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Quantifying suspended sediment sources during runoff events in headwater catchments using spectrocolorimetry

Cédric Legout • Jérôme Poulenard • Julien Nemery • Oldrich Navratil • Thomas Grangeon • Olivier Evrard • Michel Esteves

C. Legout (✉) • T. Grangeon
UJF-Grenoble 1 /CNRS / G-INP / IRD, LTHE UMR 5564, 38041 Grenoble, France
e-mail: cedric.legout@ujf-grenoble.fr

J. Poulenard
Université de Savoie, EDYTEM, Savoie Technolac, 73376 Le Bourget du Lac Cedex, France

J. Nemery
G-INP / UJF-Grenoble 1 / CNRS / IRD, LTHE UMR 5564, 38041 Grenoble, France

O. Navratil
Université de Lyon 2, EVS UMR 5600, avenue Pierre Mendès-France, 69676 Bron, France

O. Evrard
Laboratoire des Sciences du Climat et de l'Environnement (LSCE/IPSL), Unité Mixte de Recherche 8212 (CEA, CNRS, UVSQ), 91198-Gif-sur-Yvette Cedex, France

M. Esteves
IRD / UJF-Grenoble 1 / CNRS / G-INP, LTHE UMR 5564, 38041 Grenoble, France

(✉) **Corresponding author:**
Tel: +33 4 76 63 56 63
Fax: +33 4 76 82 50 01
e-mail: cedric.legout@ujf-grenoble.fr

Abstract

Purpose Increasing the understanding of the hydro-sedimentary dynamics at the catchment scale requires high temporal resolution data on suspended sediments such as their origin in addition to the common measurements of concentrations and discharge rates. Some rapid and low-cost fingerprinting methods based on spectroscopy have recently been developed. We investigated how visible spectra could be used to predict the proportion of source material in suspended sediment samples, paying particular attention to the potential alteration of the spectrocolorimetric signatures between soils and suspended sediments during transport.

Materials and methods The 22-km² catchment studied was composed of black marls, limestones, molasses, undifferentiated deposits and gypsum. Forty-eight source materials were sampled and 328 suspended sediment samples were collected at the outlet during 23 runoff events. Measurements were taken with a diffuse reflectance spectrophotometer on dried samples. As the erosion processes are particle size selective, five size fractions of source material were measured in order to assess the potential alteration of the signatures. As the biogeochemical processes occurring in the river could also affect the signatures, source materials having been immersed in the river for durations ranging from 1 to 63 days were measured. Finally, partial least-squares regression models were constructed on 81 artificial laboratory mixtures to predict the proportion of source material.

Results and discussion The spectrocolorimetric measurements discriminated the primary source materials but not the Quaternary deposits. As the gypsum was not conservative, only the black marls, molasses and limestones were used in the fingerprinting procedure. The construction of the partial least-squares regression models led to a median absolute error of 1.1%. This error increased to 3.9% when the models were applied to source samples with i) different particle sizes, ii) different durations spent in the river or iii) different origins than those used for their construction. The effect of particle size on the fingerprinting procedure was larger than the effect of biogeochemical reactions or the spatial variability of the spectrocolorimetric signatures. Half of the 23 runoff events analysed exhibited huge variations in the source proportions from one collected sample to another.

Conclusions The spectrocolorimetric fingerprinting approach proved its ability to quantify routinely the proportion of primary source materials in all suspended sediment samples collected during runoff events using automatic sequential samplers. The high temporal resolution of the predicted proportions revealed that, analysing three or four suspended sediment samples only during a runoff event would lead to a complete misunderstanding of the hydro-sedimentary processes for more than half of the investigated runoff events.

Keywords Conservative tracer properties • Diffuse reflectance spectrometry • Fingerprinting • Mountainous catchment • Partial least-squares regression • Suspended sediments • Visible range

1 Introduction

Given the importance and the recurrence of economic and environmental problems due to erosion and fine sediment transport (Pimentel et al. 1995; Owens et al. 2005; Boardman 2006; Almansa et al. 2012), decision makers' demands for efficient on- and off-site mitigation measures to limit exports of suspended sediments are becoming more insistent. Physically based distributed models are required to assess these mitigations in a context of changes in meteorological forcing and soil use. However, it is clear that at present, the performance of these models remains poor and far below the predictive expectations of decision makers (Mitas and Mitasova 1998; Nearing 1998; Jetten et al. 1999, 2003; Evans and Brazier 2005; Beven 2006, Boardman 2006). This may be due to a large extent to the fact that these models focus only on what occurs at the catchment outlet (Jetten et al. 1999) and to the associated strong likelihood of predicting the correct results for the wrong reasons (Favis-Mortlock et al. 1996; Jetten et al. 1996; Takken et al. 1999). Behind this well-known problem, additional issues associated with the spatial and temporal dynamics of processes occurring within catchments still exist. Among them, the spatio-temporal patterns of rainfall (Soler et al. 2007; Nadal-Romero et al. 2008; Mano et al. 2009; Navratil et al. 2012) and the strong spatial heterogeneity of soil erodibility is crucial (Gallart et al. 2002; Gumiere et al. 2011; Wang et al. 2009; López-Tarazón et al. 2010). In this context, gaining knowledge on the variability of sediment sources during runoff events should provide important insights to better understand the hydro-sedimentary dynamics at the catchment scale (Collins and Walling 2004; Walling 2005). Moreover, the extremely high temporal variability of suspended sediment fluxes that can occur in many environments, as reported for instance by Duvert et al. (2010) and Evrard et al. (2010) in mountainous catchments, suggests that suspended sediment sources transiting at outlets may also exhibit strong variations during runoff events. This emphasizes the need to characterize the suspended sediment source routinely on all samples collected during runoff events using automatic sequential samplers. However, conventional fingerprinting techniques based on geochemical and radionuclide measurements that have been used over the last 30 years (Walling 2005; Davis and Fox 2009) are time-consuming and rather expensive (Martínez-Carreras et al. 2010b; Poulenard et al. 2012), which may prevent routine characterization of large numbers of samples representative of various sediment sources and hydrodynamic conditions.

Because spectroscopy is a rather rapid, inexpensive, non-destructive and straightforward technique, it has been commonly used during the past 10 years in the visible (VIS), near infrared (NIR) and mid-infrared (MIR) ranges in order to quantify soil properties (Viscarra Rossel et al. 2006). More recently, spectroscopy has been applied to suspended sediment source tracing and has proved its ability to discriminate and quantify various source materials in suspended sediment samples (Poulenard et al. 2009; Martínez-Carreras et al. 2010a and b). So far, spectral reflectance data have been used in three different ways. Colour coefficients deduced from VIS spectra were used directly in an optimised mixing model as potential fingerprint properties (Martínez-Carreras et al. 2010a). VIS/NIR spectra were also used to predict the concentrations of specific geochemical fingerprints which were then used

in an optimised mixing model (Martínez-Carreras et al. 2010b). The last approach consisted in directly using NIR/MIR spectra to estimate the proportion of the different source materials in suspended sediment samples after conducting a partial least-squares regression calibration on artificial source material mixtures (Poulenard et al. 2012). However, so far and to our knowledge, there has not been any attempt to use VIS spectra and deduced colorimetric parameters as potential predictors of the proportion of the different source materials in suspended sediment samples according to the previously described approach.

Even though the measurement of VIS spectra is recognised as being a good predictor of soil constituents (Debret et al. 2011) and a simple methodology, even faster and cheaper than for infrared methods, some assumptions must be verified before using them as potential tracers in the framework of a fingerprinting study. Tracing a suspended sediment source based on soil measurements and suspended sediment at the catchment outlet assumes that the source soil signatures are preserved (Foster and Walling 1994). However, two major processes occurring during soil erosion and sediment transport at the catchment scale could affect these signatures. Firstly, erosion processes are known to be size selective (Slattery and Burt 1997; Malam Issa et al. 2006). Given that grain size is a physical chromophore (Ben-Dor et al. 1998), the signatures measured downstream on suspended sediment may differ from the source soils. Secondly, biogeochemical reactions such as iron reduction (Philips and Marion 2001) can occur during the transport of source soil particles leading to differences in spectrocolorimetric signatures.

The objectives of this study were i) to assess whether spectrocolorimetric signatures were preserved between source soil material on hillslopes and suspended material collected at the catchment outlet, ii) to quantify the fractions and associated uncertainty of each potential source material in suspended sediment samples during runoff events and iii) to assess the range of the suspended sediment source variations during runoff events at the outlet of a mountainous catchment.

2 Materials and methods

2.1 Catchment characteristics and source soil sampling

The 22-km² Galabre catchment is part of a larger mountainous instrumented area in the southern French Alps (Fig. 1a). It is located in a sedimentary area characterised by five main source material (see Fig. 1b), i.e. black marls (9%), limestones (54%), molasses (4%), undifferentiated deposits (29%) and gypsum (4%). The soils are shallow with maximum depths of 60 cm. The catchment is well covered by vegetation (forest and grassland), cropland accounting for only 2% of the total area. However, 8% of its area is considered as highly erodible. These highly erodible areas were defined as zones without vegetation and characterised by the presence of erosion features such as rills, gullies or badland morphology (Navratil et al. 2012). They were delineated in a GIS using 2004 aerial photographs and validated by field observations. These areas are assumed to be the major contributors to the suspended sediment loads since they are well connected to the hydrographic network. We

should also stress that these areas, which are considered as potential sediment sources, cannot be considered as soils because soil horizons cannot be distinguished; the materials are much more similar to the original geological material (Fig. 1b).

In September 2008, a sampling campaign was conducted. Forty-eight samples were collected of the top 5 cm of each material following a stratified sampling approach. The stratification consisted of dividing eroded areas into five homogeneous subgroups based on their lithology prior to the field campaign. Samples were then collected in eroded areas corresponding to each subgroup, depending on terrain access facility (see Fig. 1b).

2.2 Catchment outlet and monitoring station

The outlet of the Galabre catchment (lat.: 44°10'28"N, long.: 06°13'07"E) was equipped in spring 2007 to monitor suspended sediment dynamics. The water level was measured by a 24-GHz radar (Paratronic Crusoe®) every 10 min. The water-level discharge rating curve was built based on ~40 salt gauging measurements. Turbidity was measured every 10 min by infra-red light retro-diffusion (nephelometric turbidimeter WTW Visolid® 700-IQ). The turbidimeter was calibrated by using measurements of suspended sediment concentration of river water samples collected automatically (Teledyne ISCO® 176 3700) every 60 and 30 min when turbidity critical thresholds were exceeded, i.e. t_1=5 g L^{-1} SiO_2 and t_2= 20 g L^{-1} SiO_2, respectively. The suspended sediment concentration was measured by weighing the sample after drying it for 24 h at 105°C. More information on this gauging station and the associated uncertainties is provided in Navratil et al. (2011). The mean discharge was 0.256 $m^3 s^{-1}$ over the 2007–2011 recording period, with a maximum discharge of 34 $m^3 s^{-1}$. The mean suspended sediment concentration was 0.4 g L^{-1} with a maximum value of 217 g L^{-1}. The mean area-specific suspended sediment yield was 651 t km^{-2} y^{-1}.

2.3 Spectrocolorimetric measurements

Spectrocolorimetric measurements were taken on both suspended sediment samples collected during runoff events (n = 328) and on source soil materials (n = 48). It should be noted that the fingerprinting technique presented in this paper was designed to be further applied routinely on each collected suspended sediment sample once it had been dried at 105°C and weighed to obtain the suspended sediment concentration. In order to avoid a bias between suspended sediment samples and source material samples, all of them were dried at 105°C for 24 h and stored in 60 mL polystyrene straight containers before taking measurements.

Measurements were taken using a portable diffuse reflectance spectrophotometer (Konica Minolta 2600d) integrating its measurement on a 3-mm radius circle. The spectrophotometer was installed upside-down, face up, and the tubes containing the samples were placed on the measuring cell. Thus the measurement was taken directly through the base of the tube. The minimum amount of sample was roughly 100 mg. Because of the rather small measuring area and to account for the possible

heterogeneity within the samples, four measurements were taken on each sample, the container being shaken between each measurement. During a measurement, the spectrophotometer emits a standard Xenon arc light source and measures the ratio between the light reflected from the sample and from a calibrated white standard. Spectral reflectances were measured between 360 and 740 nm with a 10-nm resolution. All measurements were taken with the D65 standard illuminant, the 10° angle observer and with the specular component excluded. Raw data collected were the spectral reflectance percentage for each of the 39-wavelength class. From these raw data we also derived 8 components of various colorimetry models (Viscara Rossel et al. 2006). XYZ tristimulus values were calculated based on the colour-matching functions defined in 1931 by the International Commission on Illumination (CIE, 1931). We then transformed the standardised tristimuli to the CIE L*a*b* and the CIE L*u*v* cartesian coordinate systems using the equations given in CIE (1978).

The spectrophotometer was calibrated before each set of measurements by making a zero and a white calibration. Control measurements were also taken regularly during and at the end of a set of measurements. These latter consisted in measurements on red, green and yellow panels as well as six contrasted soil samples.

2.4 Assessment of the conservation of the colour-based signatures

2.4.1 Particle size measurements and fractioning

Particle size distributions were measured using a laser diffraction sizer (Malvern, Mastersizer 2000) in the 0.01- to 2000-µm range. As the objective of these measurements was to identify the particle size selectivity during erosion processes, absolute particle size distribution rather than the effective particle size distribution were measured on the <63-µm size fraction on a selection of 17 soil samples and 47 suspended sediment samples. Particle size distributions measured after 10 min of sonication with maximum stirring and pumping conditions, at 1000 and 2500 rpm, respectively, were considered as absolute particle size distributions.

Source soils were fractioned in order to assess to what extent the size of particles was responsible for the colour-based signatures. For each source material, black marls, limestones and molasses, five source soil samples were sieved to five size fractions: bulk soil, <200, <100, <63 and <20 µm.

2.4.2 In situ biogeochemical experiment

To assess a possible alteration of the colour-based signatures during the transit of suspended sediment, source soil samples were immersed for various durations in the Galabre River. The experiment was conducted on the <63-µm size fraction of the potential source materials. The samples were composite samples consisting of a mix of three to five individual samples from the same lithology. For each composite source material, 2 g of soil were introduced in two successive nylon porous bags with a 20-µm mesh size. Preliminary trials revealed that both the mesh size and the double layer provided a good compromise for the renewal of water in the bags without clogging by

external suspended sediment with limited initial material loss. Indeed the comparison of the mass before and after immersion led to a low median mass loss of 5% (statistically significant according to a Wilcoxon signed ranked test). A similar comparison for the D10, D50 and D90 on the dispersed particle size distributions did not reveal the existence of any significant difference. Forty-five bags were immersed in the river in March 2009. Then three triplicates of each source material were collected after 1, 7, 14, 35 and 63 days. Spectral properties were measured on each sample collected, once oven dried for 24 h at 105°. We emphasize that this experiment was conducted with immersion durations more than four times longer than those reported in Poulenard et al. (2012) with the same source materials.

2.4.3 Statistical tests

To assess whether groups of measurements were significantly different, statistical tests of group comparisons were done. As the groups compared did not exhibit equality in their variance, the Dunn nonparametric test was used at the 0.01 probability level. This test was applied to address three goals. It was used to assess the extent to which particle size selectivity occurred during sediment transfer. For each dispersed size fraction, a comparison was made between suspended sediment and source materials. The Dunn test was also applied to assess potential changes in source soil signatures i) between various particle size fractions and ii) between various duration times spent in the river. Each colorimetric parameter value group was compared to the group measured on the <63-µm size fraction and to the group measured after 1 day in the river, respectively for i) and ii). These comparisons were done for each parameter L*, a*, b*, u*, v* and for each source material.

2.5 Construction of predictive models

Partial least-squares regression models were constructed following the methodology presented by Poulenard et al. (2012) to quantify the proportion of each source material in the suspended sediment samples collected during runoff events. Partial least-squares regression models were constructed by establishing relationships between spectral measurements together with derived colorimetric parameters (47 X-explanatory variables) and proportions of source materials in various samples (Y-variable), as described by Wold et al. (2001). At the end of the discriminant analysis of source materials by spectrocolorimetry (section 3.1.), only three primary source materials were retained for the construction of the partial least-squares regression models (i.e., black marls, limestones and molasses). Thus, 81 artificial laboratory mixture samples were prepared by mixing, in known proportions, these three primary source materials that were immersed for 1 day (Fig. 2). The distribution of the mixtures in the ternary diagram was a compromise between covering the whole triangle area and having a number of samples that were well distributed on each axis. As the spectral measurements were repeated four times on each sample, the number of samples used for the partial least-squares regressions reached 324. This data set was randomly divided, one half being used for

calibration, the remaining half for validation. Independent partial least-squares regression models were constructed for each primary source material type. Finally, the quality of the tracing procedure was then checked by summing the three predicted proportions and verifying that this sum was close to 100%.

3 Results and discussion

3.1 Source soil discrimination

The first step of the proposed tracing approach was to assess whether the spectrocolorimetric measurements were able to discriminate the various source materials in the Galabre catchment. The factorial discriminant analysis performed on the values of each colorimetric parameter for the 48 source material samples revealed that spectrocolorimetry provided a way to distinguish all groups of samples. The cumulative percentage of discrimination of the first two factors was 100%. The parameter a* exhibited a correlation of 0.99 with the first factor while L* exhibited a correlation of 0.95 with the second factor. As illustrated by Fig. 3 showing the scattering of L* and a* parameters, 78% of the samples were grouped in four sets. Samples with L* values comprised between 33.3 and 38.3 and a* values between 1.5 and 1.9 corresponded to black marls. Molasses were clearly discriminated from black marls by L* values ranging from 53.3 to 56.5 and a* values ranging from 0.7 to 1.1. Limestones were fully discriminated from the two previous source material types by higher a* values ranging from 9.2 to 10.1. The fourth group, gypsisols, was also well discriminated from the other source materials with the highest L* values ranging from 66.8 to 71.7. The remaining 22% were samples covering the entire range of L* and a* variations without showing any direct affiliation to one of the four previous groups. The latter samples appeared to comprise a mix of the other source materials. This was expected because these samples were sampled on steep slopes in areas labelled as undifferentiated deposits. The classification table (i.e. confusion table) used to appraise the results of the predictive quadratic discriminant analysis confirmed that black marls, molasses, limestones and gypsisols were accurately classified (100% correct), whereas undifferentiated deposits were classified with a lower accuracy (73% correct). As no proper colorimetric signature was found for these materials that are a mix of the four others, they were no longer considered as a primary source material in the subsequent tracing approach based on spectrocolorimetric measurements. Among the four remaining potential source materials, the gypsisols showed by far the least conservative behaviour during their transfer by the flow. Indeed gypsum is known to be highly soluble in water (Porta 1998) and the Diffuse Reflectance Infrared Fourier Transform Spectrometry measurements taken by Poulenard et al. (2012) revealed the absence of gypsum in suspended sediment samples collected at the outlet of the Galabre catchment. Thus the gypsisol potential source material was removed from the subsequent steps of the tracing approach.

3.2 Effect of particle size on source signature

The particle size selectivity of erosion and transport processes occurring in the Galabre catchment was assessed by comparing the dispersed particle size distributions measured on 17 of the 48 source material samples and on 47 of the 328 suspended sediment samples. Figure 4a shows evidence that the <63-µm size fraction of the suspended sediment samples was enriched in particles smaller than 8 µm and depleted in particles coarser than 16 µm. In order to assess down to which size fraction the erosion and transport processes were size selective, we calculated the class weights considering first the <31-µm size fraction only (see Fig. 4b) and then the <16-µm size fraction only (see Fig. 4c). Figure 4b shows that, even when focusing on the <31-µm size fraction, the suspended sediment samples were still depleted in the coarsest size fractions. However, when considering the <16-µm size fraction only, no statistical difference according to the Dunn test was observed between the suspended sediment and the source materials (see Fig. 4c). This analysis did not allow for a precise identification of the critical size, below which particle size selectivity no longer existed. It is likely that this size limit was located somewhere in the 16- to 31-µm range for the runoff events studied and in the Galabre mountainous catchment. Nevertheless, it underlined the need for considering particle size selectivity in fingerprinting approaches far below 63 µm and certainly down to particle size around roughly 20 µm. In the following, we investigated the extent to which the spectrocolorimetric signatures varied between the various particle size fractions.

Figure 5 shows the same trend for all the colorimetric parameters and the source materials. Considering the three source materials, the average increase of the colorimetric values from the bulk samples to the <20-µm size fraction were 11%, 40%, 23%, 28% and 24%, respectively, for L*, a*, b*, u* and v*. These changes were quite high and remained in agreement with already published data on the colour–particle size relationship (Torrent and Barron, 1993; Sánchez-Marañón et al., 1997; Sánchez-Marañón et al., 2004; Gunal et al., 2008). However, these changes fall to 6%, 5%, 6%, 7% and 7%, respectively, for L*, a*, b*, u* and v* when comparing the <63-µm size fraction to the <20-µm size fraction. As no significant statistical difference was found between the two latter fractions according to the Dunn test (see Fig. 5), we assumed that constructing the partial least-squares regression models on the <63-µm size fraction should lead to representative predicted proportions of source materials in the suspended sediment samples. Nevertheless, the changes observed on the colorimetric parameters certainly generated uncertainty in the predicted source proportions (see section 4.4). It should be noted that some particles reaching 300 µm in size were sometimes sampled during runoff events. However, for the 47 suspended sediment samples in which we analysed particle size distribution, the >63-µm size fraction accounted for an average of only 1.1% of the entire sample particle size distribution. Thus, even though the change in colorimetric parameters associated with coarse particles was high, this effect can generally be ignored when comparing the <63-µm size fraction to the <200-µm size with values of −5%, −16%, −11%, −13%, −11%, respectively, for L*, a*, b*, u* and v*,.

3.3 Effect of immersion duration on source signature

Colorimetric parameters L*, a*, b*, u* and v* generally exhibited low variations according to the immersion time of source samples in the river (Fig. 6). Indeed, the variations that affected the original source material (day 0) remained lower than 10% for the whole set of parameters, source materials and immersion durations. This means that no major differences were observed i) between measurements taken on original source materials (day 0) and measurements taken on the materials having been immersed in the river and ii) between the various measurements taken for increasing immersion durations.

However, looking at the small variations in detail highlighted differences between source materials. For each parameter, the relative differences between t = 1 day and the subsequent durations were calculated. Throughout all immersion durations, the differences were found to be lower than 2.6% on average for the limestone samples, whereas they were higher for the molasses and black marls. For example, the black marls exhibited average differences of 6.3, 3.8, 7.3, 5.5 and 6.6%, respectively, for the L*, a*, b* u* and v* parameters. The greater differences observed for molasses and black marls than for limestones were also confirmed by statistical tests of group comparisons shown in Fig. 6 as gray circles. Doing the same analysis but over all the parameters for each immersion duration led to small average differences (i.e. less than 3.2%) for limestones. No clear trend was noted with increasing residence time in the river flow. Larger differences were obtained, however, for the molasse and the black marl samples. The largest differences were obtained for the last two immersion durations (days 35 and 63) with average values of 7.2 and 9.8% for the molasses and black marls, respectively. This trend was also confirmed by statistical tests, as shown in Fig. 6.

Overall, this detailed analysis showed that the black marls and molasses may be more sensitive to colorimetric variations during their transit times than the limestone material. It also underlined that, for the two most sensitive materials, the longest periods (i.e. longer than 1 month) in the river were associated with the largest variations of the spectrocolorimetric signatures. This result complements similar work conducted by Poulenard et al. (2009, 2012) on the effect of short immersion durations of less than 1 month on infrared spectra. Whatever spectral range is used, this highlights the need for further investigation with longer times spent in the river, as the transfer time distribution of suspended sediments within rivers could be longer than the 65-day duration tested in this study, as demonstrated by Bonniwell et al. (1999) and Evrard et al. (2010) in mountainous headwater catchments. Even if the variations of the colorimetric parameter values with the time spent in the river water were rather small for our experimental conditions, the impact of this associated signature alteration on the final fingerprinting procedure will be discussed in the following section.

3.4 Colour-based mixing models

Figure 7 shows the performance of the three partial least-squares regression models constructed independently for the three source materials. The determination coefficients were similar for each model (0.99), whereas the root mean square errors were slightly different with values of 1.83, 2.28 and 1.55, for black marls, molasses and limestones, respectively. Considering the whole data set used in the construction of the partial least-squares regression models (i.e. training and validation) led to a median sum of the three predicted source proportions of 100.0% with minimum sums of 97.7% and maximum sums of 103.3%. These rather good results for the sums were only representative of the laboratory mixtures made with the three source soil materials sieved to 63 µm and immersed in the flow for 1 day. We then assessed the performance of these partial least-squares regression models when predicting proportions of source samples with different particle size distribution or different immersion durations than those used to construct the models. As mentioned by Martínez-Carreras et al. (2010a and 2010b) and by Poulenard et al. (2012), error could also propagate in the models because of the spatial variability of the source material signature. Even if the variability of the colorimetric parameters within a group of source material samples was rather low (see Fig. 3), we assessed the errors generated by this spatial variability.

The overall absolute errors were larger, with values of 3.9%, 1.6% and 8.4%, respectively, for the median, the first quartile and the third quartile, whereas these values reached only 1.1%, 0.5% and 2.1% for the training and validation data set used during the construction of the partial least-squares regression models. Errors for the samples that were immersed for different durations in the river (Table 1) were rather small with a median value of 3.1%. Whilst these latter allowed to isolate the errors associated with the alteration of the signatures due to immersion, errors in Table 2 included not only the effect of particle size, but also the effect of the spatial variability of the source material samples within a single group of source material. The measurements were indeed conducted on individual samples, whereas the models were calibrated on composite samples sieved to 63 µm. Thus the median error of 3.3% corresponding to the <63-µm size fraction reflects the effect of spatial heterogeneity of the source materials. It was however not possible to precisely isolate the effect of the size fractions. It should be noted that the median error increased to 11.5% when considering the other size fractions (Table 2). This suggests that the effect of particle size selectivity on the spectrocolorimetric fingerprinting procedure was larger than the effect of spatial heterogeneity or biogeochemical reactions that may have occurred during the particle transit times. The 3rd quartile errors, which was considered to be more realistic than the median error to account for the range of uncertainty, was below 20% for the smallest size fractions, i.e. <63 µm and <20 µm (see Table 2). As on average 98.9% of the suspended sediment samples were smaller than 63 µm, the overall maximum error could reasonably be considered smaller than 20% when applying this spectrocolorimetric fingerprinting procedure to predict the proportion of a source material in suspended sediment sampled during runoff events. However, this uncertainty was only valid in the range of conditions tested in this

study. The uncertainty would be larger if i) suspended sediments had transit times longer than 63 days, ii) particle sizes were finer than 20 µm or larger than 63 µm and iii) suspended sediments came from non-sampled source materials.

As reported previously, calculating the sum of the predicted proportions for the three material sources obtained with the three independent partial least-squares regression models provided a way to control the reliability of the predictions. As the gypsum source material was not retained in the colour-based fingerprinting procedure, we assessed whether the latter control procedure was able to identify that a problem occurred when we conducted our fingerprinting approach on the samples. Therefore VIS measurements were conducted on the <63-µm fraction of 20 gypsum source material samples as if they were suspended sediments sampled during runoff events. The three partial least-squares regression models were then applied to the measurement data sets in order to obtain predicted proportions of black marls, molasses and limestones. The sum of the three predicted proportions was on average 145% with maximum values of 180%, suggesting that the control procedure could detect problems during the fingerprinting approach. This control procedure should be considered as a necessary but not a sufficient condition to confirm the reliability of the method. When the sum is very different from 100%, as for the gypsum samples, there is definitely a problem with the model. However the sum might be close to 100% and there will be no guarantee that the model is correct.

3.5 Prediction of source material proportion in suspended sediment samples collected during runoff events

The uncertainty associated with the spectrocolorimetric fingerprinting procedure could be considered as rather high, in comparison with errors reported by the conventional fingerprinting approach studies based on geochemistry and radionuclide properties (Collins et al. 2012). However, one may wonder if these errors are acceptable given the range of variations in the proportions of sources during a runoff event. In order to assess how much the suspended sediment source varied during runoff events at the Galabre river outlet, we applied the partial least-squares regression models to predict the proportions of black marls, limestones and molasses during 23 runoff events recorded and sampled between November 2007 and November 2011. On average, for the 328 suspended sediment samples collected and analysed, the sum of the three predictions reached 106%. For 18 out of the 23 runoff events analysed, the corresponding sums remained below 120% for all the intra-event suspended sediment samples (Fig. 8). For four of the five remaining runoff events, only one or two suspended sediment samples were characterised by unusually high sum values (maximum, 141%). However, almost half (11) of 23 suspended sediment samples collected during the remaining 07/07/10 runoff event were characterised by predicted black marl proportions larger than 120% (see Fig. 8).

For the 23 runoff events, the predicted limestone proportions remained small (10% on average), which should be considered as negligible regarding the estimated uncertainty associated with the

colour-based fingerprinting procedure. Only 18 suspended sediment samples exhibited predicted limestone proportions higher than 20%. The suspended sediment samples were therefore mostly composed of black marls and molasses, both exhibiting concomitant variations in their proportions, as illustrated by the numbers in figure 8 showing their temporal evolution during the 08/11/11 runoff event. In order to assess the value of applying spectrocolorimetric tracing to the maximum of samples within runoff events, we calculated the variation of each predicted black marl proportion from one sample to the next collected automatically during a runoff event. We restricted this analysis to black marls because they exhibited concomitant variations in their proportions with molasses. The runoff events were then classified into three different groups based on an a priori criteria, i.e. the number of samples within an event characterised by variations higher than 50% (Table 3). Events from the first group had predicted proportions smaller than 10%, i.e. remaining stable throughout the runoff event. Events from the second group had only one sample with variations higher than 50%. The highest variations were observed in the early moments of runoff events, decreasing rapidly to values smaller than 25%. Events from the third group were characterised by highly variable predicted proportions from one sample to another. More than half of the 23 runoff events were considered as highly variable. Even though the first two groups of runoff events could be well characterised in terms of source material dynamics by analysing no more than three or four suspended sediment samples during an event, applying the same strategy for runoff events of the last group would lead to a complete misunderstanding of the hydro-sedimentary processes.

For two of the 23 runoff events (22/11/07 and 12/08/08), proportions of sources determined by two other tracing methods were available, i.e. the method combining diffuse reflectance infrared Fourier transform spectrometry with partial least-squares regression (Poulenard et al. 2012) and a more conventional geochemical fingerprinting method (Navratil et al. 2012). Figure 9 shows a general good agreement between the methods if the uncertainty associated with the predicted black marl proportions is considered. The differences between the different fingerprinting techniques may be largely due to i) the ability of each method to consider the variability of the source materials' fingerprinting properties from the step of selecting the most discriminating tracers to the predictive model construction step, ii) the potential alteration of the selected fingerprinting properties during the transit of particles in the watershed, recognising that different techniques are more or less sensitive to these alterations depending on the properties selected.

To conclude with the potentiality of the spectrocolorimetric fingerprinting procedure, it is clear that two main limitations remain in comparison with conventional fingerprinting methods. The first one is the lack of discrimination compared to sources other than the primary source materials, such as the undifferentiated deposits in this catchment. As mentioned by Martínez-Carreras et al. (2010c), this lack of discrimination may also be a limitation for larger catchments characterised by a greater variability in the colorimetric signatures. This issue should be further investigated, for example by combining the method presented in this study with conventional fingerprinting methods. The second

limitation is the rather high errors on the predicted proportions of source materials. Even if these limitations exist, the main advantages of the procedure (i.e., low cost and rapidity) facilitate the achievement of numerous measurements and hence high-resolution predictions of proportions of primary source materials in suspended sediment samples, which is essential for better understanding the behaviour of headwater catchments exhibiting highly variable hydro-sedimentary dynamics.

4 Conclusions

The colour-based fingerprinting approach conducted in a 22-km² mountainous catchment demonstrated that four of the five main source type materials, i.e. black marls, limestones, molasses and gypsisols, could be discriminated by means of spectral measurements conducted in the visible range. However, it was not possible to fingerprint the undifferentiated deposits, composed of a mix of the four other source materials in various proportions. This should be considered as the technique's main limitation. The colour-based fingerprinting approach was found to be able to discriminate the primary source materials.

As the suspended sediment samples were enriched in particle sizes finer than (roughly) 20 µm in comparison with source materials, which is rather small for a rapidly flowing river, the conservativeness of the colour-based signatures was challenged. Another debated issue was the potential alteration of spectrocolorimetric signatures during the transit of the suspended sediments in the hydrographic network, as suspended sediment transit times within the river channel can be larger than the concentration time of the catchment. The experiments designed to answer these two questions revealed that the effect of particle size on the colour signature was higher than the effect of the duration of sediment immersion in the river water. A maximum 16% variation of the colorimetric parameters was measured between the <63 µm fractions and the other size fractions observed during runoff events, whereas a maximum variation of 10% was measured in the samples having been immersed between 1 and 63 days. Nevertheless, these rather high variations did not generate excessive uncertainty through the partial least-squares regression mixing the calibration and prediction procedure, because an error of 20% should reasonably be associated with the predicted proportions of source materials in suspended sediment samples. Such uncertainty remained much higher than the uncertainty associated with the conventional fingerprinting approach and could certainly be reduced. Since the effect of particle size was found to be significant, we could for instance have considered applying correction factors, as is done in mixture models of conventional fingerprinting approaches. This would mean routinely measuring the particle size distributions, which is time-consuming, and could reduce one of the main advantages of this alternative method, i.e. analytical rapidity.

Finally, the application of the partial least-squares regression models to 23 runoff events revealed that the predicted proportions of black marls and molasses were highly variable within runoff events that occurred in the Galabre catchment from November 2007 to November 2011. The data set produced

with this colour-based fingerprinting approach on a significant number of runoff events, each being well documented, should now be analysed considering the positioning of the source materials in the catchment, the spatiotemporal meteorological radar data, the time series of discharges and concentrations at the outlet. This should offer new insights into the hydrosedimentary processes and assessing the performance of distributed hydrological models.

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650 **List of figures**

651

652 **Fig. 1** Location of the Galabre catchment (a) with maps of the eroded areas, lithology and sampling
653 sites (b).

654 **Fig. 2** Artificial laboratory samples prepared by mixing the three source materials (i.e. black marls,
655 limestones and molasses) in controlled proportions.

656 **Fig. 3** Source material discrimination considering L* and a* parameters. The spectroscopic
657 measurements were taken on the <63-µm size fraction. The number of collected source samples are in
658 parentheses.

659 **Fig. 4** Boxplot of the dispersed size fractions for suspended sediments and source material samples.
660 Black circles and white triangles correspond to outliers. The percentages were calculated considering
661 (a) the <63-µm size fraction, (b) the <31-µm fraction and (c) the <16-µm fraction. The symbol * at
662 the end of each fraction label indicates that the two populations, i.e. suspended sediment and source
663 material, were significantly different according to the Dunn test.

664 **Fig. 5** Colorimetric parameter values for various size fractions of (a) molasses, (b) limestones and (c)
665 black marl samples. Gray circles indicate that measurements were significantly different from those
666 performed on the <63-µm fraction according to Dunn test.

667 **Fig. 6** Various colorimetric parameter values with time spent in the river for (a) molasse, (b)
668 limestone and (c) black marl samples. Gray circles indicate that measurements were significantly
669 different from those taken after 1 day in the river according to the Dunn test.

670 **Fig. 7** Results of the partial least-squares regression models for (a) molasses, (b) limestones and (c)
671 black marls. Each model was constructed independently with the same set of 81 artificial laboratory
672 mixtures.

673 **Fig. 8** Predicted source material proportions in suspended sediment samples collected at the outlet of
674 the Galabre catchment using the partial least-squares regression models presented in Fig. 7. For each
675 of the 23 runoff events, a set of 5 to 23 suspended samples were collected during the event
676 and four measurements were conducted with the spectrophotometer on each sample (black
677 circles). The numbers above each group of four circles illustrate the temporal evolution of the
678 proportions of black marls and molasses during the 08/11/11 runoff event.

679 **Fig. 9** Comparison of the black marl proportions predicted by the partial least-squares regression
680 model presented in Fig. 7c and by other fingerprinting methods (Poulenard et al. 2012; Navratil et al.
681 2012). The samples were collected during the 22/11/07 and 12/08/08 runoff events. Error bars
682 correspond to the estimated uncertainty. The dashed line is the 1:1 line.

List of tables

Table 1 Statistics of the absolute errors between actual and predicted proportions calculated using the partial least-squares regression models presented in Fig. 7 detailed for each source material and for various immersion durations in the river. Different letters given in brackets after the median error indicate significant differences between immersion times according to the Dunn test.

Table 2 Statistics of the absolute errors between actual and predicted proportions calculated using the partial least-squares regression models presented in Fig. 7 detailed for each source material and for various size fractions.

Table 3 Statistics of the variations from one suspended sediment sample to the next collected during a flood event of the predicted black marl proportion.

Table 1 Statistics of the absolute errors between actual and predicted proportions calculated using the partial least-squares regression models presented in Fig. 7 detailed for each source material and for various immersion durations in the river. Different letters given in brackets after the median error indicate significant differences between immersion times according to the Dunn test.

	Immersion time (days)	Number of samples	Median error (%)	1st quartile (%)	3rd quartile (%)
Black marl	0	12	1.7 (a b)	0.8	13.5
	7	36	2.8 (a b)	0.5	4.7
	14	36	1.2 (a)	0.5	4.0
	35	36	4.0 (b)	2.1	6.9
	63	36	2.5 (a b)	1.0	3.8
Molasse	0	12	12.9 (a)	5.0	15.9
	7	36	3.2 (b c)	1.6	5.0
	14	36	2.2 (c)	1.0	4.9
	35	36	6.0 (a)	2.4	9.2
	63	36	5.6 (a)	3.2	8.6
Limestone	0	12	3.8 (a)	3.2	12.3
	7	36	2.1 (b)	0.8	3.3
	14	36	0.5 (c)	0.3	1.5
	35	36	5.0 (a)	3.8	6.8
	63	36	4.4 (a)	2.4	6.6
All source samples	All immersion times	468	3.1	1.2	6.0

706 **Table 2** Statistics of the absolute errors between actual and predicted proportions calculated
707 using the partial least-squares regression models presented in Fig. 7 detailed for each source
708 material and for various size fractions
709

	Size fraction (µm)	Number of samples	Median error (%)	1st quartile (%)	3rd quartile (%)
Black marl	<200	20	15.3	12.5	21.7
	<100	20	15.6	8.1	20.2
	<63	20	2.7	1.5	12.8
	<20	20	5.5	3.8	14.8
Molasse	<200	20	19.3	14.6	24.5
	<100	20	16.7	11.3	24.4
	<63	20	5.4	1.8	18.3
	<20	20	11.1	8.9	17.3
Limestone	<200	20	1.9	0.7	5.9
	<100	20	1.9	0.8	3.6
	<63	20	3.0	1.6	3.9
	<20	20	7.7	6.0	12.9
All source samples	<63	60	3.3	1.8	16.6
All source samples	All sizes except <63µm	180	11.5	4.2	19.4

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712 **Table 3** Statistics of the variations from one suspended sediment sample to the next collected
713 during a flood event of the predicted black marl proportion.
714

Runoff event	Number of samples with variation > 50%	Mean variation (%)	Std. Dev. (%)	Range (%)
03/05/11	0	3	4	7
14/10/08	0	0	1	3
22/11/07	1	11	15	42
11/01/08	1	13	13	39
29/05/08	1	11	18	76
12/08/08	1	5	15	60
03/03/09	1	13	8	21
14/12/10	1	13	22	46
30/05/11	1	9	24	68
18/06/08	3	11	27	81
19/09/08	2	6	16	58
31/10/08	6	46	40	100
19/11/08	5	46	47	106
24/06/10	2	34	42	98
15/09/10	3	25	40	110
10/11/10	2	19	20	50
09/06/11	4	25	33	84
05/07/11	2	85	4	5
19/07/11	3	12	28	87
30/08/11	2	18	41	92
28/09/11	2	8	19	60
08/11/11	9	39	33	91

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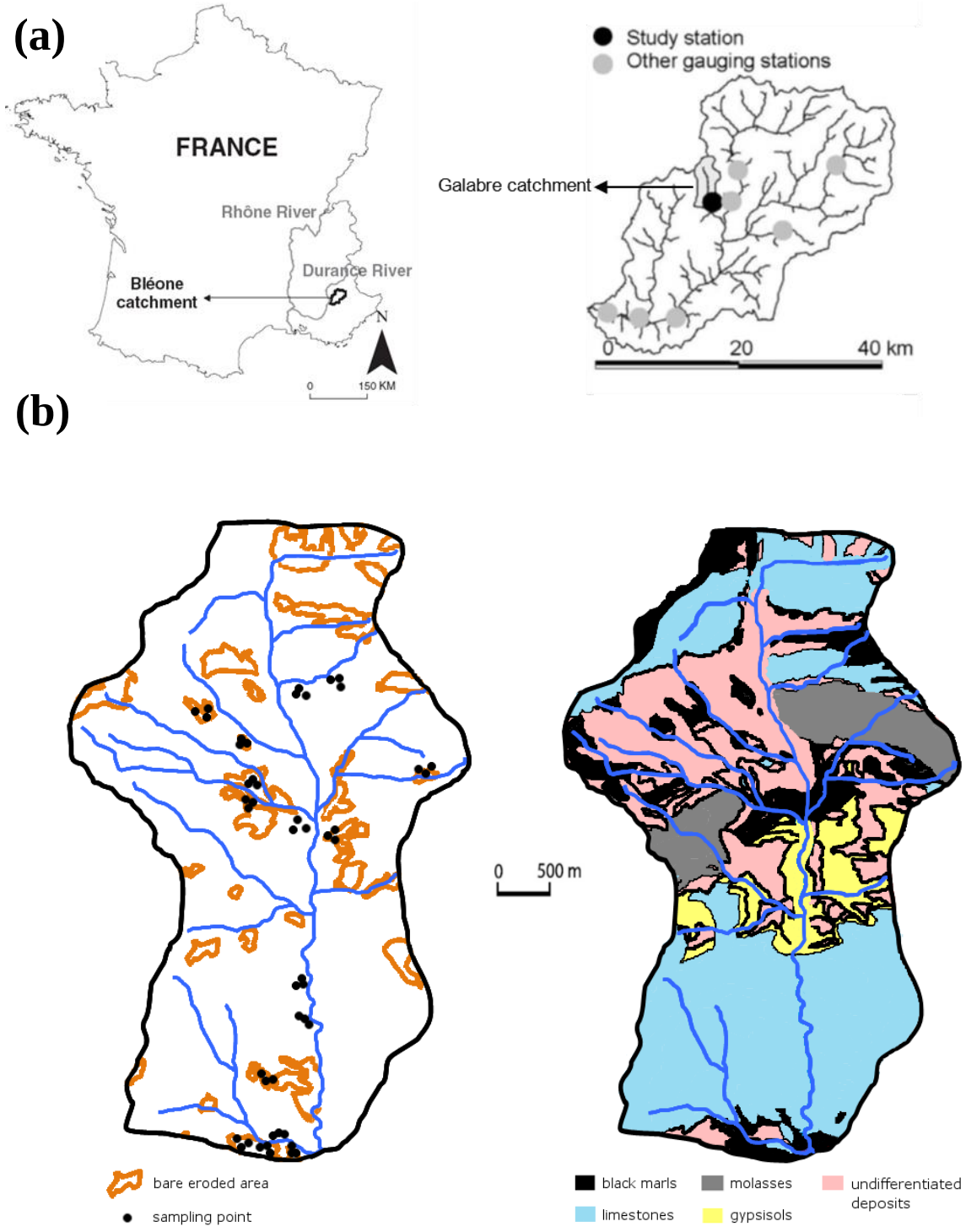

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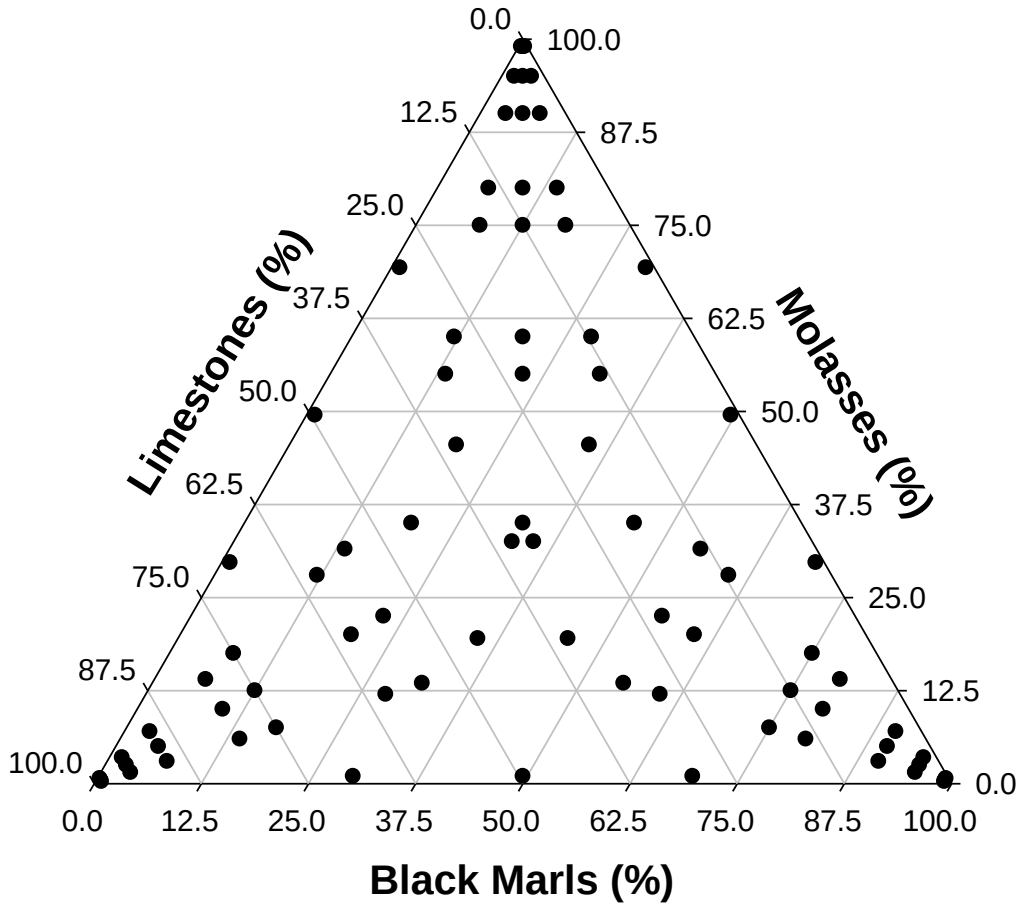

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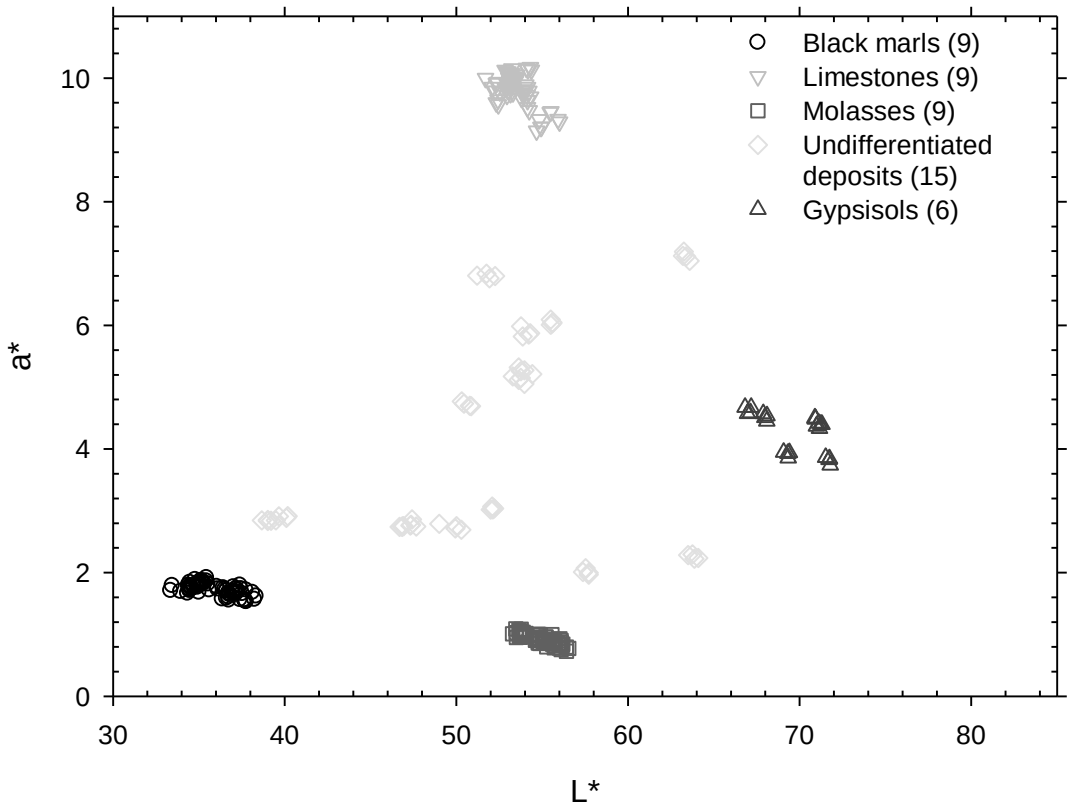

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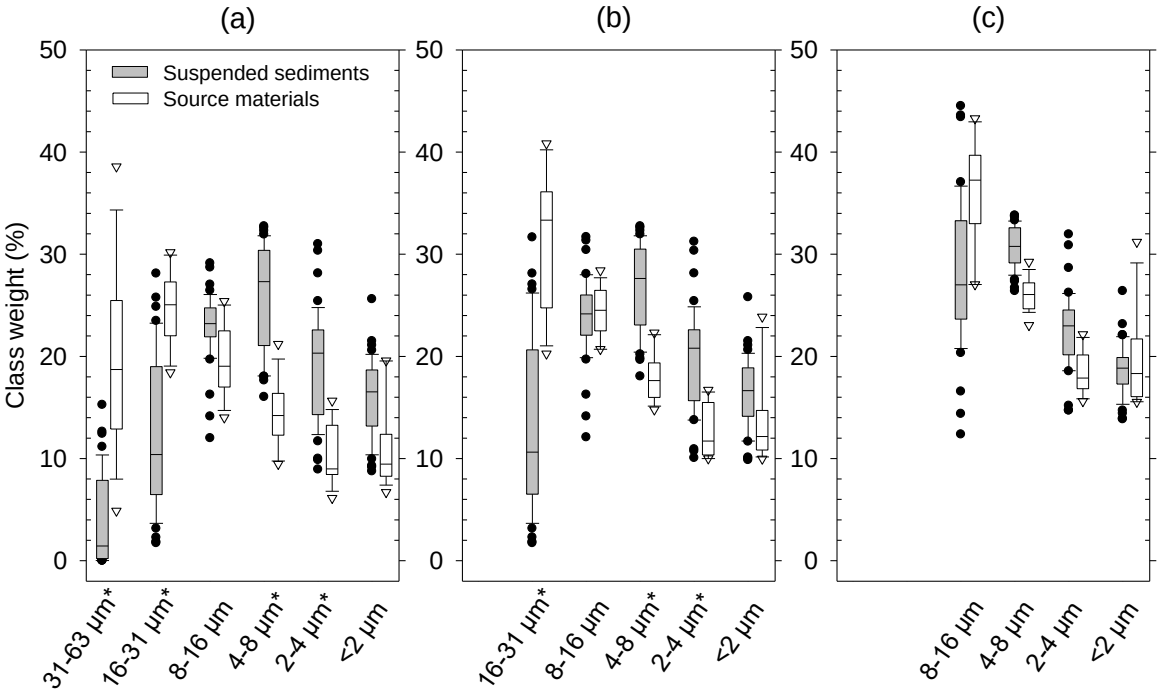

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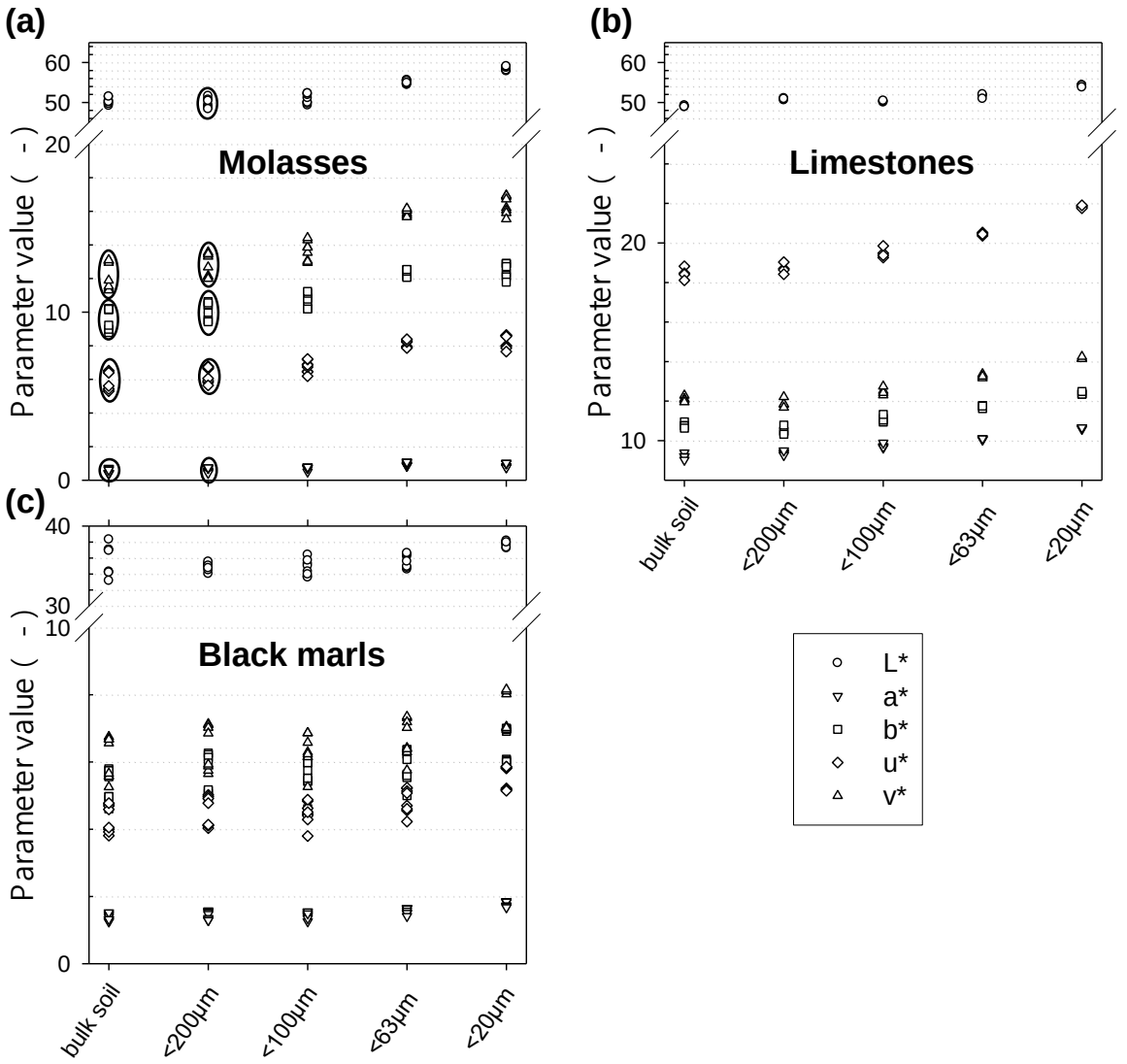

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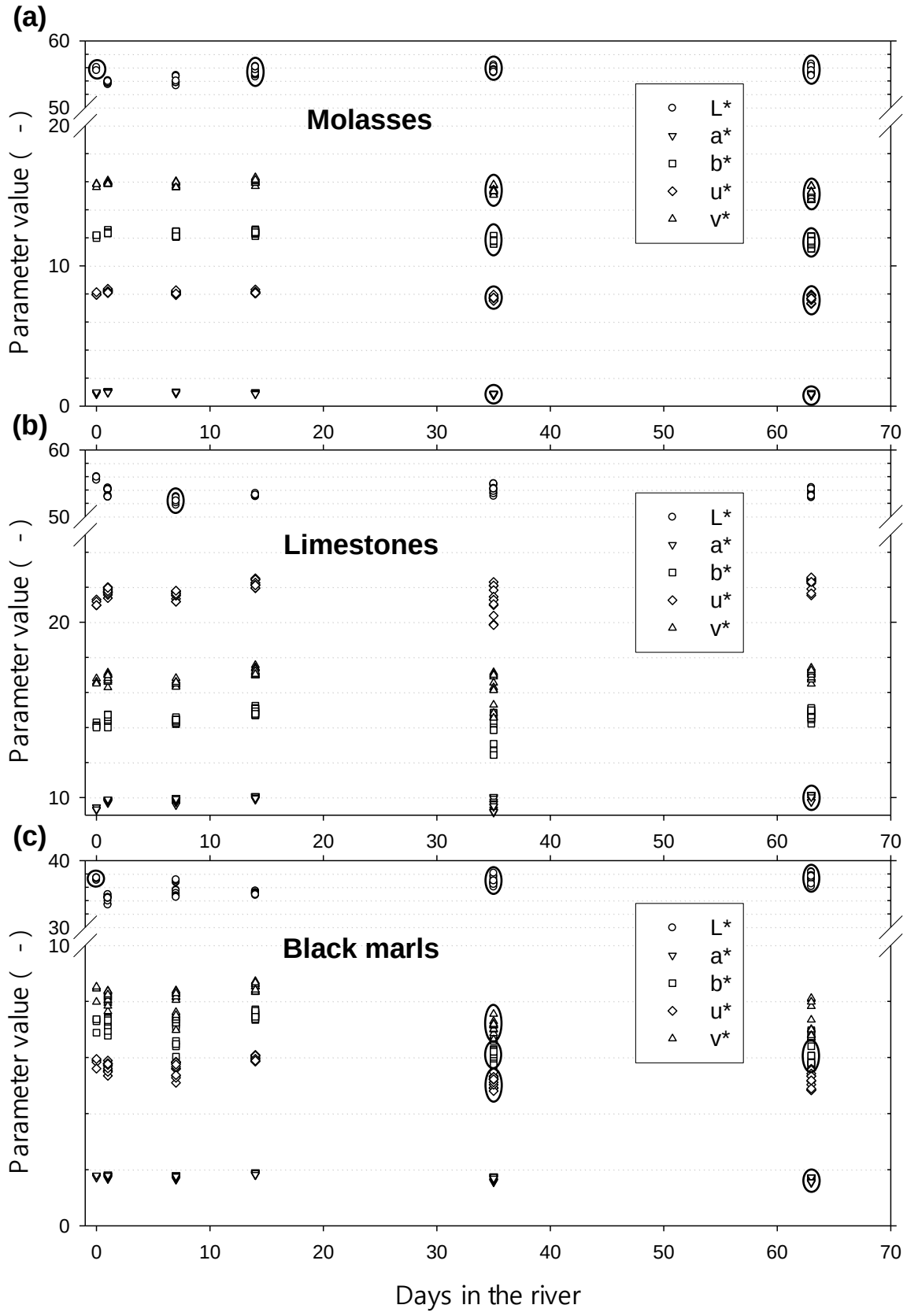

Fig. 6 Various colorimetric parameter values with time spent in the river for (a) molasse, (b) limestone and (c) black marl samples. Gray circles indicate that measurements were

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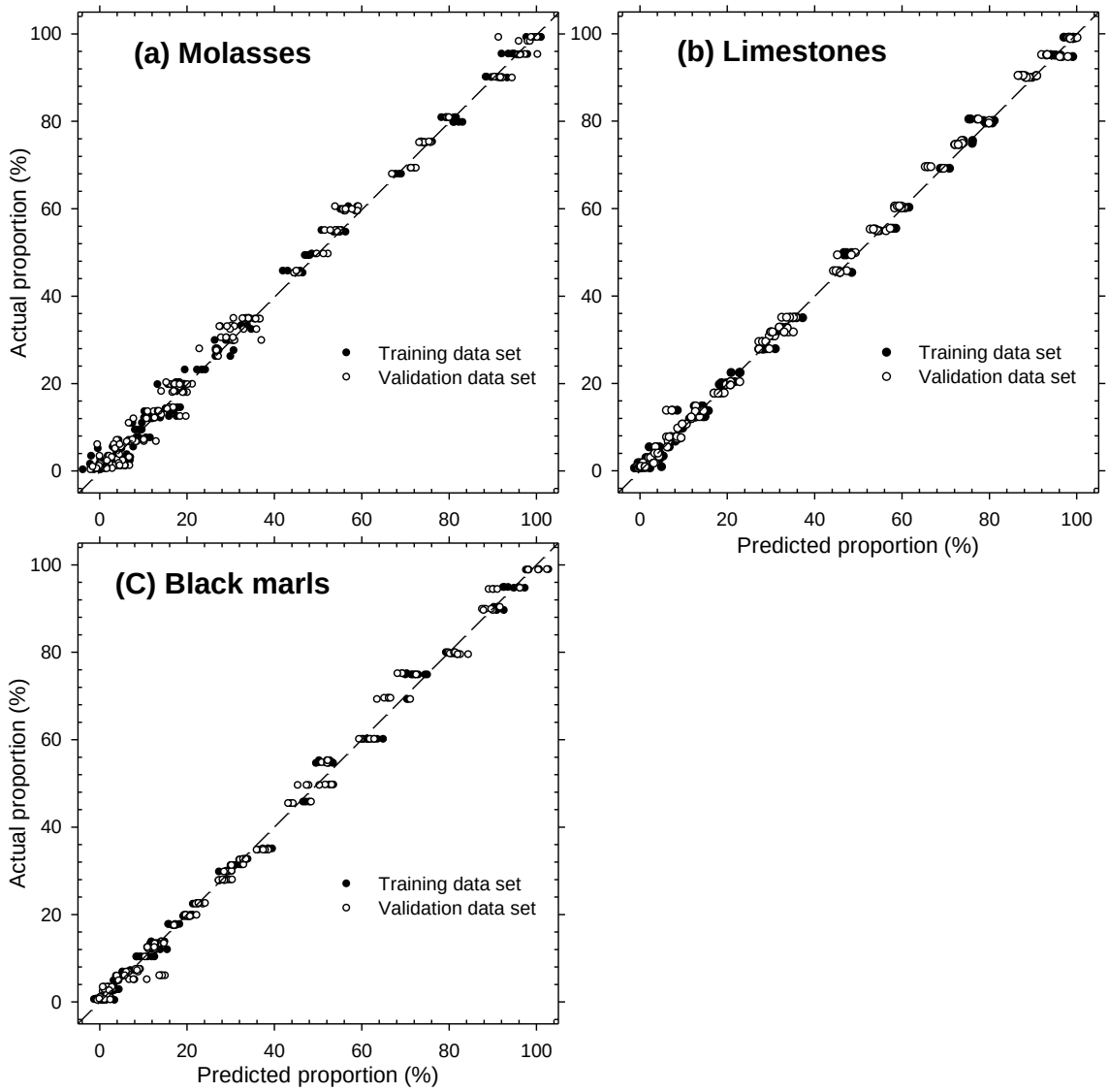

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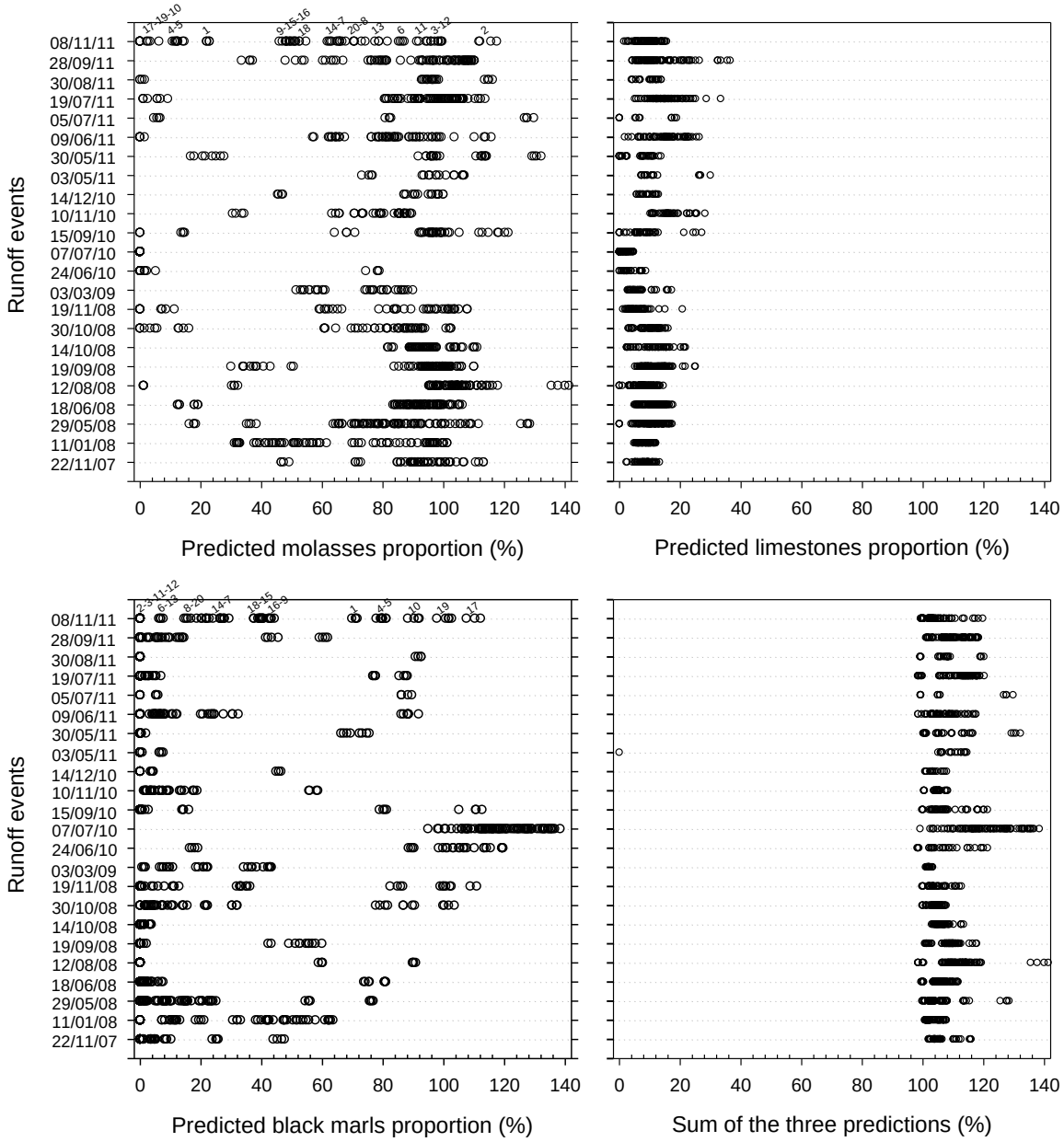

Fig. 8 Predicted source material proportions in suspended sediment samples collected at the outlet of the Galabre catchment using the partial least-squares regression models presented in Fig. 7. For each of the 23 runoff events, a set of 5 to 23 suspended samples were collected during the event and four measurements were conducted with the spectrophotometer on each sample (black circles). The numbers above each group of four circles illustrate the temporal evolution of the proportions of black marls and molasses during the 08/11/11 runoff event.

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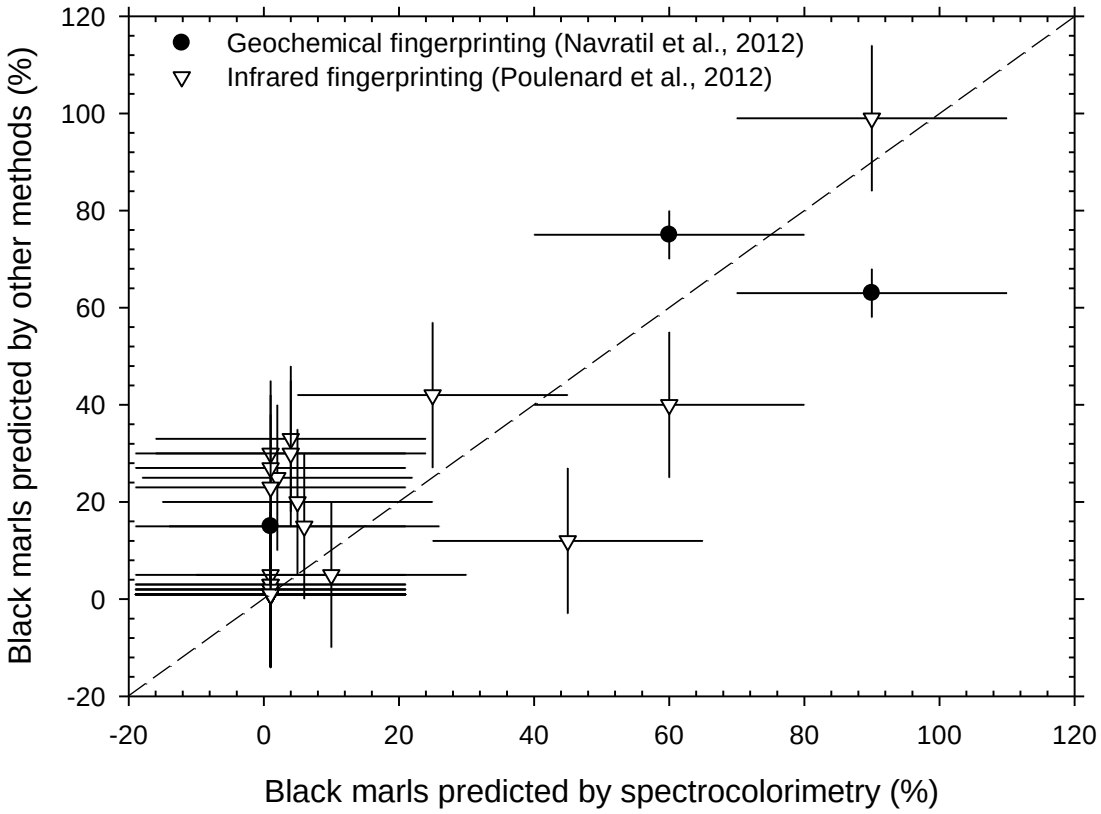

Fig. 9 Comparison of the black marl proportions predicted by the partial least-squares regression model presented in Fig. 7c and by other fingerprinting methods (Poulenard et al. 2012; Navratil et al. 2012). The samples were collected during the 22/11/07 and 12/08/08 runoff events. Error bars correspond to the estimated uncertainty. The dashed line is the 1:1 line.

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