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1 **High-resolution prediction of organic matter concentration with**
2 **hyperspectral imaging on a sediment core**

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- 1 **Keywords:** Hyperspectral Imaging, Chemometrics, Near-Infrared Spectroscopy, High
- 2 Resolution Analysis, Organic Matter
- 3

4 **Abstract**

5

6 In the case of environmental samples, the use of a chemometrics-based prediction model is
7 highly challenging because of the difficulty in experimentally creating a well-ranged
8 reference sample set. In this study, we present a methodology using short wave infrared
9 hyperspectral imaging to create a partial least squares regression model on a cored
10 sediment sample. It was applied to a sediment core of the well-known Lake Bourget
11 (Western Alps, France) to develop and validate a model for downcore high resolution LOI550
12 measurements used as a proxy of the organic matter. In lake and marine sediment, the
13 organic matter content is widely used, for example, to reconstruct carbon flux variations
14 through time. Organic matter analysis through routine analysis methods is time- and
15 material-consuming, as well as not spatially resolved. A new instrument based on
16 hyperspectral imaging allows high spatial and spectral resolutions to be acquired all along a
17 sediment core. In this study, we obtain a model characterized by a 0.95 r prediction, with
18 0.77 wt% of model uncertainty based on 27 relevant wavelengths. The concentration map
19 shows the variation inside each laminae and flood deposit. LOI550 reference values obtained
20 with the loss on ignition are highly correlated to the inc/coh ratio used as a proxy of the
21 organic matter in X-ray fluorescence with a correlation coefficient of 0.81. This ratio is also
22 correlated with the averaged subsampled hyperspectral prediction with a r of 0.65.

23

24 **1. Introduction**

25

26 The organic matter is usually used for sediment studies. For example, it can be used to
27 estimate the carbon stocks over time. Among different methods, the organic matter can be
28 approximated through Loss of Ignition at 550°C (Heiri et al., 2001), which are a widely used
29 method in paleo-environmental studies. All these methods are time-consuming, relatively
30 expensive, destructive and have low spatial resolution (0.5-1 cm sampling).

31 Hyperspectral imaging is a method at the interface of spectroscopy and imaging. The
32 ability to predict the organic matter has been demonstrated based on visible (Vis, 400-800
33 nm) and near-infrared (NIR, 800-2500 nm) spectroscopy, known as Vis-NIR spectroscopy (Li
34 et al., 2015; Nawar and Mouazen, 2017; Van Exem et al., 2018; Viscarra Rossel and Behrens,
35 2010). Predictions are still efficient with only NIR spectroscopy (Clairotte et al., 2016; Leach
36 et al., 2008; Zornoza et al., 2008). Mid-infrared (MIR, 2500-25000 nm) spectroscopy also has
37 the same ability (Clairotte et al., 2016; Rosén et al., 2011; Vohland et al., 2014). X-ray
38 fluorescence (XRF) spectroscopy is also used as an indirect qualitative proxy of the organic
39 matter (Bajard et al., 2016; Chawchai et al., 2016; Croudace and Rothwell, 2015; Lintern et
40 al., 2016).

41 Chemometrics methods can be used to extract relevant information from spectral
42 bands by comparison with discrete sample measurements and can be used downstream to
43 predict the organic matter or other variables. Partial least squares regression (PLSR) has
44 probably been the most used method to extract organic matter information from spectra
45 (Clairotte et al., 2016; Dhawale et al., 2015; Nawar and Mouazen, 2017; Viscarra Rossel and
46 Behrens, 2010; Vohland et al., 2014). However, other methods can be used with their

47 specific conditions. For instance, the artificial neural network (ANN) and the support vector
48 machine (SVM) require a large dataset. A comparison of different chemometrics methods
49 show that advanced methods such as ANN, SVM, and Multivariate Adaptive Regression
50 Splines (MARS) can slightly improve the performance (Kuang et al., 2015; Li et al., 2015;
51 Viscarra Rossel and Behrens, 2010). Transferring a model between several samples can be
52 very interesting, and PLSR is better than ANN to model local variations, while they are quite
53 similar for global variations (Wijewardane et al., 2016). In order to improve model
54 performance and robustness, spectral variable selection is achieved to reduce the spectral
55 collinearity. As a side effect, this reduction makes chemical interpretation easier (Peng et al.,
56 2014; Viscarra Rossel and Behrens, 2010; Vohland et al., 2014). Furthermore, coupling
57 spectroscopic datasets have been shown to improve model performance (Clairotte et al.,
58 2016) by the increase of the spectral and thus chemical information.

59 Chemometrics methods have been widely used in the biochemistry and the
60 pharmacology domains. These methods are usually based on an experimentally built sample
61 set in which the target concentrations are known or spiked. A direct chemometrics approach
62 is promising to predict concentrations in environmental solids such as sediments, soils, and
63 biological tissues. The challenge is here to propose a procedure designed to build a robust
64 model based on a natural dataset only. Indeed, we can expect that the range and spread of
65 real target values of a learning dataset is less robust than a model generated with an
66 experimentally designed dataset.

67 The aim of this study is to propose a way to build a PLSR model with hyperspectral
68 data on a natural environmental sediment using the opportunity of its heterogeneity to
69 generate robust models without the constitution of an experimental set. We applied this
70 method to predict the organic matter content in a sediment core by the way of a PLSR

71 model. A sample from the Lake Bourget was used and analyzed with short-wave infrared
72 (SWIR, 900-2500 nm) hyperspectral imaging. The loss on ignition (LOI) was the reference
73 method for the organic matter values. LOI is predicted from a hyperspectral image and a
74 variable selection applied to increase the robustness of the model. Predictions were
75 validated with LOI550 measurements and compared with the inc/coh ratio calculated with
76 XRF as a qualitative proxy of the organic matter. Finally, the pixel prediction validity with the
77 scale law (micrometer and millimeter) is discussed.

78

79 **2. Materials and methods**

80

81 **2.1. Site descriptions**

82

83 Lake Bourget (231.5 masl, 18 km long, and 2.8 km wide) is a hard-water lake at the
84 northwestern edge of the French Alps (figure 1). The lake was formed between the Pre-
85 Alpine and Jura Mountain ranges within the Molasse Basin by the retreat of Wurmian
86 glaciers. Two small rivers (Leyse and Sierroz) usually flow into Lake Bourget, which then
87 flows into the Rhone River by the Saviere Channel. However, during flooding of the Rhone
88 River, the water-current of this channel is reversed, and river water flows into Lake Bourget.

89 In the northern deep basin, flood deposits from the Rhone contribute to a variable
90 sediment fraction. During such flood events, the Lake Bourget catchment area is 4,600 km²,
91 including tributaries draining part of the Jura Mountains and the Inner Alps. Otherwise,
92 excluding the Rhone, it is 580 km². Over the last 10,000 years, the river-borne silicate
93 fraction has ranged between 10 and 40% of the bulk sediment, with the remaining amount

Science of the Total Environment

94 composed of carbonate depending on past climate conditions (Arnaud et al., 2012, 2005;
95 Debret et al., 2010; Giguët-Covex et al., 2010; Jenny et al., 2014).

96 In 2009, sediment (LDB09-P101, length = 54 cm, width = 9 cm) was cored in the
97 northern basin of Lake Bourget (N45 45.334, E5 51.332, 145 m water depth) in the frame of
98 the IPER-RETRO program (ANR-08-VUL 005, (Perga et al., 2015)). This core was selected for
99 this study because it contains both seasonally paced bioinduced millimeter lamina as well as
100 interbedded deposits brought by Rhone River flood events.

101

102 2.2. Sample preparation and LOI550 measurement

103

104 The core was sampled every ca. 2 cm in 5 mm slices cautiously avoiding the mixing of
105 different sediment facies (i.e., lamina and flood deposits for example). However, in this 5
106 mm, there can be several lamina which are around 2 mm thick. Discrete samples were dried
107 at 60 °C for 72 h then crushed (Basma et al., 1994).

108 The LOI was measured following the methodology detailed in (Heiri et al., 2001). Briefly, the
109 protocol is as follows: (1) heat to 550 °C over 4 h to estimate the organic content and (2)
110 heat to 950 °C over 2 h to estimate the mineral carbon content. At each step, the sample
111 was weighed to calculate the loss of weight (wt%) with equations (1) and (2).

112

$$LOI550 \text{ (wt\%)} = \frac{m_0 - m_1}{m_0} * 100 \quad (1)$$

$$LOI950 \text{ (wt\%)} = \frac{(m_1 - m_2)}{m_0} * 100 \quad (2)$$

113

114 where m_0 is the initial weight of dried sediment, m_1 is the weight after the first step,
115 and m_2 is the weight at the end.

116 The uncertainty of this method is 0.14 wt% ($\alpha = 0.05$, $n = 63$) for LOI550 values and
117 0.04 wt% ($\alpha = 0.05$, $n = 63$) for LOI950 values. It was estimated with 7 samples and 9
118 replicates each from several cores.

119

120 2.3. SWIR hyperspectral imaging acquisition

121

122 Hyperspectral imaging consists of acquiring an image with high spatial resolution, in which
123 each pixel contains spectral information with a continuous spectral resolution.

124 The core was analyzed in less than 15 minutes with the SWIR hyperspectral camera
125 (Specim Ltd., Finland) with the lens OLES22,5 at the M2C lab, University of Normandie-
126 Rouen. It covers the SWIR range between 968 nm and 2574 nm with a reflectance spectral
127 resolution of 12 nm (144 wavelengths) and a spatial theoretical resolution of 200 μm in both
128 directions all along the core. The spectral unit is reflectance by 10,000 ($R \times 10,000$).

129 The protocol followed to acquire the hyperspectral image is detailed in (Butz et al.,
130 2015). The core was cleaned before acquisition. Then, the camera was calibrated with a
131 spectralon reference (white), and the shutter was closed (black) for determining the spectral
132 dimensions. Spatial calibration was achieved by the way of imaging a known object for its
133 shape (squared pixels) and color (intensity). Deviation was checked at the end of the
134 acquisition in the same manner, and no deviation was observed.

135

136 2.4. X-ray fluorescence spectroscopy

137

138 The relative contents of major elements were analyzed by X-ray fluorescence (XRF) at a 200
139 μm resolution on the surface of the sediment core with an ITRAX XRF Core Scanner (Cox
140 Analytical Systems) at the CEREGE laboratory in 2010. The split core surface was first
141 covered with a 4- μm -thick Ultralene film to avoid contamination and desiccation of the
142 sediment. The X-ray beam was generated with a molybdenum tube at 35 kV and 30 mA, with
143 a runtime of 15 s. Compton (incoherent) and Rayleigh (coherent) scattering data were
144 extracted from it, and the inc/coh ratio was calculated. It has been used in many studies as a
145 qualitative proxy of organic matter (Bajard et al., 2016; Chawchai et al., 2016; Croudace and
146 Rothwell, 2015; Lintern et al., 2016).

147

148 2.5. Data analysis

149

150 Data acquisition was performed using Specim hardware ENVI 4.8. The data was then
151 converted, processed and analyzed with MATLAB (R2017a, MathWorks). Several free and
152 open MATLAB toolboxes were used and are detailed afterwards.

153 A key point to predict the LOI550 from hyperspectral imaging is the coupling of the
154 volume of the sample at 5 mm resolution with surface pixels of approximately 0.2 mm. The
155 proposed method is composed of four main steps. (1) A bootstrapping selection in the
156 hyperspectral spectra of the LOI sampling area was performed to construct several datasets.
157 (2) Then, PLSR was used to model LOI550 thanks to these spectra and the discrete LOI550
158 measurements for all the datasets. (3) The 10 optimal models were retained based on their
159 performances. (4) Wavelengths highly correlated with LOI550 were identified with variable

160 selection on the retained models in (3). A final reduced model was estimate with these
161 wavelengths. The complete workflow followed in this study is presented in Figure 2.

162

163 2.5.1. Spectral preprocessing

164

165 Spectral bands between 968-1127 nm (15 wavelengths) and 2418-2574 nm (15 wavelengths)
166 were excluded from the processing because of their very low signal-to-noise ratio. In fact,
167 noise is known to artificially increase the prediction of a chemometrics model (Tetko et al.,
168 1995). 39 wavelengths of H₂O absorption bands (between 1094 and 1176 nm, 1339 and
169 1465 nm, and 1773 and 2005 nm) were removed as proposed by (Gomez et al., 2015).
170 Consequently, 75/144 wavelengths were retained (figure 3).

171 In order to produce a robust model, some data in the spectra and LOI550 values have
172 been removed based on two standard deviations of the Mahalanobis distance in a principal
173 component analysis space (Mark and Tunnell, 1985). These data were due to spectral
174 artifacts (specular reflection, not enough signal, too noisy) or aberrant values. Pixels that
175 correspond to high surface variations (gap areas for example) were removed by setting a
176 lower limit for the standard deviation of a spectrum. This threshold must be set for each
177 image and based on the spectrum regions without noisy bands. For Lake Bourget images, a
178 standard deviation limit is set at 250 R x 10,000 (reflectance per 10,000).

179 Several standard spectral preprocessing (detrend, standard normal variate (SNV),
180 Savitzky-Golay derivatives) were tested to correct spectra from the scattering effect and/or
181 to normalize spectra (Vidal and Amigo, 2012). Finally, in order to optimize the prediction
182 model, the data were preprocessed by the way of an autoscaling by mean-centering and
183 standardizing each wavelength (Z-score).

184

185 2.5.2. Spectral sub-sampling

186

187 Our goal is to build a regression model between a set of 20 data of LOI and a set of 20

188 regions of thousands of pixels on the image which correspond to the sampling area.

189 Different techniques could be used to generate a representative value of the spectrum used

190 for regression with LOI data, (mean, bootstrap, min or max, mode or median spectrum). The

191 limit of a mean spectrum for each sampling area leads to smooth spectral variabilities;

192 resulting model were not relevant. We applied a bootstrapping procedure rather than a

193 mean spectrum assuming that LOI could be better explained by a specific spectrum of the

194 region of interest than by the mean spectrum of this region. Bootstrapping was used to

195 randomly select 100 spectra in each sampling area to generate 100 datasets of 20 spectra.

196

197 2.5.3. Partial least squares regression

198

199 PLSR was used to establish a relationship between the LOI550 values and SWIR

200 hyperspectral imaging. This method is based on the extraction of orthogonal predictors (also

201 called latent variables, LV) corresponding to the maximum variability in the spectral bands

202 used as predictors linked to one or several predicted variable(s) (Wold et al., 1984).

203 Each of the 100 bootstrapped datasets was divided in a calibration set (13 data) and a

204 validation set (the 7 unused data). For each of the 100 bootstrapped datasets, a PLSR model

205 is generated based on the calibration set, and then applied to the validation set in order to

206 assess the performances of the prediction.

207 The optimal number of latent variables was estimated by the use of the Durbin
 208 Watson test (Durbin and Watson, 1950) which is similar to a signal-to-noise ratio and was
 209 used to improve the robustness of the model.

210 Performances of the prediction model were estimated using the coefficient of
 211 correlation, r , and the uncertainty of both data sets (calibration and validation sets). They
 212 are calculated by equations (3) and (4).

$$r = \sqrt{1 - \frac{\sum_{i=1}^n (y_i - \hat{y}_i)^2}{\sum_{i=1}^n (y_i - \bar{y}_i)^2}} \quad (3)$$

$$\text{Model uncertainty} = 2 \times \sqrt{\frac{\sum_{i=1}^n (\hat{y}_i - y_i)^2}{n}} \quad (4)$$

213 where y_i is a LOI550 reference value, \hat{y}_i is a LOI550 predicted value, \bar{y}_i is the mean
 214 LOI550 reference value, and n is the number of values.

215

216

217 2.5.4. Variable selection

218

219 Variable selection algorithms were used to decrease the redundancy between neighboring
 220 wavelengths and remove non-informative ones to make the models more robust and easier
 221 to interpret chemically. The algorithms that were used can be found in MathWorks and are
 222 detailed in (Leardi and Lupiáñez, 1998; Li et al., 2014). The genetic algorithm was the
 223 method that gives the optimal model performance, as it aims is to solve an optimization
 224 problem by finding the lowest number of wavelengths to have the optimal prediction
 225 performance. It is inspired by natural selection, where wavelengths that are highly
 226 correlated to the LOI550 are first selected and then the optimal combination is chosen.

227 The GA-PLSR of the 10 best performing bootstrapping models were used to increase the
228 certainty for the selected wavelengths. Then, the wavelengths are ranked by their number of
229 occurrences. PLSR models are calculated by increasing the number of ranked selected
230 wavelengths. Finally, a model is chosen with the optimal r and model uncertainty. At last, a
231 geochemical map is estimated by the prediction of all the hyperspectral pixels to observe the
232 distribution down and across the core. Once an optimal model is created, it can be used
233 theoretically without other sampling on other cores sampled in the similar sedimentation
234 environment.

235

236 **3. Results**

237

238 3.1. Lithology and OM content

239

240 The Lake Bourget sediment core presents three main units, which were described in detail in
241 (Giguet-Covex et al., 2010). The uppermost one, between 0 cm and 18 cm, presents
242 millimeter-thick biochemical varve and corresponds to anoxic conditions at the lake-
243 sediment interface, with LOI550 values greater than 6 wt% (Giguet-Covex et al., 2010; Jenny,
244 2013). The second unit, between 18 cm and 26 cm, presents disturbed varve and LOI550
245 values that are stable at 6 wt%. In the lowermost unit, between 26 cm and 54 cm, there are
246 fuzzy laminated structures, and the LOI550 values are quite stable at 5 wt%. Flood-triggered
247 deposits (Jenny et al., 2014) are also present in the two first units, with a major one between
248 13.5 cm and 14.5 cm. Twenty measurements of the LOI were performed with a range

249 between 4.97 wt% and 8.60 wt% and a mean value of 6.41 wt% along with a standard
250 deviation of 1.37 wt%. LOI550 variations according to the depth can be seen in figure 4.d.

251

252 3.2. Organic matter predictive models

253

254 Four PLSR models are presented in table 1 to illustrate the importance of removing water
255 bands and wavelength selection.

256 Having a high number of LVs can increase the r of calibration but decrease the model
257 robustness because more LVs increase the calibration noise, which is not present in the
258 validation set. This is shown between models with and without water bands (table 1 blue
259 and green). When the number of LVs is higher, the calibration r is too, but the validation r is
260 lower.

261 Wavelength selection leads to increase the performance of the prediction model.

262 This is visible with a number of latent variables (LV) that is smaller (6-8) and an uncertainty
263 that decreases when less wavelengths are used.

264 Finally, the best compromise was found with a model with 27 wavelengths, validated
265 with 6 latent variables, and a prediction r of 0.95 ($p < 0.05$). A model uncertainty of 0.77
266 wt% ($\alpha = 0.05$, $n = 20$) for LOI550 prediction by hyperspectral imaging was found, whereas it
267 is 0.14 wt% ($\alpha = 0.05$, $n = 20$) for the LOI550 analysis. This is in agreement with PLSR models
268 developed with spectroscopic devices in the literature (Clairotte et al., 2016; Leach et al.,
269 2008; Li et al., 2015). This uncertainty is quite important because of the low number of
270 LOI550 values and their low dispersion. We expect that a greater and spreader set of LOI
271 values should lead to a more accurate PLSR model.

272

273 3.3. Wavelength correlation with organic matter

274

275 Variable selection algorithms are dependent on the spectral preprocessing (Peng et al.,
276 2014). First models with O-H bands show that they were selected as relevant, whereas some
277 organic bands were missing. These models, however, were less robust in terms of prediction.
278 These results could depend on O-H water bands that disturb the model. Removing O-H
279 wavelengths can increase the performance and robustness if other bands can add relevant
280 information to replace the missing information of organic matter O-H bands.

281 The genetic algorithm allows the number of wavelengths to be reduced to 27 (figure
282 3). They can be divided into three main classes, organic, carbonate and clay bands according
283 to (Peng et al., 2014; Viscarra Rossel and Behrens, 2010). Organic bands correspond to C-H
284 bonds (1205, 1217, 1622, 1735, 1746, 1757, 2250, 2261, 2272, 2306, 2317, and 2328 nm), C-
285 O bonds (2127 and 2138 nm), and N-H bonds (2093, 2105, and 2116 nm). Bands associated
286 with C=O bonds (1487 and 1510 nm) corresponds to organic or carbonate bands, and these
287 may discriminate the lamina type (dark or light). For clay bands, 5 bands were selected
288 (2149, 2160, 2183, 2228, and 2239 nm). The three other bands are not directly associated
289 with chemical bonds (1273, 1555, and 1566 nm). Some bands are spectrally close (for
290 example, 1205-1217 nm and 1746-1757 nm), which could reveal some band shape changes
291 due to organic mineral interaction.

292

293 3.4. Range, prediction and confidence intervals

294

Science of the Total Environment

295 The PLSR model was made with LOI550 measurements that have a range of 4.97 wt% to 8.60
296 wt%. We assume that LOI550 model intercept at the origin (there is no organic matter
297 spectroscopic signal when there is no organic matter in the sediment). Then we consider
298 that we can predict LOI550 in the range 0 wt% to 8.60 wt%. 93 % of the data are included in
299 it and have a minimal prediction error of 2.25 wt% ($\alpha = 0.05$) in the center of the calibration
300 (6.26 wt%).

301 Prediction and confidence intervals were calculated thanks to the complete dataset
302 (figure 5.c). The prediction error map (figure 5.b) shows side effects (right and left), which
303 can be due to surface variation or illumination. This observation is also visible in the
304 concentration map. Obviously, areas with high surface variations (gap, fissures) will not be
305 used in the LOI550 profile, and their prediction errors are more important than other
306 predicted values at the same depth. Figure 5.e shows that the prediction error is high in the
307 middle of light lamina (near 2.90 wt%), whereas it is low for the dark lamina (near 2.30 wt%).
308 Predictions of these light lamina concentrations have a range between 9-12 wt% (figure 5.d).
309 These predictions, out of the calibration range, must be interpreted cautiously.

310

311 3.5. Prediction distribution

312

313 The LOI550 concentration map in figure 4.c shows the three lithology units. A horizontal
314 merging is used to estimate a time series of LOI550 (figure 4.e) prediction to be compared
315 with LOI550 reference values (figure 4.d). The first unit presents LOI550 prediction values
316 that oscillate with a maximum near 11 wt% and a minimum of 4 wt%, and the global trend is
317 a decrease from 11 wt% to 6 wt%, which is similar to the reference values. The second unit is
318 characterized by a lower variation between 5-7 wt% and a steady trend at approximately 6

319 wt%. The last unit is quite homogeneous at 5 wt%. Floods can be characterized with a rapid
320 decrease in the prediction value, for example, the one between 13.5 and 14.5 cm.

321 Focusing on unit 1, the variations of the average LOI550 predicted values (figure 6.a,
322 blue curve) appear to closely match the varve laminations, with high values for light lamina
323 and low values for black lamina. This is also in agreement with the LOI550 reference values
324 (green line) by averaging a 5 mm thickness. In the LOI550 concentration map (figure 6.b), the
325 sequence of varve is observable along the core with 200 μm resolution. Even if values are
326 out of the range, a qualitative study can be made. Variations inside light lamina show that
327 the middle has a higher concentration than the edges, and for dark lamina, an opposite
328 trend exists, with the lowest values in the middle. There can be mixing between lamina
329 inside the sediment or inside the spectra. Additionally, it is heterogeneous across lamina
330 with LOI550 variations. In a flood, the average LOI550 predicted values (figure 6.c) present
331 an upward decreasing trend from 5 wt% to 6.5 wt%. The LOI550 concentration map (figure
332 6.d) shows that values vary a lot, approximately 3 wt% across the core.

333

334 **4. Discussion**

335

336 4.1. Comparison of LOI550 with the inc/coh ratio by XRF

337

338 In order to discuss this prediction, we compare this prediction with another proxy of organic
339 matter which can be measured at a similar spatial resolution. The incoherent to coherent
340 ratio was calculated with an XRF core scanner on this core. This ratio is used as an indirect
341 qualitative proxy of the organic matter, whereas the LOI550 is quantitative. To ensure the

Science of the Total Environment

342 pertinency of the comparison of PLSR model and inc/coh proxy, we compare first with
343 LOI550 with this proxy for this sample.

344 This ratio has been subsampled, the 25 pixels corresponding to 5 mm of LOI550 were
345 averaged. LOI550 measurements and the inc/coh are correlated ($r = 0.81$; $p < 0.05$) and can
346 thus be compared. Figure 4.d,e show that differences are mainly in unit 2 with inc/coh
347 values similar to unit 1, whereas LOI550 measurements between these two units are
348 decreasing. This could be due either to the surface state (oxidation) or to the difference
349 between a surface (inc/coh) and a volume (LOI550) measurement.

350 The hyperspectral quantitative prediction can also be compared with the inc/coh
351 ratio when resampled at the same resolution. Figure 4.f shows the ratio variations along the
352 core, and the three units are characterized with high, medium, and low oscillations in the
353 hyperspectral prediction as well as variation in the flood deposit. The correlation coefficient
354 between the LOI550 prediction and inc/coh is 0.65 ($p < 0.05$). With the high-resolution
355 image on varved lamina (figure 6.a, c), it is easier to show and compare both variations. The
356 LOI550 quantitative prediction and inc/coh qualitative ratio are in agreement for varve
357 lamina and flood deposits. When the varve are not parallel or mixed, XRF cannot detect
358 them, whereas hyperspectral imaging can, and that can be seen at a 4 cm depth. Between
359 depths of 3.2 cm and 3.6 cm, values of inc/coh and predicted LOI550 are steady because of
360 the presence of irregularly shaped varve. For hyperspectral imaging, it is possible to see
361 them on the concentration map, and with image processing, it will be possible to adjust the
362 varve sequence. For the flood (figure 6.c), the inc/coh ratio increases faster down the core
363 than the hyperspectral prediction, which may indicate that one of the two methods is biased
364 by grain size variations.

365

366 4.2. Micrometric surface prediction and volume analysis

367

368 The analysis of the LOI550 vs inc/coh leads to suspect a difference between surface vs
369 volume measurement. This volume-surface correlation is noted $r_{V/S}$. LOI550 measurements
370 and the average predicted values are correlated with a $r_{V/S}$ of 0.73 ($p < 0.05$) and a root
371 mean square error (RMSE) of 1.72 wt%.

372 Some points between depths of 6 cm and 12 cm are affected by a surface variations
373 such as the gap on the top right of the core (figure 4.a, c), and without this area, the
374 correlation $r_{V/S}$ increased to 0.81 ($p < 0.05$). This induces a loss of spectral intensity and thus
375 weaker LOI550 prediction values. Cores need to have as large as possible of a plane surface
376 to have a correct prediction.

377 The $r_{V/S}$ is weaker than that of the model due mainly to chemical properties. The
378 surface state can be the main explanation, as the oxidation of some chemical compounds
379 can induce intensity variations on the selected bands in some pixels. That is why the core
380 needs to be cleaned before beginning, and the acquisition needs to be fast for no
381 reappearance of surface states between the first and the last spectra. The other differences
382 can mean that the surface and volume sediment analysis don't evaluate the same property
383 for the organic matter content.

384

385 4.3. Proposed methodology

386

387 The proposed methodology seems to be relevant with the validation of PLSR models by XRF
388 comparison and by the characteristics of the chemical bonds selected with the variable

389 selection algorithm. However, based on the concentration map and selected spectral bands,
390 we can wonder if a unique PLSR model is the optimal method in a sediment characterized by
391 three different mineralogical patterns: the two types of lamina (light and dark) and the
392 homogeneous part. If PLSR models were created for each of these three patterns
393 independently, prediction could be more accurate with different selected wavelengths. With
394 our LOI measurements, it is not possible to estimate a model by the type of lamina because
395 the sampling resolution of an operator does not allow the ability to distinguish between
396 them. Improvement of such a model could occur by the way of a higher sampling resolution
397 that is closer to the lithology of the sediment core.

398

399 4.4. Outlook for PLSR application on sediment cores and other 400 environmental matrices

401

402 Quantitatively predicting proxies at high resolution along and across the core in less than an
403 hour, from the acquisition to the prediction, is very effective and is not done by any other
404 methods at this time. This is an important advance for the study of sediment cores to infer
405 the paleo-environment and paleo-climate. The high spatial resolution allows us to look inside
406 the laminae, and the spectral dimensions allow chemical variations to be studied with
407 further work to identify the patterns of organic matter. The high-resolution approach is
408 relevant in some type of sedimentary environments where there are successive deposits as
409 the lamina or the varve and even in some homogenous sediment. In the case of a very
410 homogeneous sediment such as those subject to bioturbation or redistribution, the high

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411 resolution loses some interests, but the detection of specific compounds may still keep an
412 interest for a global characterization (without chronology).

413 The use of other proxies may help to improve the quality of the predictions. With this
414 application on the Lake Bourget core, grain size effects seem to skew the LOI550 modeling.
415 Predicting several proxies at the same time can make the model more robust. For example, if
416 the grain size has a real effect on the LOI550 prediction, creating a unique model could
417 increase the robustness. Furthermore, the spatial and the spectral dimensions of the
418 hyperspectral images may be combined in the data processing to improve our understanding
419 of the sediment records. For instance, thanks to lamina, chemical, physical and biological
420 variations could be estimated at the seasonal scale. In the Lake Bourget core, organic carbon
421 fluxes could be estimated for each type of laminae (dark or light) and compared in eutrophic
422 and non-eutrophic parts of the core (Jenny, 2013).

423 Creating a universal model that can be applied to several sedimentation sites (lake,
424 marine, etc.) and types (eutrophic, detrital, etc.) needs standardized parameters. Obviously,
425 the hyperspectral acquisition is a critical step that need to follow a strict protocol (Butz et al.,
426 2015). Even if a model seems to be applied to a core which was not used on the model
427 generation, some few chemical verifications may be achieved in order to avoid unexpected
428 bias. As a first step, the model could be theoretically transferred on samples cored in similar
429 sedimentary environments to keep the same type of matrix effects.

430 Obviously, with all these considerations, this methodology can be transferred to
431 other natural heterogeneous samples, for example speleothems, soils, ice cores, and trees,
432 to infer the paleo-environment, paleo-climate, soil health, and pollution.

433

434 **5. Conclusion**

435

436 Hyperspectral imaging is a high resolution (200 μm), nondestructive and fast analysis
437 method (15 minutes). Coupling hyperspectral imaging and partial least squares regression
438 shows great possibilities for the creation of quantitative predictive models and the
439 prediction for any kind of natural sample at high resolution. In this study, a methodology was
440 proposed to estimate a robust PLSR model using the heterogeneity of the sample without
441 the constitution of a specific calibrated concentration range.

442 It was applied to LOI550 prediction and it was validated with LOI550 measurements
443 with selected near-infrared wavelengths that correspond to relevant chemical bonds. It was
444 also successfully compared with the inc/coh XRF qualitative ratio used as a proxy of the
445 organic matter. Therefore, this methodology seems to be relevant and allows for the organic
446 matter content to be quantitatively inferred at high resolution along and across the core.
447 This proxy for laminated or varve sediment could be precise at the seasonal scale with the
448 200 μm pixel size.

449 This methodology must be tested on other cores or heterogeneous samples to verify
450 its relevance. The “universality” of the model generated from this dataset, should be applied
451 on different lake systems in order to test the ability to predict organic matter in other
452 environments and to set the limitations of this. It may be used on other proxies that are
453 characteristic in the basin catchment. Predicting several proxies at the same time may also
454 be studied to create a robust model that is not disturbed by some chemical or physical
455 variabilities. The proposed methodology applied to sediment cores has great possibilities to
456 more precisely infer the paleo-climate and paleo-environment that are recorded in the core
457 inside each sediment structure.

458

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460

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465 **References**

466

467 Arnaud, F., Revel, M., Chapron, E., Desmet, M., Tribovillard, N., 2005. 7200 years of Rhône
468 river flooding activity in Lake Le Bourget, France: a high-resolution sediment record of
469 NW Alps hydrology. *Holocene* 15, 420–428.
470 <https://doi.org/10.1191/0959683605hl801rp>

471 Arnaud, F., Révillon, S., Debret, M., Revel, M., Chapron, E., Jacob, J., Giguet-Covex, C.,
472 Poulénard, J., Magny, M., 2012. Lake Bourget regional erosion patterns reconstruction
473 reveals Holocene NW European Alps soil evolution and paleohydrology. *Quat. Sci. Rev.*
474 51, 81–92. <https://doi.org/10.1016/j.quascirev.2012.07.025>

475 Bajard, M., Sabatier, P., David, F., Develle, A.-L., Reyss, J.-L., Fanget, B., Malet, E., Arnaud, D.,
476 Augustin, L., Crouzet, C., Poulénard, J., Arnaud, F., 2016. Erosion record in Lake La Thuile
477 sediments (Prealps, France): Evidence of montane landscape dynamics throughout the
478 Holocene. *The Holocene* 26, 350–364. <https://doi.org/10.1177/0959683615609750>

479 Basma, A.A., Al-Homoud, A.S., Al-Tabari, E.Y., 1994. Effects of methods of drying on the
480 engineering behavior of clays. *Appl. Clay Sci.* 9, 151–164. [https://doi.org/10.1016/0169-](https://doi.org/10.1016/0169-1317(94)90017-5)
481 [1317\(94\)90017-5](https://doi.org/10.1016/0169-1317(94)90017-5)

482 Butz, C., Grosjean, M., Fischer, D., Wunderle, S., Tylmann, W., Rein, B., 2015. Hyperspectral
483 imaging spectroscopy: a promising method for the biogeochemical analysis of lake
484 sediments. *J. Appl. Remote Sens.* 9, 1–20. <https://doi.org/10.1117/1.JRS.9.096031>

485 Chawchai, S., Kylander, M.E., Chabangborn, A., Löwemark, L., Wohlfarth, B., 2016. Testing
486 commonly used X-ray fluorescence core scanning-based proxies for organic-rich lake
487 sediments and peat. *Boreas* 45, 180–189. <https://doi.org/10.1111/bor.12145>

- 488 Clairotte, M., Grinand, C., Kouakoua, E., Thébault, A., Saby, N.P.A., Bernoux, M., Barthès,
489 B.G., 2016. National calibration of soil organic carbon concentration using diffuse
490 infrared reflectance spectroscopy. *Geoderma* 276, 41–52.
491 <https://doi.org/10.1016/j.geoderma.2016.04.021>
- 492 Croudace, I.W., Rothwell, R.G., 2015. Micro-XRF studies of sediment cores : applications of a
493 non-destructive tool for the environmental sciences. [https://doi.org/10.1007/978-94-](https://doi.org/10.1007/978-94-017-9849-5)
494 [017-9849-5](https://doi.org/10.1007/978-94-017-9849-5)
- 495 Debret, M., Chapron, E., Desmet, M., Rolland-Revel, M., Magand, O., Trentesaux, A., Bout-
496 Roumazeille, V., Nomade, J., Arnaud, F., 2010. North western Alps Holocene
497 paleohydrology recorded by flooding activity in Lake Le Bourget, France. *Quat. Sci. Rev.*
498 *29*, 2185–2200. <https://doi.org/10.1016/J.QUASCIREV.2010.05.016>
- 499 Dhawale, N.M., Adamchuk, V., Prasher, S.O., Viscarra Rossel, R.A., Ismail, A.A., Kaur, J., 2015.
500 Proximal soil sensing of soil texture and organic matter with a prototype portable mid-
501 infrared spectrometer. *Eur. J. Soil Sci.* 66, 661–669. <https://doi.org/10.1111/ejss.12265>
- 502 Durbin, J., Watson, G.S., 1950. Testing for Serial Correlation in Least Squares Regression: I.
503 *Biometrika* 37, 409–428. <https://doi.org/10.2307/2332391>
- 504 Giguet-Covex, C., Arnaud, F., Poulénard, J., Enters, D., Reyss, J.-L., Millet, L., Lazzaroto, J.,
505 Vidal, O., 2010. Sedimentological and geochemical records of past trophic state and
506 hypolimnetic anoxia in large, hard-water Lake Bourget, French Alps. *J. Paleolimnol.* 43,
507 171–190. <https://doi.org/10.1007/s10933-009-9324-9>
- 508 Gomez, C., Drost, A.P.A., Roger, J.M., 2015. Analysis of the uncertainties affecting predictions
509 of clay contents from VNIR/SWIR hyperspectral data. *Remote Sens. Environ.* 156, 58–
510 70. <https://doi.org/10.1016/j.rse.2014.09.032>
- 511 Heiri, O., Lotter, A.F., Lemcke, G., 2001. Loss on ignition as a method for estimating organic

Science of the Total Environment

- 512 and carbonate content in sediments: reproducibility and comparability of results. *J.*
513 *Paleolimnol.* 25, 101–110. <https://doi.org/10.1023/A:1008119611481>
- 514 Jenny, J.-P., 2013. Réponses des grands lacs périalpins aux pressions anthropiques et
515 climatiques récentes : reconstitutions spatio-temporelles à partir d'archives
516 sédimentaires. HAL. Université Grenoble Alpes.
- 517 Jenny, J.-P., Wilhelm, B., Arnaud, F., Sabatier, P., Giguet Covex, C., Mélo, A., Fanget, B.,
518 Malet, E., Ployon, E., Perga, M.E., 2014. A 4D sedimentological approach to
519 reconstructing the flood frequency and intensity of the Rhône River (Lake Bourget, NW
520 European Alps). *J. Paleolimnol.* 51, 469–483. [https://doi.org/10.1007/s10933-014-9768-](https://doi.org/10.1007/s10933-014-9768-4)
521 4
- 522 Kuang, B., Tekin, Y., Mouazen, A.M., 2015. Comparison between artificial neural network and
523 partial least squares for on-line visible and near infrared spectroscopy measurement of
524 soil organic carbon, pH and clay content. *Soil Tillage Res.* 146, 243–252.
525 <https://doi.org/10.1016/j.still.2014.11.002>
- 526 Leach, C.J., Wagner, T., Jones, M., Juggins, S., Stevenson, A.C., 2008. Rapid determination of
527 total organic carbon concentration in marine sediments using Fourier transform near-
528 infrared spectroscopy (FT-NIRS). *Org. Geochem.* 39, 910–914.
529 <https://doi.org/10.1016/j.orggeochem.2008.04.012>
- 530 Leardi, R., Lupiáñez, A., 1998. Genetic algorithms applied to feature selection in PLS
531 regression: how and when to use them. *Chemom. Intell. Lab. Syst.* 41, 195–207.
532 [https://doi.org/10.1016/S0169-7439\(98\)00051-3](https://doi.org/10.1016/S0169-7439(98)00051-3)
- 533 Li, H., Xu, Q., Liang, Y., 2014. libPLS: An Integrated Library for Partial Least Squares
534 Regression and Discriminant Analysis. *PeerJ Prepr.*
535 <https://doi.org/10.7287/peerj.preprints.190v1>

- 536 Li, S., Shi, Z., Chen, S., Ji, W., Zhou, L., Yu, W., Webster, R., 2015. In Situ Measurements of
537 Organic Carbon in Soil Profiles Using vis-NIR Spectroscopy on the Qinghai-Tibet Plateau.
538 Environ. Sci. Technol. 49, 4980–4987. <https://doi.org/10.1021/es504272x>
- 539 Lintern, A., Leahy, P.J., Zawadzki, A., Gadd, P., Heijnis, H., Jacobsen, G., Connor, S., Deletic,
540 A., McCarthy, D.T., 2016. Sediment cores as archives of historical changes in floodplain
541 lake hydrology. Sci. Total Environ. 544, 1008–1019.
542 <https://doi.org/10.1016/j.scitotenv.2015.11.153>
- 543 Mark, H.L., Tunnell, D., 1985. Qualitative near-infrared reflectance analysis using
544 Mahalanobis distances. Anal. Chem. 57, 1449–1456.
545 <https://doi.org/10.1021/ac00284a061>
- 546 Nawar, S., Mouazen, A.M., 2017. Predictive performance of mobile vis-near infrared
547 spectroscopy for key soil properties at different geographical scales by using spiking and
548 data mining techniques. CATENA 151, 118–129.
549 <https://doi.org/10.1016/j.catena.2016.12.014>
- 550 Peng, X., Shi, T., Song, A., Chen, Y., Gao, W., 2014. Estimating soil organic carbon using
551 VIS/NIR spectroscopy with SVMR and SPA methods. Remote Sens. 6, 2699–2717.
552 <https://doi.org/10.3390/rs6042699>
- 553 Perga, M.-E., Frossard, V., Jenny, J.-P., Alric, B., Arnaud, F., Berthon, V., Black, J.L., Domaizon,
554 I., Giguët-Covex, C., Kirkham, A., Magny, M., Manca, M., Marchetto, A., Millet, L.,
555 Paillès, C., Pignol, C., Poulenard, J., Reyss, J.-L., Rimet, F., Sabatier, P., Savichtcheva, O.,
556 Sylvestre, F., Verneaux, V., 2015. High-resolution paleolimnology opens new
557 management perspectives for lakes adaptation to climate warming. Front. Ecol. Evol. 3,
558 72. <https://doi.org/10.3389/fevo.2015.00072>
- 559 Rosén, P., Vogel, H., Cunningham, L., Hahn, A., Hausmann, S., Pienitz, R., Zolitschka, B.,

Science of the Total Environment

- 560 Wagner, B., Persson, P., 2011. Universally Applicable Model for the Quantitative
561 Determination of Lake Sediment Composition Using Fourier Transform Infrared
562 Spectroscopy. *Environ. Sci. Technol.* 45, 8858–8865.
- 563 Tetko, I. V., Livingstone, D.J., Luik, A.I., 1995. Neural network studies. 1. Comparison of
564 overfitting and overtraining. *J. Chem. Inf. Model.* 35, 826–833.
565 <https://doi.org/10.1021/ci00027a006>
- 566 Van Exem, A., Debret, M., Copard, Y., Vanni re, B., Sabatier, P., Marcotte, S., Laignel, B.,
567 Reyss, J.-L., Desmet, M., 2018. Hyperspectral core logging for fire reconstruction
568 studies. *J. Paleolimnol.* 59, 297–308. <https://doi.org/10.1007/s10933-017-0009-5>
- 569 Vidal, M., Amigo, J.M., 2012. Pre-processing of hyperspectral images. Essential steps before
570 image analysis. *Chemom. Intell. Lab. Syst.* 117, 138–148.
571 <https://doi.org/10.1016/J.CHEMOLAB.2012.05.009>
- 572 Viscarra Rossel, R.A., Behrens, T., 2010. Using data mining to model and interpret soil diffuse
573 reflectance spectra. *Geoderma* 158, 46–54.
574 <https://doi.org/10.1016/j.geoderma.2009.12.025>
- 575 Vohland, M., Ludwig, M., Thiele-Bruhn, S., Ludwig, B., 2014. Determination of soil properties
576 with visible to near- and mid-infrared spectroscopy: Effects of spectral variable
577 selection. *Geoderma* 223, 88–96. <https://doi.org/10.1016/j.geoderma.2014.01.013>
- 578 Wijewardane, N.K., Ge, Y., Wills, S., Loecke, T., 2016. Prediction of Soil Carbon in the
579 Conterminous United States: Visible and Near Infrared Reflectance Spectroscopy
580 Analysis of the Rapid Carbon Assessment Project. *Soil Sci. Soc. Am. J.* 80, 973–982.
581 <https://doi.org/10.2136/sssaj2016.02.0052>
- 582 Wold, S., Ruhe, A., Wold, H., Dunn, III, W.J., 1984. The Collinearity Problem in Linear
583 Regression. The Partial Least Squares (PLS) Approach to Generalized Inverses. *SIAM J.*

584 Sci. Stat. Comput. 5, 735–743. <https://doi.org/10.1137/0905052>

585 Zornoza, R., Guerrero, C., Mataix-Solera, J., Scow, K.M., Arcenegui, V., Mataix-Beneyto, J.,

586 2008. Near infrared spectroscopy for determination of various physical, chemical and

587 biochemical properties in Mediterranean soils. Soil Biol. Biochem. 40, 1923–1930.

588 <https://doi.org/10.1016/j.soilbio.2008.04.003>

589

590 **Tables**

591

592 *Table 1: Performance of complete and reduced PLSR models for the LOI550 prediction without removing water bands in blue*

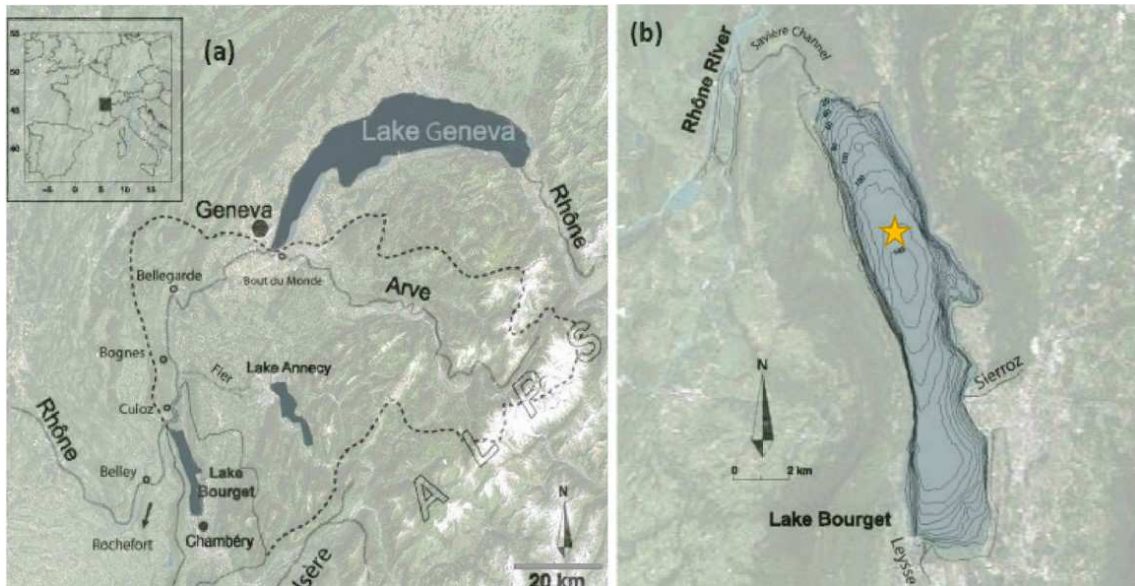
593 *and after removing them in green.*

Wavelengths	Latent Variable	r calibration	r prediction	Model uncertainty (wt%)
121	8	0.99	0.80	1.40
21	7	0.96	0.88	1.20
75	7	0.99	0.92	1.02
27	6	0.98	0.95	0.77

594

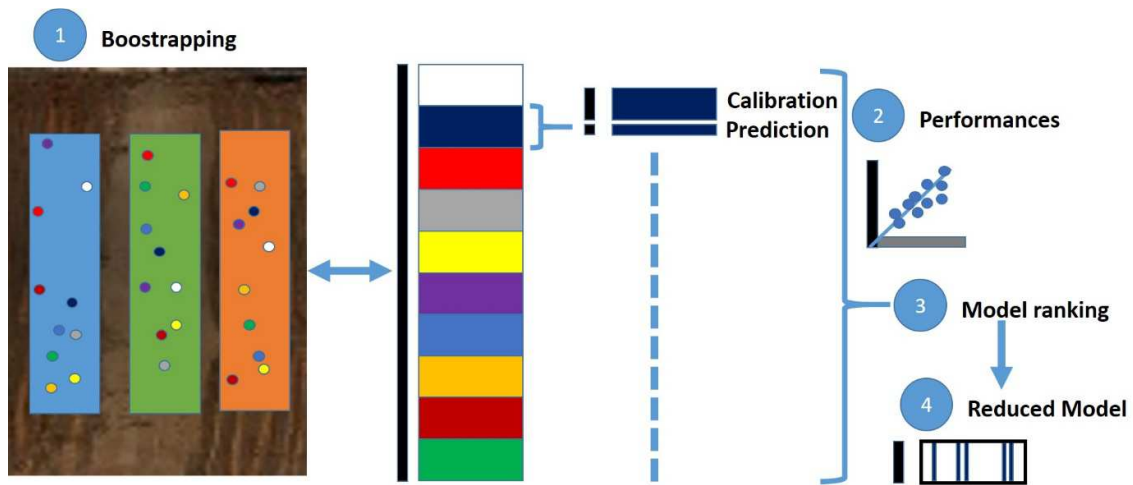
595

596 **Figure captions**



597

598 *Figure 1: (a) Location and catchment area of Lake Bourget. (b) Bathymetry, tributaries and effluents of the lake.*



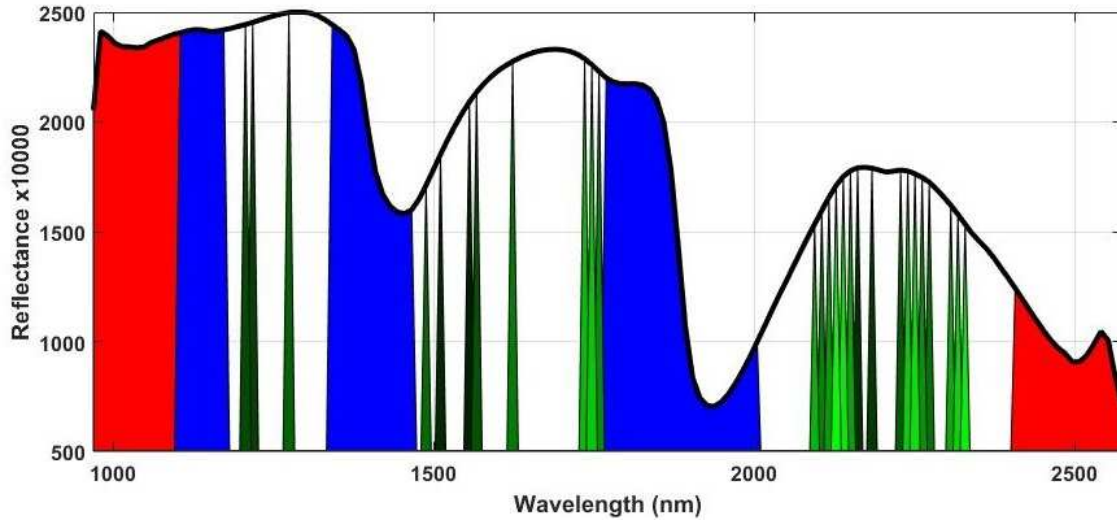
599

600 *Figure 2: The four principal steps followed to create a model: (1) dataset creations with bootstrapping in the sampling area*

601 *that are associated with the corresponding LOI550 value, (2) create models, estimate performances and estimate the*

602 *regression coefficients, (3) rank the models based on their performances, and (4) reduce the number of wavelengths with 10*

603 *optimal models and create the reduced model.*



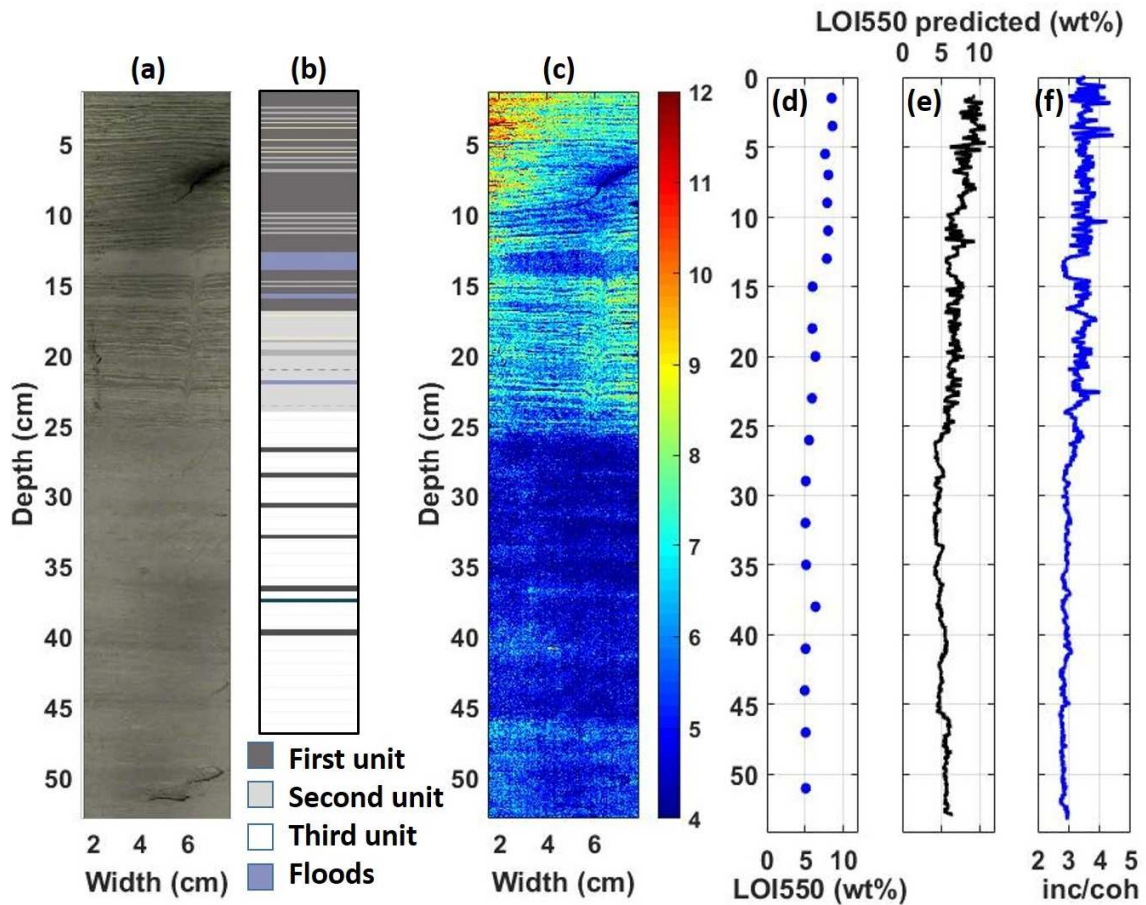
604

605 *Figure 3: 27 most correlated wavelengths to LOI550 are highlighted with a green gradient (light green: most), the water*

606

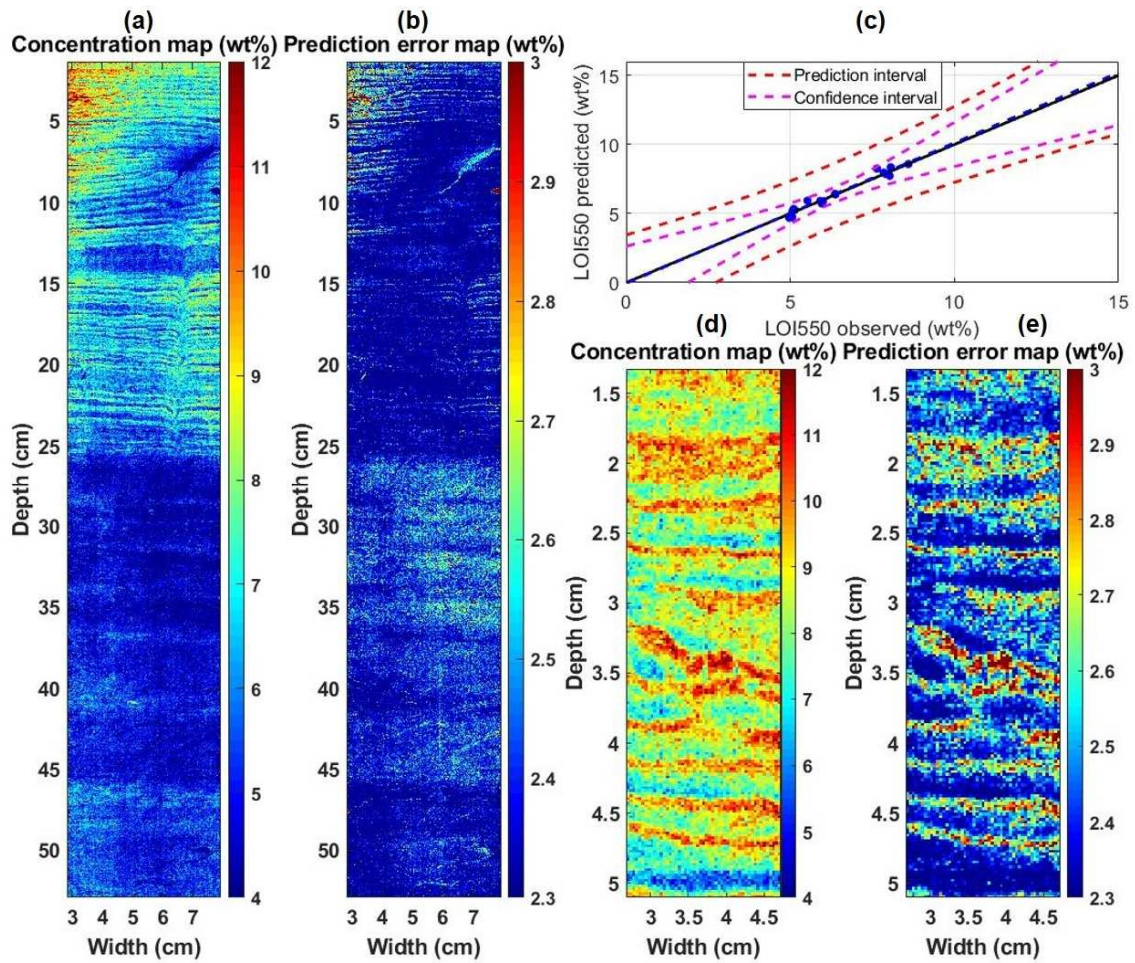
bands are in blue, and the noise bands are in red on the mean spectrum in black.

607



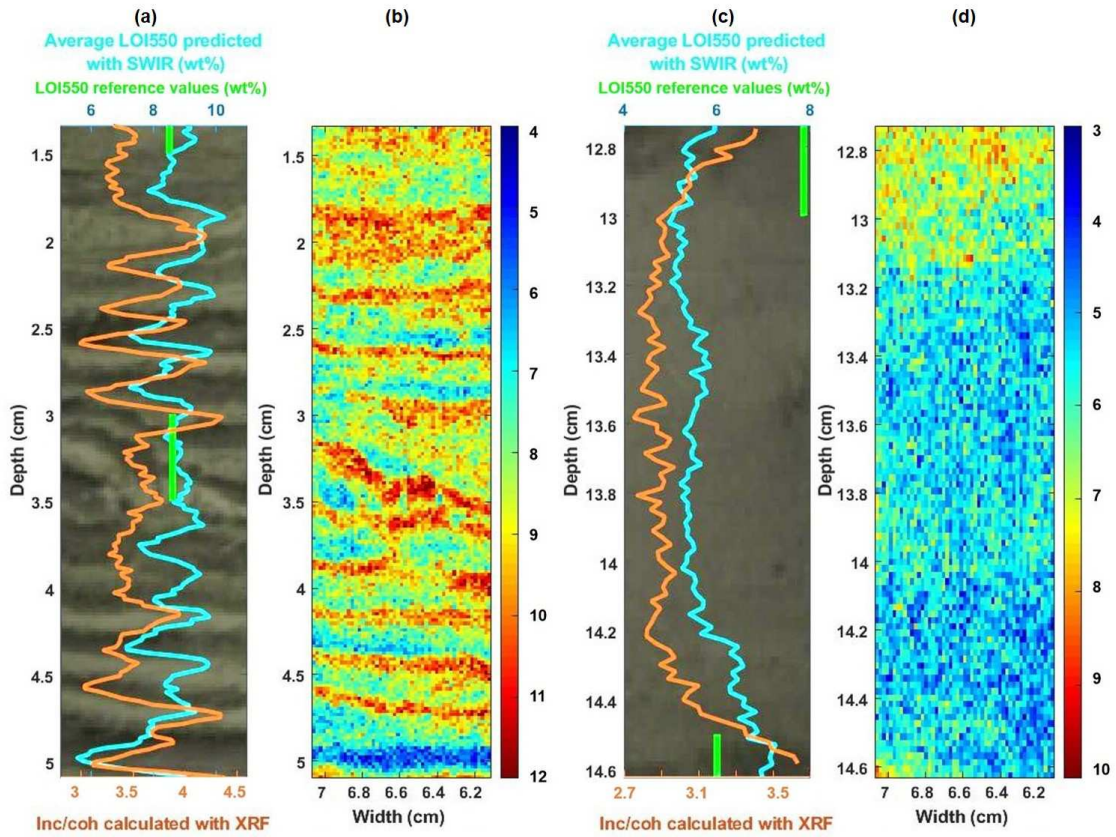
608

609 Figure 4: Lake Bourget (a) RGB image, (b) lithology units, (c) LOI550 predicted concentration map with the reduce model, (d)
 610 LOI550 reference values, (e) average LOI550 predicted values, and (f) inc/coh ratios.



611
 612 Figure 5: (a) Concentration map of the core with its prediction error map (b). (c) Prediction and confidence intervals of the
 613 LOI550 model. (d) Concentration map of a varved area and his prediction error map (e).

614
 615



616

617 *Figure 6: Zoom in for two areas on unit 1: varve (a-b) and flood (c-d). RGB image (a-c) with LOI550 reference values (green*

618 *line) predicted by SWIR data (blue curve) and the inc/coh ratio (orange curve) as well as LOI550 concentration maps (b-d).*

619