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

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39 **Abstract**

40 In mountainous catchments, large quantities of sediment are exported within very
41 short periods leading to numerous environmental problems (e.g. reservoir siltation).
42 The origin of suspended sediment during two distinct floods was determined by
43 conducting an original fingerprinting method coupling Diffuse Reflectance Infrared
44 Fourier Transform Spectroscopy (DRIFTS) and a chemometric technique (i.e. Partial
45 Least Squares – PLS – analysis). Samples of the potential sediment sources were
46 collected in badland areas developed on various substrates (i.e. molasse, marly
47 limestones, black marls and gypsum) in the Galabre 20 km²-catchment located in the
48 French Southern Alps. DRIFTS spectra provided a way to discriminate between the
49 different potential sediment sources. Furthermore, the use of mid-infrared spectra
50 allowed the direct quantification of the gypsum proportion in sediment. This
51 contribution was systematically null at the catchment outlet because of the rapid
52 dissolution of gypsum in the river. A PLS model was then constructed to estimate the
53 contribution of the three other potential sources to the sediment flux during the
54 floods. This model was developed and validated using a set of 45 "experimental"
55 samples that were prepared in the laboratory in order to contain various proportions
56 of the three remaining sources. By introducing DRIFTS spectra into the PLS model,
57 we could predict the proportions of those sources in the mixed 'experimental'
58 samples with a confidence interval of ca. $\pm 10\%$. The model was then applied to the
59 sediment collected during the two selected floods in order to outline their origin. Black
60 marls provided the highest contribution of sediment during both events, but the
61 analysis also revealed a significant contribution of molasse. Results also showed the
62 remobilisation of sediment originated from molassic substrates that deposited on the
63 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,

69 **1. Introduction**

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

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

94 One of the strategies that dominated to assess the origin of sediment during
95 floods consisted in analysing hysteresis relationships between the river discharge
96 and Suspended Sediment Concentrations (SSC) (Asselman, 2000). Given that flow
97 velocity – correlated with discharge – controls suspended sediment transport (Klein,
98 1984; Seeger et al., 2004), variations of the relationship between SSC and discharge
99 are traditionally attributed to variations in the quantity of material that is available for
100 transport by the river (Williams, 1989). This suspended material can then either
101 originate from recent hillslope erosion or from the resuspension of sediment stored
102 temporarily in the river bed (Bronsdon and Naden, 2000). Different hysteresis
103 patterns are thus traditionally interpreted by drawing hypotheses on the type and the
104 location of erosion areas involved (Lefrançois et al., 2007; Lenzi and Marchi, 2000;
105 Duvert et al., 2010).

106 To decrease the uncertainties associated with this ‘classical’ monitoring
107 approach, sediment fingerprinting methods were developed in the 1980s to identify
108 unambiguously the sources of sediment (see Walling, 2005, for a review of
109 fingerprinting studies). During the last decades, this approach has been increasingly
110 applied to identify and ‘trace’ several distinctive characteristics of the source material
111 that can be compared to the same characteristics measured on river suspended
112 sediment samples (see Collins and Walling, 2004 and references therein; Foster et
113 al., 2007; Minella et al., 2008). The choice of potential fingerprinting properties is
114 generally guided by the availability of analytical facilities at the laboratory. The most
115 frequently used tracers are radionuclides (^{137}Cs , unsupported ^{210}Pb , ^7Be), and
116 various chemical elements (Stutter et al., 2009). Measurement of those properties
117 was greatly facilitated during the last years, e.g. by the development of Inductively
118 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).

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

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

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

169 **2. Materials and methods**

170

171 **2.1. Study Site**

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

187 **2.2. Monitoring and Sampling**

188 A monitoring station was installed at the outlet of the catchment (22 km²) in October
189 2007. It measured water level with a high frequency (10 minutes) using the radar
190 technique (24GHz, Paratronic Crusoe). A rating curve was constructed to calculate
191 discharges based on the 10 min. frequency water level measurements. Suspended
192 Sediment Concentrations (SSC) were also recorded continuously using a turbidity
193 sensor (WTW, Visolid 700 IQ sensor, time step 10 min). An automatic sampler was
194 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

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

225 These soil samples were compared to suspended sediment samples collected
226 at the monitoring station during two contrasted heavily loaded floods (Figure 2a and
227 2b) identified on the records available in order to determine the proportion of each
228 source to the SS flux at the outlet.

229 The first selected flood lasted six days (21/11/2007 - 27/11/2007). Two flood
230 peaks resulted from low intensity long-lasting winter precipitation (total rainfall depth
231 of 125 mm; mean rainfall intensity of $\approx 1.0 \text{ mm h}^{-1}$ derived from hourly time-step
232 records). The first SSC peak reached 22 g L^{-1} with a maximum discharge of 0.45 m^3
233 s^{-1} and the second reached 60 g L^{-1} with a maximum discharge of $4.2 \text{ m}^3 \text{ s}^{-1}$ (Figure
234 2b). A third peak discharge ($5.9 \text{ m}^3 \text{ s}^{-1}$) occurred afterwards, but it did not lead to any
235 significant increase in SSC. Overall, during this flood, the SSC peak led the
236 discharge peak. It was characterised by a clockwise SSC-discharge relationship.

237 The second flood that we selected occurred between 12/08/08 and 14/08/08
238 (Figure 2c). It was typically triggered by a short and heavy summer storm (total
239 rainfall depth of 24.3 mm; mean rainfall intensity of 5.8 mm h^{-1} , derived from 10 min.
240 time-step records). Peak SSC reached 140 g L^{-1} with a maximum peak discharge of
241 $0.81 \text{ m}^3 \text{ s}^{-1}$. SSC peak occurred later than peak discharge, defining an anticlockwise
242 SSC–discharge relationship.

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

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

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

255 **2.3. Spectroscopic and chemometric analyses**

256 *Spectroscopic measurements*

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

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

268 500 ml of river water. The scraping was in this case easy. We have also studied the
269 filters by DRIFTS . Background signal / noise (?) was checked on clean filters, and
270 reliable spectra were obtained with 25 mg of materials in the filters. The spectra
271 obtained by the two methods were similar (data not shown). We have finally preferred
272 to apply the scraping technique on the suspended sediment to have the same nature
273 of samples (i.e. a powder) for both soils and suspended sediment.

274 A ThermoNicolet 380 spectrometer equipped with a liquid-nitrogen cooled
275 MCT (Mercury – Cadmium – Telluride) detector was used to perform the Fourier
276 Transform Infrared (FT-IR) analysis. Spectra were obtained using the diffuse
277 reflectance (DRIFTS) measurement technique. The spectra scan range was 4000 –
278 650 cm^{-1} at a resolution of 2 cm^{-1} with 32 co-added scans per spectrum. Results
279 were then compiled using the OMNIC[®] (version 7.3) software provided by the
280 spectrometer manufacturer (ThermoNicolet, USA). This software facilitated the
281 measurement of the peak areas that were relevant to determine the DRIFTS
282 properties.

283 *Statistical analysis and PLS model*

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

293 Relationships between DRIFTS spectra ('x' variates) and the corresponding
294 weight contribution of the sediments sources datasets ('y' variates) were assessed
295 using Partial Least Square (PLS) analyses. PLS regression models are powerful
296 tools for analyzing multivariable data (Martens and Naes, 1992). These models offer
297 a solution to derive quantitative predictions related to chemical mixtures (Wold et al.,
298 2001). In this study, we derived separate PLS models for each sediment source.
299 When drawing up a PLS model, the first step consists in determining the number of
300 components that will provide the best compromise between the description of the
301 calibration set and the model predictive power. The Kennard and Stone - KS-CV -
302 validation method was then conducted to confirm the number of components to
303 introduce into the model (Kennard and Stone, 1969). It provided an evaluation of the
304 uncertainty associated with the predictions generated by the PLS model when it was
305 applied to an unknown sample. To this end, the KS-CV algorithm selected samples
306 for which the predictors were the most distant, as indicated by their high Euclidean
307 distances. For this training subset, the lowest predictive standard error (PRESS)
308 value was found for three components. The predicted values for the test set were
309 then compared to the actual values by calculating root mean-square errors of
310 prediction (RMSEP). Independent PLS models were constructed to estimate the
311 proportions of each main potential sources of sediment.

312 ***2.4. Conservativeness of DRIFTS properties in river***

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

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

321 **3. Results and discussion**

322 ***3.1. Discrimination of sediment sources by DRIFTS analysis***

323 Figure 3a shows the typical DRIFTS spectra derived for the main lithological sources
324 of sediment (i.e., topsoil collected in badlands areas) found in the Galabre catchment.

325 A preliminary qualitative analysis of those DRIFTS spectra allowed us to distinguish
326 the major types of materials. Soils developed on gypsum substrates are
327 characterized by the peaks that are classically associated with CaSO_4 (Farmer,
328 1974) located around 3500 cm^{-1} and between $2370 - 2060\text{ cm}^{-1}$. DRIFTS spectra of
329 the soils developed on other substrates consisted clearly of a mixture of carbonates
330 (with the corresponding peaks at $2800-3000\text{ cm}^{-1}$, $2430-2640\text{ cm}^{-1}$, 1800 cm^{-1} etc.),
331 aluminosilicates in the $3500-3700\text{ cm}^{-1}$ region and quartz (e.g. at $796/776\text{ cm}^{-1}$). A
332 simple calculation of the peak areas corresponding to those main constituents
333 provided a first way to discriminate the lithological origin of sediment (Figure 3b).

334 Given the existence of specular distortions (Reeves et al., 2005), this approach
335 cannot provide a quantitative estimation of the sediment composition. This method
336 constitutes a semi-quantitative approach to exploit information contained in the
337 spectra. Soils developed on molasses were characterized by large calcite (CaCO_3)
338 peak areas (between 2430 and 2640 cm^{-1} in Figure 3b) and large aluminosilicate
339 peak areas (3500 and 3700 cm^{-1}). This result was consistent with the composition of
340 this marine molassic material dominated by carbonated sandstones (Haccard et al.,
341 1989). In contrast, black marls exhibited a large aluminosilicate peak area and a
342 small CaCO_3 peak area. Then, soils developed on marly limestones displayed large

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

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

356 ***3.2. Determining the contribution of gypsisols to sediment***

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

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

376 **3.3 Determination of the sediment origin during the selected floods**

377 *Construction of the PLS model*

378 Quantifying the contribution of the three relevant sources to sediment collected
379 in the river required the preparation of 45 experimental samples by mixing the three
380 remaining types of sources (i.e. black marls, marly limestones and molasses) in
381 various proportions (Figure 4a). Samples corresponding to those three source types
382 consisted themselves in a mix of several (from 3 to 5) individual subsamples
383 collected in different parts of the catchment. Twenty-five samples (chosen randomly)
384 were used for validation set and 20 samples for calibration. Figures 4b, 4c and 4d
385 show that there was a good agreement between the actual proportions of the
386 different sources in the experimental mixed samples and the corresponding
387 proportions calculated by the PLS model. R^2 coefficient varied between 0.992 and
388 0.997. Resulting RMSEP varied between 1.9 and 3.5. Given we wanted to assess the
389 contribution of different sediment sources in a mixed sample, these errors remained
390 acceptable. During the calibration step, variations of the contributions predicted by
391 the model with a 95% confidence interval fluctuated by $\pm 10\%$ (dotted line on Figure
392 6b, c and d). We subsequently used this confidence interval to quantify the

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

399 *Conservativeness of DRIFTS signatures*

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

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

414 *Application of the PLS model to the suspended sediment*

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

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

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

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

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

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

482 Then, during the second rising stage of the flood (23 November), the bulk of
483 sediment originated from hillslopes and was supplied by black marls with a
484 progressively increasing contribution of molasse material throughout time. Behaviour
485 during this stage was similar to the one observed during the 12-13 August 2008 flood
486 and can be associated with the sediment supply by the succession of lithological
487 sources located along the river. We attributed the relatively low marly-limestone
488 contribution ($\pm 10\%$ throughout the event) calculated during the two flushing stages of
489 21-27 November 2007 flood to the limited stock of marly-limestone material available
490 in the river, which was probably due to the winter low-intensity rainfall regime that led
491 to a low mobilisation of such materials.

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

497 **3.4 Interest and limit of the DRIFTS-PLS fingerprinting approach**

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

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

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

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

533 **4. Conclusions**

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

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

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564

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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 2430-2640 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 2370-2060 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

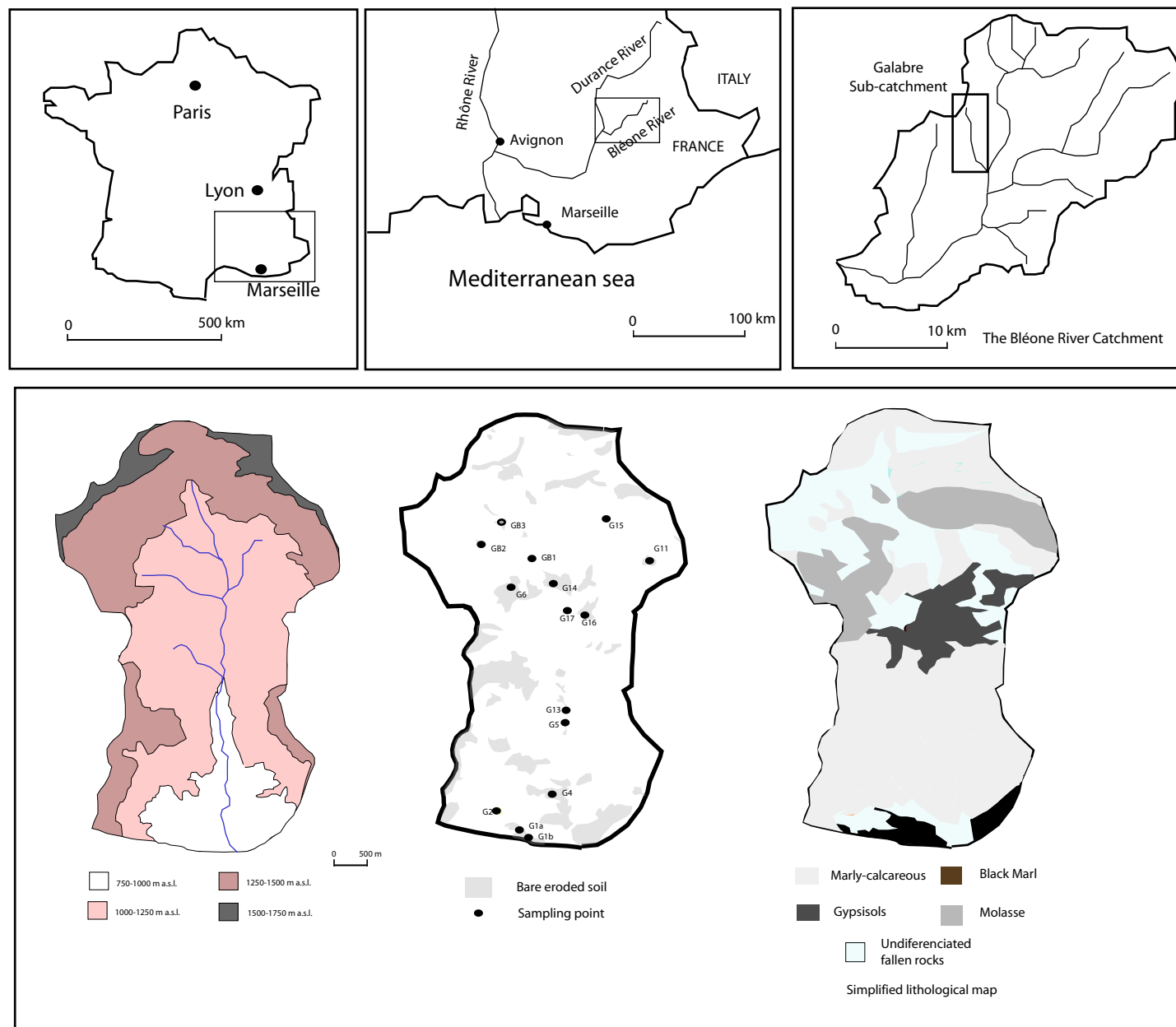
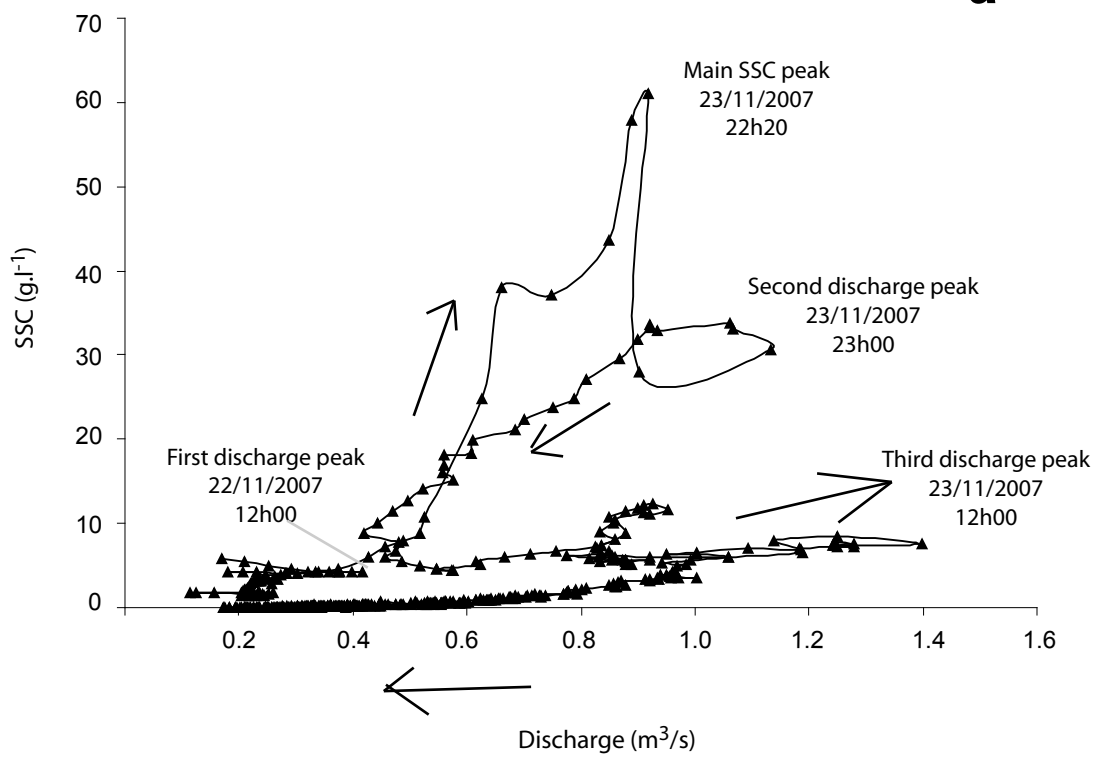


Figure 2

22/11/2007 event



12/08/2008 event

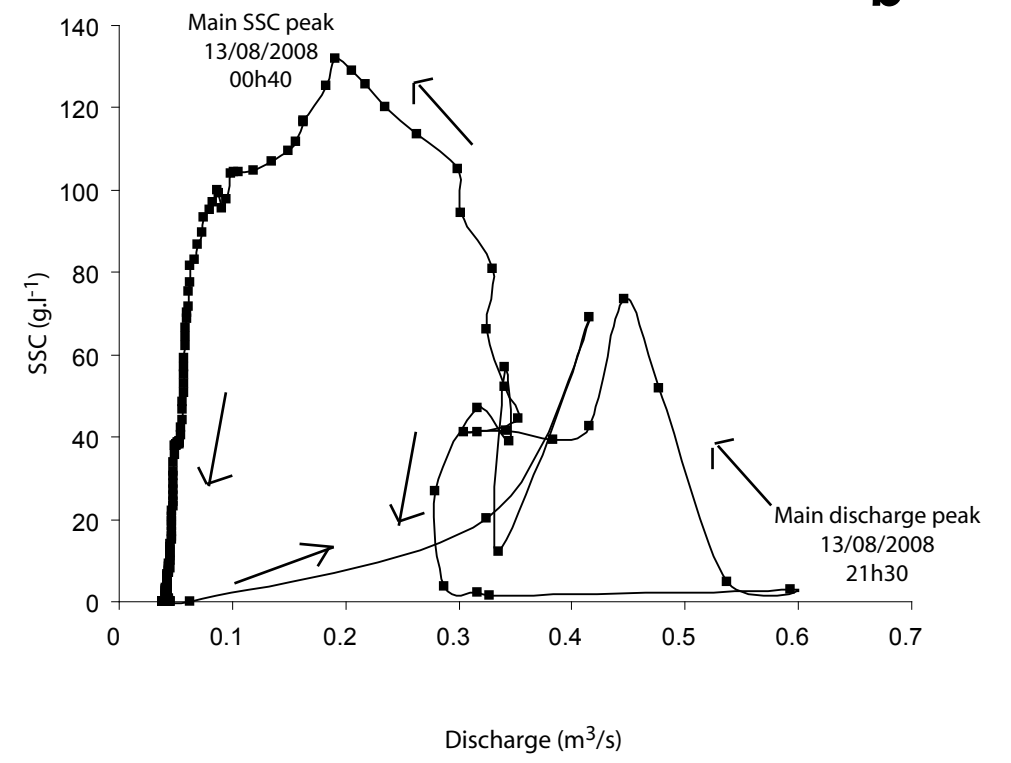


Figure 3

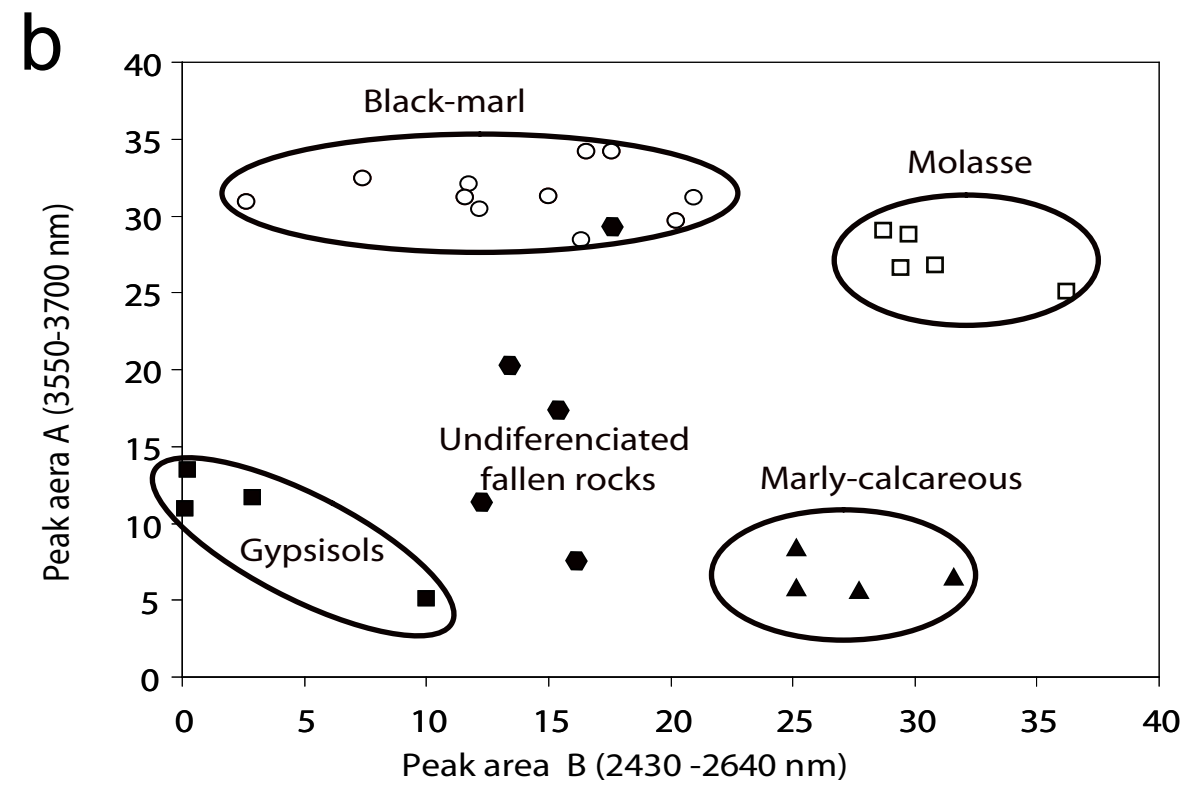
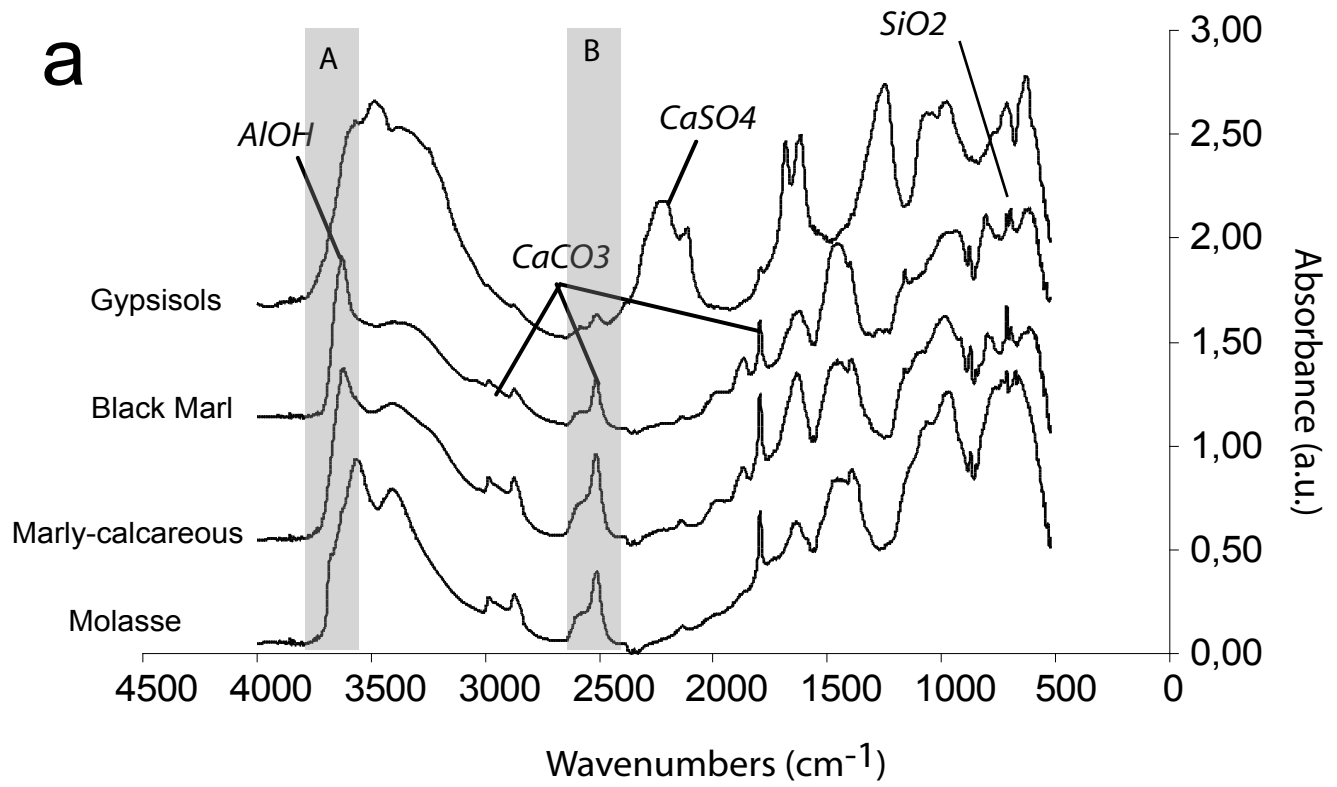


Figure 4

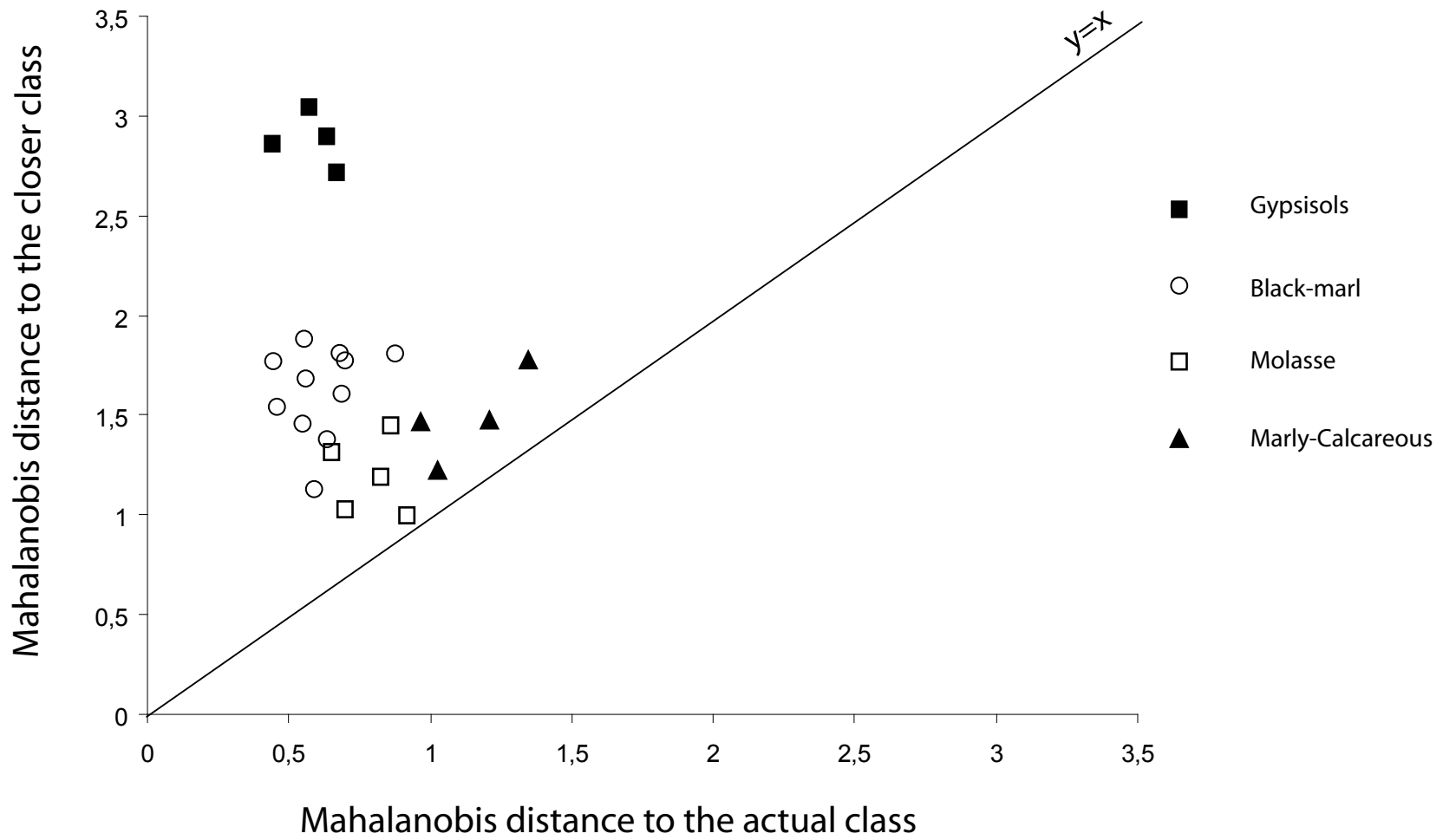


Figure 5

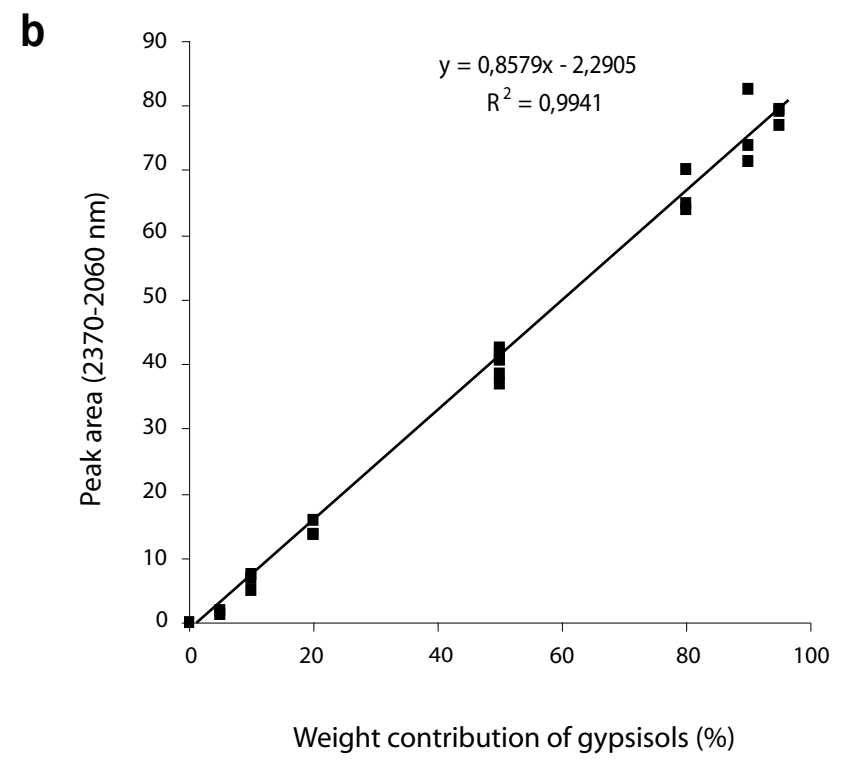
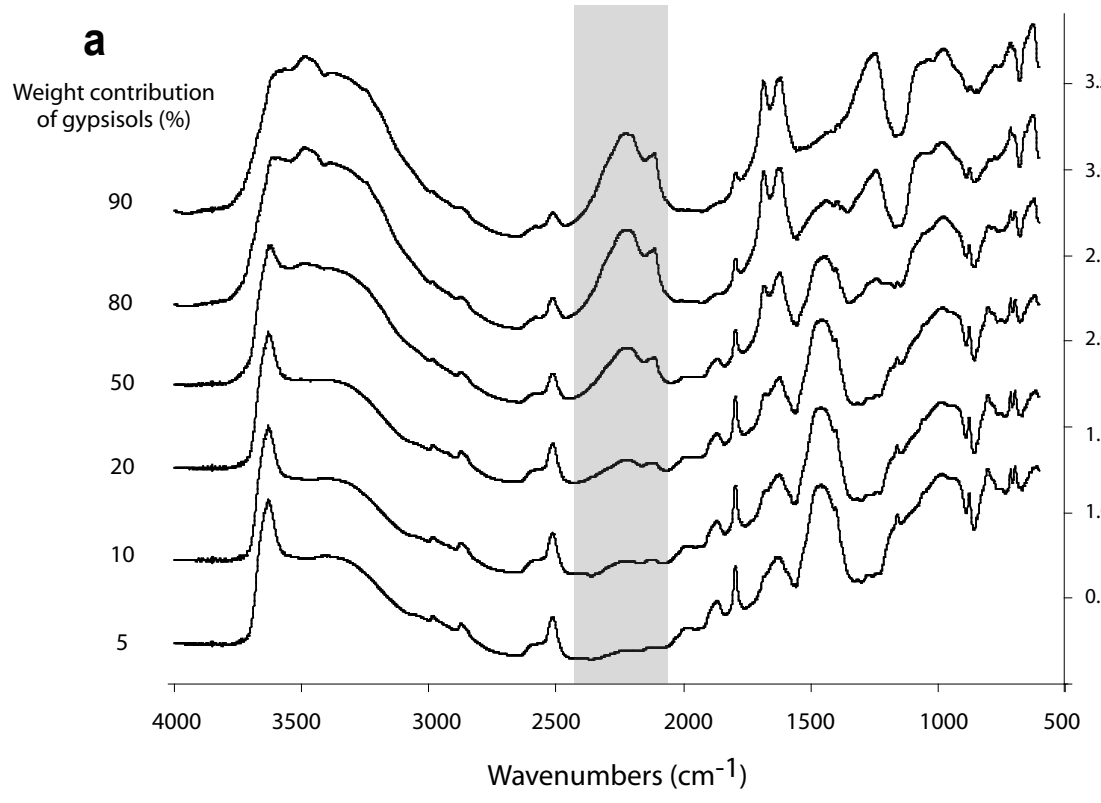
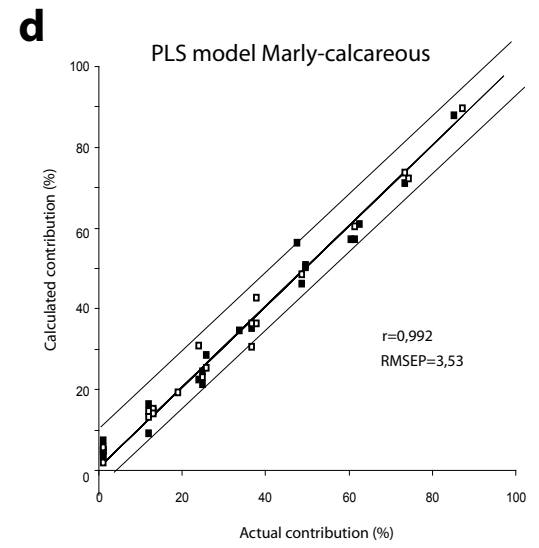
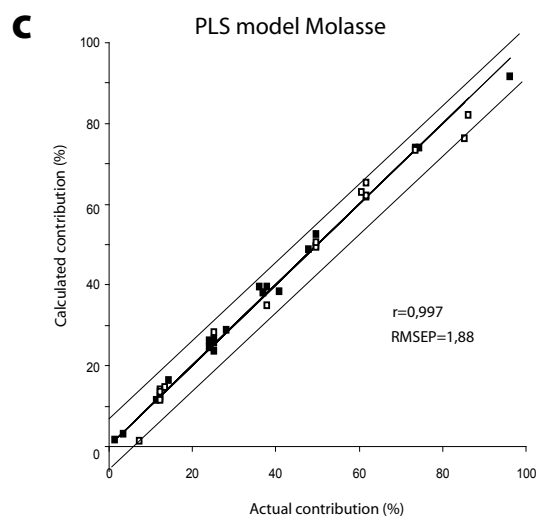
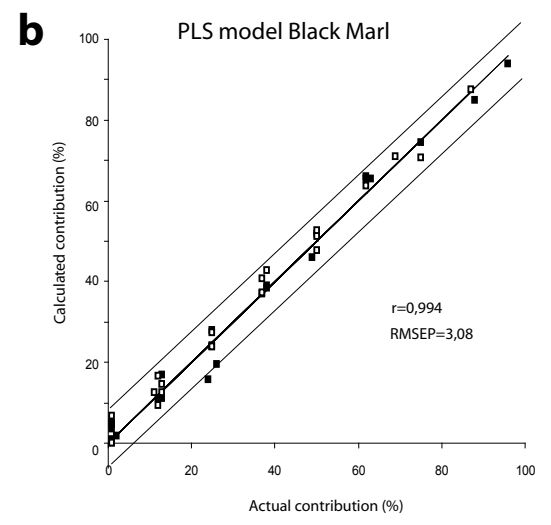
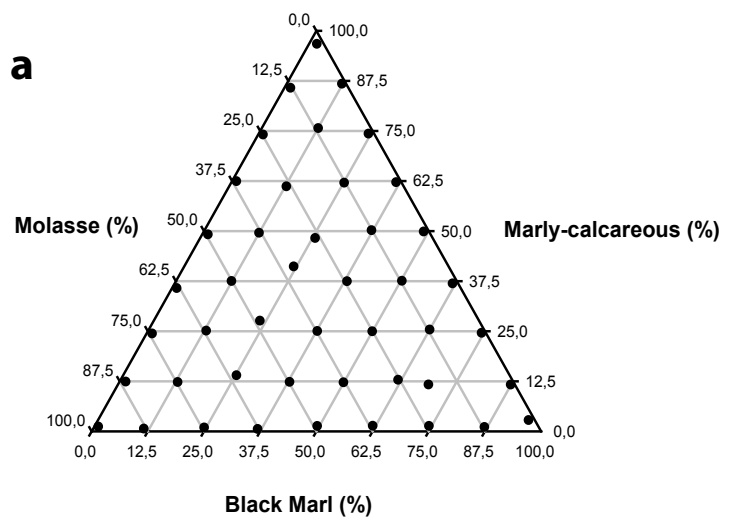


Figure 6



— $y=x$

■ Calibration

□ Validation

Figure 7

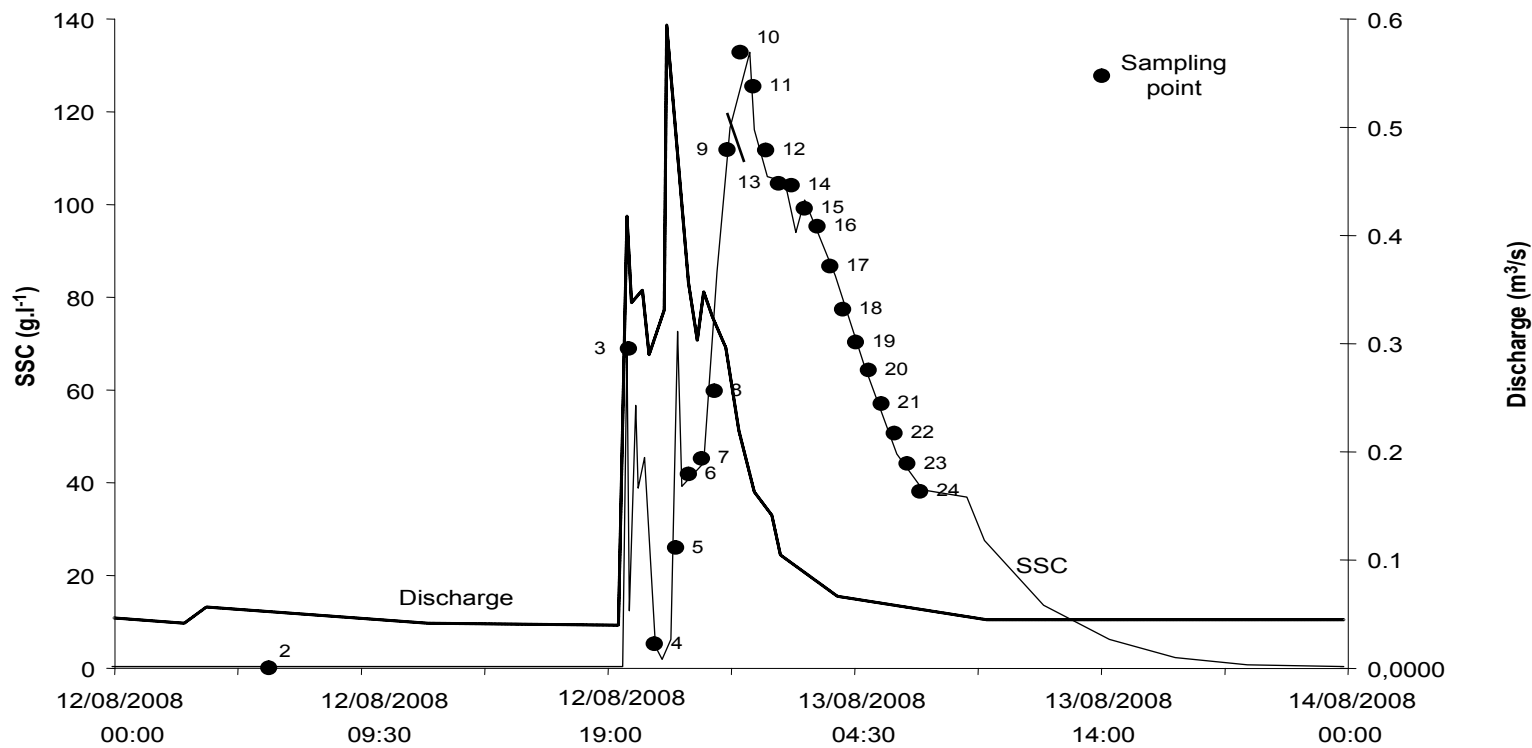
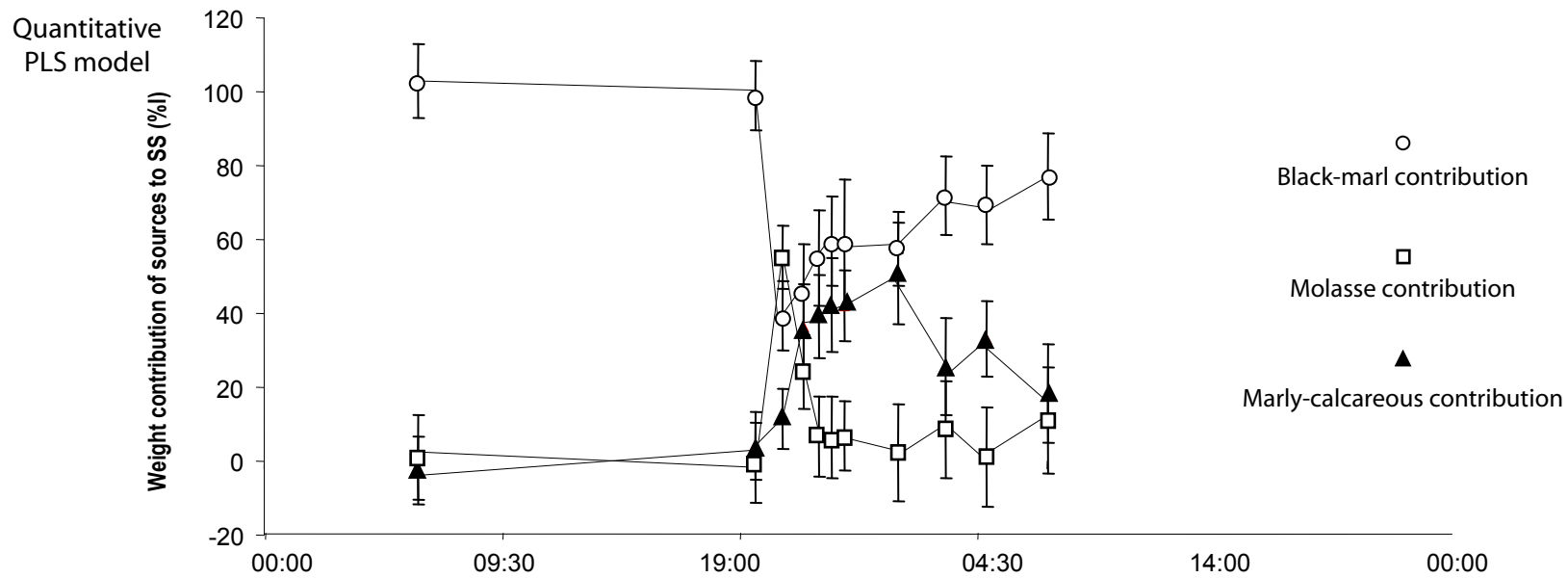


Figure 8

Quantitative
PLS model

