; mean rainfall intensity of $\approx 1.0 \text{ mm h}^{-1}$ derived from hourly time-step records). The first SSC peak reached 22 g L^{-1} with a maximum discharge of $0.45 \text{ m}^3 \text{ s}^{-1}$ and the second reached 60 g L^{-1} with a maximum discharge of $4.2 \text{ m}^3 \text{ s}^{-1}$ (Figure 2b). A third peak discharge ($5.9 \text{ m}^3 \text{ s}^{-1}$) occurred afterwards, but it did not lead to any significant increase in SSC. Overall, during this flood, the SSC peak led the discharge peak. It was characterised by a clockwise SSC-discharge relationship.

The second flood that we selected occurred between 12/08/08 and 14/08/08 (Figure 2c). It was typically triggered by a short and heavy summer storm (total rainfall depth of 24.3 mm; mean rainfall intensity of 5.8 mm h^{-1} , derived from 10 min. time-step records). Peak SSC reached 140 g L^{-1} with a maximum peak discharge of $0.81 \text{ m}^3 \text{ s}^{-1}$. SSC peak occurred later than peak discharge, defining an anticlockwise SSC–discharge relationship.

Those two floods are representative of the contrasting hydrological behaviour of the Galabre River catchment, which justifies their selection in the framework of this study.

Preliminary analysis by combustion of acidified samples in a LECO CS 125 analyser (Coynel et al, 2005) showed that the organic carbon content of suspended sediment collected during floods was lower than 0.9%. Those values are of the same order of magnitude (0.5 to 1.2 %) as the ones measured in the black marls of the highly erodible catchment of Draix (Southern French Alps) and that are considered to provide fossil organic carbon (Copard et al., 2006).

Absolute grain size distribution measurements were performed by laser diffraction (Malvern Mastersizer 2000) on the 30 soil samples as well as on all the samples of suspended sediment collected during the two selected floods.

2.3. Spectroscopic and chemometric analyses

Spectroscopic measurements

Absolute grain size distribution measurements showed that the suspended sediment material that we collected was systematically $< 63 \mu\text{m}$ (Table 1). In order to reduce the impact of the different grain size distributions between the source material and the suspended sediment (Horowitz and Elrick, 1987), spectroscopic analyses were conducted on all the suspended sediment material and on the $< 63 \mu\text{m}$ fraction obtained by sieving of the soil samples.

Dry suspended sediment collected on the filters were scraped carefully, avoiding to extract pieces of the filter itself, and then gently crushed. To conduct a DRIFTS analyze in good conditions, 100 mg of material were required. The suspended sediment concentrations were always larger than 1 g L^{-1} . There was therefore always more than 500 mg of material available on the filter when filtering

500 ml of river water. The scraping was in this case easy. We have also studied the filters by DRIFTS . Background signal / noise (?) was checked on clean filters, and reliable spectra were obtained with 25 mg of materials in the filters. The spectra obtained by the two methods were similar (data not shown). We have finally preferred to apply the scraping technique on the suspended sediment to have the same nature of samples (i.e. a powder) for both soils and suspended sediment.

A ThermoNicolet 380 spectrometer equipped with a liquid-nitrogen cooled MCT (Mercury – Cadmium – Telluride) detector was used to perform the Fourier Transform Infrared (FT-IR) analysis. Spectra were obtained using the diffuse reflectance (DRIFTS) measurement technique. The spectra scan range was 4000 – 650 cm^{-1} at a resolution of 2 cm^{-1} with 32 co-added scans per spectrum. Results were then compiled using the OMNIC[®] (version 7.3) software provided by the spectrometer manufacturer (ThermoNicolet, USA). This software facilitated the measurement of the peak areas that were relevant to determine the DRIFTS properties.

Statistical analysis and PLS model

In order to avoid any CO₂ (gas) interference, analyses were only performed on wavelengths comprised in the ranges of 3800–2400 cm^{-1} and 2300–650 cm^{-1} . Principal component analyses (PCA) were carried out to determine the natural clustering of samples in the DRIFTS dataset, in order to evaluate the overall variability and any potential overlap between the different sample classes. Discriminant Analyses (DA) were then conducted using the PCA scores as input data into the TQ-Analyst[™] software (version 7.2). Mahalanobis distances were used to determine whether the different classes of source material could be discriminated with a high level of confidence (De Maesschalck et al., 2000).

Relationships between DRIFTS spectra ('x' variates) and the corresponding weight contribution of the sediments sources datasets ('y' variates) were assessed using Partial Least Square (PLS) analyses. PLS regression models are powerful tools for analyzing multivariable data (Martens and Naes, 1992). These models offer a solution to derive quantitative predictions related to chemical mixtures (Wold et al., 2001). In this study, we derived separate PLS models for each sediment source. When drawing up a PLS model, the first step consists in determining the number of components that will provide the best compromise between the description of the calibration set and the model predictive power. The Kennard and Stone - KS-CV - validation method was then conducted to confirm the number of components to introduce into the model (Kennard and Stone, 1969). It provided an evaluation of the uncertainty associated with the predictions generated by the PLS model when it was applied to an unknown sample. To this end, the KS-CV algorithm selected samples for which the predictors were the most distant, as indicated by their high Euclidean distances. For this training subset, the lowest predictive standard error (PRESS) value was found for three components. The predicted values for the test set were then compared to the actual values by calculating root mean-square errors of prediction (RMSEP). Independent PLS models were constructed to estimate the proportions of each main potential sources of sediment.

2.4. Conservativeness of DRIFTS properties in river

To test the conservative behaviour of the DRIFTS properties of source materials after a prolonged immersion in the river, given proportions of different sediment sources (also used for calibration and validation of the PLS model) were placed in microporous bags in the river. Bags were then removed after a stay of 1 day, 1 week and 2 weeks in the river. We analysed three replicates representative of

each set of conditions (stay duration, initial proportion of sources). DRIFTS measurements were computed on each sample in order to estimate the conservative behaviour of those properties.

3. Results and discussion

3.1. Discrimination of sediment sources by DRIFTS analysis

Figure 3a shows the typical DRIFTS spectra derived for the main lithological sources of sediment (i.e., topsoil collected in badlands areas) found in the Galabre catchment. A preliminary qualitative analysis of those DRIFTS spectra allowed us to distinguish the major types of materials. Soils developed on gypsum substrates are characterized by the peaks that are classically associated with CaSO_4 (Farmer, 1974) located around 3500 cm^{-1} and between $2370 - 2060\text{ cm}^{-1}$. DRIFTS spectra of the soils developed on other substrates consisted clearly of a mixture of carbonates (with the corresponding peaks at $2800\text{-}3000\text{ cm}^{-1}$, $2430\text{-}2640\text{ cm}^{-1}$, 1800 cm^{-1} etc.), aluminosilicates in the $3500\text{-}3700\text{ cm}^{-1}$ region and quartz (e.g. at $796/776\text{ cm}^{-1}$). A simple calculation of the peak areas corresponding to those main constituents provided a first way to discriminate the lithological origin of sediment (Figure 3b). Given the existence of specular distortions (Reeves et al., 2005), this approach cannot provide a quantitative estimation of the sediment composition. This method constitutes a semi-quantitative approach to exploit information contained in the spectra. Soils developed on molasses were characterized by large calcite (CaCO_3) peak areas (between 2430 and 2640 cm^{-1} in Figure 3b) and large aluminosilicate peak areas (3500 and 3700 cm^{-1}). This result was consistent with the composition of this marine molassic material dominated by carbonated sandstones (Haccard et al., 1989). In contrast, black marls exhibited a large aluminosilicate peak area and a small CaCO_3 peak area. Then, soils developed on marly limestones displayed large

CaCO₃ peak areas (e.g. 2430 and 2640 cm⁻¹ in Figure 3b) and relatively low aluminosilicates peak areas (3500 and 3700 cm⁻¹). Gypsisols were associated with small calcite and aluminosilicates peak areas. Finally, the soils developed on steep slopes and from undifferentiated materials, appear, as expected, constituted by mixtures of the other substrates

Discriminant analyses were conducted on the DRIFTS spectra in order to validate the potential use of the entire spectra to outline the main origin of sediment. In a graph plotting the Mahalanobis distance to the actual class centre vs. the Mahalanobis distance to the nearest class, all samples were located above the y=x line (see supplementary data 1). This result indicates that the distance to the centre of the real class was always shorter than the second closer one. We could therefore confidently say that DRIFTS spectra discriminates the main sediment sources present in the Galabre River catchment.

3.2. Determining the contribution of gypsisols to sediment

The DRIFTS spectra corresponding to an experimental set of samples constituted of marly limestones mixed with various proportions of gypsisols (i.e., soils developed on gypsum badlands) were acquired (supplementary data 2). We observed a direct linear relationship between the proportion of gypsum in the sample and the area of the peak corresponding to CaSO₄ (2370-2060 cm⁻¹; see supplementary data 2). We observed similar results with all the other types of material used for the preparation of the experimental samples (i.e. molasses, black marls and a mix of them). It was therefore possible to estimate directly the proportion of gypsum based on the area of this peak. This result confirms the ones obtained by previous studies (e.g. Böke et al., 2004) that outlined the relevance of infrared data to assess the proportion of gypsum in soils. Regarding suspended sediment samples

collected during the two selected floods, we calculated a null contribution of gypsisols using this method (the peak area at 2370-2060 cm^{-1} was indeed systematically null or negative). The absence of gypsum in suspended sediment at the outlet was expected, given the high solubility of this material in water (Porta, 1998) and the relatively large distance (> 3 km) from gypsisols sources to the river outlet. Given the non conservative behaviour of gypsum during its transfer in the river, we removed this potential source from the subsequent steps of the analysis to focus on the three remaining sources (i.e. black marls, marly-limestones and molasses).

3.3 Determination of the sediment origin during the selected floods

Construction of the PLS model

Quantifying the contribution of the three relevant sources to sediment collected in the river required the preparation of 45 experimental samples by mixing the three remaining types of sources (i.e. black marls, marly limestones and molasses) in various proportions (Figure 4a). Samples corresponding to those three source types consisted themselves in a mix of several (from 3 to 5) individual subsamples collected in different parts of the catchment. Twenty-five samples (chosen randomly) were used for validation set and 20 samples for calibration. Figures 4b, 4c and 4d show that there was a good agreement between the actual proportions of the different sources in the experimental mixed samples and the corresponding proportions calculated by the PLS model. R^2 coefficient varied between 0.992 and 0.997. Resulting RMSEP varied between 1.9 and 3.5. Given we wanted to assess the contribution of different sediment sources in a mixed sample, these errors remained acceptable. During the calibration step, variations of the contributions predicted by the model with a 95% confidence interval fluctuated by $\pm 10\%$ (dotted line on Figure 6b, c and d). We subsequently used this confidence interval to quantify the

uncertainties associated with our estimations of the suspended sediment composition. This uncertainty is only associated with the use of PLS models. Extra uncertainty due to spatial variability could only be taken into account by using several samples to prepare each reference in the mixture. Thus a part of the uncertainty associated with the measurement and/or the spatial variability of the DRIFTS signatures could not be taken into account in this study.

Conservativeness of DRIFTS signatures

Figure 5 shows the location of samples in a ternary diagram (i.e., three samples with a clear dominance of a single source located in the three poles of the diagram and one sample with equal proportions of the three sources located at the centre of the diagram) before and after immersion in the river. The “initial sample” corresponds to the actual proportions of sources in the experimental samples that we prepared in laboratory and before immersion. The points after immersion correspond to the proportions estimated by the PLS models applied to the DRIFTS spectra.

The difference between the PLS estimations and the actual values systematically varied between 5% and 15% for the dominant source and was in the same order of magnitude as PLS uncertainties. Furthermore, this error did not increase with longer immersion periods in the river. This experiment demonstrated i) that the DRIFTS signature was sufficiently conservative to be used as a potential fingerprint property and ii) that our PLS model provided reliable estimations of suspended sediment composition.

Application of the PLS model to the suspended sediment

Figures 6 and 7 show the evolution of discharge and SSC throughout the selected floods and the evolution of the sediment flux composition calculated by the DRIFTS-PLS procedure.

Comparison of the mean absolute particle size between source samples used to construct the model and the suspended sediment samples (Table 1) demonstrated relatively large grain size differences. The proportion of clay size particles remained stable, but the content of fine silt sized particles ($<16\ \mu\text{m}$) was significantly larger in suspended sediment than in soil samples. This difference in the grain size distribution of particles could potentially induce a bias in our estimations. Further studies could usefully estimate how this grain size difference potentially affected the infrared spectra and how it influenced our estimations of the suspended sediment composition. However, even though the three models used to estimate the contribution of the three different sources were independent, the sum of the contributions they provided was systematically very close to 100% (Figures 6 and 7). Each model estimates the proportion of a source, independently of the two other sources. The application of these three models to experimental mixtures leads inevitably to a sum of 100%. However, when these three models are applied to real sediment samples, the sum of the three proportions may well be very far from 100% (as we have observed in other cases when a source was lacking for example). The fact that the sums of three contributions calculated on the sediment sampled during the floods were close to 100%, highlights that i) all the main relevant sources of sediment in the Galabre River catchment, at least for the two studied floods, were sampled, and ii) the grain size effect was probably minor and that our models could cope with limited differences caused by changes in absolute particle size distributions or by variations of material residence time in the river..

During the 12-13 August 2008 flood, peak SSC occurred after peak discharge, defining an anticlockwise loop. As outlined by Lenzi and Marchi (2000) and Lefrançois et al. (2007) this relationship would mean that sediment conveyed by the

river at the beginning of the flood originated from distant parts of the catchment where erosion occurred. Results of combined DRIFTS – PLS fingerprinting (Figure 8) showed that there was a clear dominance of the black marl contributions all throughout the flood ($40 \pm 10\%$ to $100 \pm 15\%$ of sediment) and mainly during the first flush. Then, during peak discharge (but before SSC maximum), marly-limestones were the main sediment supplier (providing temporarily $60 \pm 7\%$ of sediment). Molasse contribution increased with SSC and was maximal ($50 \pm 13\%$) during peak SSC. Finally, black marl dominated again during the recession stage. Unfortunately, we had no information on the spatial pattern of rainfall that triggered this flood. Evolution of sediment sources during the flood could indeed have been associated with changes of rainfall pattern. We can nevertheless hypothesise that a homogeneous rainfall pattern occurred in the Galabre River catchment during this event because the succession of the sediment sources determined by our model corresponds to the succession of lithologies along the river. The black marls contribution, which clearly dominated all throughout the flood and especially during the first flush can be explained either by the high erodibility and sensitivity of this material to erosion (Mathys et al., 2005) and by their location in the vicinity of the outlet. This interpretation would confirm the dominant sediment supply by hillslope erosion during this flood.

The interpretation of the event of November 2007 is complicated by the succession of several stages with different behaviours. During the first stage that occurred in the morning of 22 November, the bulk of sediment was supplied by molasse material ($60 \pm 15\%$ of sediment; Figure 7). In the catchment, this substrate is the most distant to the outlet. We therefore hypothesise that sediment exported during this stage corresponded to sediment that deposited previously on the riverbed

and that was exported during the first rising stage. This interpretation is consistent with the classical meaning given to synchronous SSC and Q peaks associated with the resuspension of sediment deposited in the channel that were less and less available throughout the flood (Lenzi and Marchi, 2000; Jansson, 2002 ; Goodwin et al., 2003; Lefrançois et al., 2007). This resuspension is also consistent with the high capacity of riverbeds in this type of mountainous catchments to store temporarily huge amounts of fine sediment as demonstrated by Navratil et al. (2010) in nearby catchment. The contribution of black marls that are the most erodible material was rather low during this first stage. This fact is probably due to the location of black marls in the close vicinity of the outlet. The river sections where black marls can be directly supplied to the watercourse draining correspond to less than 10% of the river network in the catchment. Thus, the stock of black marls already present in the river was inevitably limited in comparison with the potential stock supplied to the river by the two other sources.

Then, during the second rising stage of the flood (23 November), the bulk of sediment originated from hillslopes and was supplied by black marls with a progressively increasing contribution of molasse material throughout time. Behaviour during this stage was similar to the one observed during the 12-13 August 2008 flood and can be associated with the sediment supply by the succession of lithological sources located along the river. We attributed the relatively low marly-limestone contribution ($\pm 10\%$ throughout the event) calculated during the two flushing stages of 21-27 November 2007 flood to the limited stock of marly-limestone material available in the river, which was probably due to the winter low-intensity rainfall regime that led to a low mobilisation of such materials.

The total load of sediment exported by both floods (Table 2) shows similar proportions with about 60 to 70% of sediments from the black marls, about 10% from marly-limestone and about 20% to 30% from molasses. We have however seen that during peaks or during the main flood stages (Table 2), the range of contribution could vary dramatically particularly between the marly-limestones and the molasses.

3.4 Interest and limit of the DRIFTS-PLS fingerprinting approach

The proposed method proved to be effective in a small mountainous catchment where there are only a few potential sediment sources (i.e. badlands developed on different sedimentary rock types). However, its application to catchments characterised by more complex sources of sediment (variations in soil types and land uses) is more uncertain. To test it, a combination of the DRIFTS method with the conventional fingerprinting technique could usefully be carried out to this end.

Evrard et al. (2011) conducted a conventional fingerprinting study using sediment geochemistry and radionuclide concentrations as potential input properties to a Monte Carlo mixing model to quantify the contribution of different lithological sources to river sediment in the entire Bléone catchment. This study was carried out on riverbed sediment, and only one of the analysed samples was collected in the vicinity of the Galabre River monitoring station. This sediment was sampled on 22 April 2009 after a widespread flood. Mixing model outputs showed that the bulk of this sediment was provided by black marls (77%), with a minor contribution of marly limestones (20%) and molasse/Quaternary deposits (3%). However, the results of our study show that sediment source contributions vary from one flood to another as well as within a single flood. Indeed, at the event scale, the contribution of Black marls found by the DRIFTS-PLS approach (Table 2) was in the same order of

magnitude (i.e., about 70%). In contrast, the relative contribution of marly-limestone and molasse greatly differed. However, a comparison based on a single sample is not really relevant. In future, both approaches should therefore be conducted on the same samples of suspended sediment collected during floods to allow for a fully relevant comparison of both techniques.

Furthermore, our approach is only relevant to estimate primary sources of sediment (*sensu* Collins and Walling, 2004) and not to quantify contributions of suspended material provided by secondary sources (i.e sediment already mobilized during the previous flood and stored in the river). Still, this information is essential to understand the hydrosedimentary functioning of such mountainous catchments characterised by a large capacity to store fine particles in the river bed and deliver them later (Navratil et al., 2010). The capacity of the DRIFTS approach to provide information on sediment supply by secondary sources should therefore be investigated. Furthermore, over the longer term, novel tools could be developed to monitor *in situ* spectroscopic properties of suspended sediment. Use of spectrometers with 4 cm⁻¹ resolution and 64 scans should also be tested.

4. Conclusions

This study aimed to assess the potential advantages of a methodology combining DRIFTS and chemometric techniques for sediment source apportionment during floods in a mountainous catchment affected by severe erosion and massive sediment exports. DRIFTS properties provided a way to discriminate various lithological sediment sources in a sedimentary catchment. It allowed a straightforward quantification of the gypsum proportion in sediment. Combining DRIFTS measurements with the PLS method provided quantitative information on the type of sediment supplied to the river during different flood types. Despite several limitations

associated with the low number of sources considered and the PLS method calibration process that relies on mixed samples prepared in laboratory, this alternative sediment fingerprinting method is original and benefits from the simplicity and the rapidity of DRIFTS measurements (> 30 samples h^{-1}). Once calibrated, it has the potential to provide higher resolution information on suspended sediment composition and its evolution throughout time than traditional Q – SSC studies. This knowledge is important to improve our understanding of the flood sediment dynamics. Indeed, even though conventional sediment fingerprinting has proved to be useful for documenting remobilisation of sediment stored in river channel networks, the infrared spectroscopy method provides a way to conduct fast and cheap fingerprint property measurements on large quantities of samples. This type of results could provide datasets required for calibration and validation of river sediment transfer models. In future, developing a way to avoid the constitution of artificial mixtures for the PLS calibration step should be investigated. Furthermore, the reliability of field spectrometers to monitor *in situ* DRIFTS properties of suspended sediment directly in the river should be assessed.

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Figure captions

Figure 1- Location of the Galabre River catchment, and presentation of its topography and lithology. Location of the samples of the potential sediment sources collected in the catchment.

Figure 2 – (a) Records of discharge and SSC on the Galabre River between Oct. 2007 and Oct. 2008 on the Galabre catchment. (b) Detailed records of the selected winter flood. (c) Detailed records of the selected summer flood. Circles indicate the characteristics of the suspended sediment samples collected by automatic sampler and analysed with the DRIFTS method.

Figure 3 - (a) Characteristical DRIFTS spectra of the main lithological sources of sediment (b) Location of the sediment source of sediment in a graph plotting the area of peak $2430\text{-}2640\text{ cm}^{-1}$ area vs. the area of peak 3500 and 3700 cm^{-1}

Figure 4 - Discriminant analysis of the source of sediments. Mahalanobis distance to the actual class center *versus* the Mahalanobis distance to the closer class.

Figure 5 - (a) DRIFTS spectra of mixture of gypsisols with other sources of sediment with various proportion of gypsisols (b) relationship between the percentage of gypsisols and the $2370\text{-}2060\text{ cm}^{-1}$ surface peak area.

Figure 6 - (a) Ternary diagram with the position of the experimental mixtures prepared for the PLS calibration. Relationship between actual and PLS calculated percentage of sediment sources in experimental mixture for Black Marl (b) ; Molasse (b) ; Marly-limestone (d)

Figure 7 – Ternary diagram with the position of sample immersed in the river during 1 day, 1 week and 2 weeks. The actual initial proportion of sources within the sample is indicated by black circles. The apportionment after immersion is calculated by DRIFTS-PLS.

Figure 8 – Records of discharge, SSC, and quantitative determination of sediment sources using the DRIFTS-PLS method for the 12/13 August 2008 flood.

Figure 9 – Records of discharge, SSC, and quantitative determination of sediment sources using the DRIFTS-PLS method for the 21/26 November 2007 flood.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Quantitative
PLS model