

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

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## Science of the Total Environment

- 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 (Leysse 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 km<sup>2</sup>,  
91 including tributaries draining part of the Jura Mountains and the Inner Alps. Otherwise,  
92 excluding the Rhone, it is 580 km<sup>2</sup>. 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

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

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

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

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  $\mu\text{m}$  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  $\mu\text{m}$  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- $\mu\text{m}$ -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 H<sub>2</sub>O 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

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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



## Science of the Total Environment

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  $\mu\text{m}$  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

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

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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

## Science of the Total Environment

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

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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

## Science of the Total Environment

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.

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434 **5. Conclusion**

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

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

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

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460

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589

590 **Tables**

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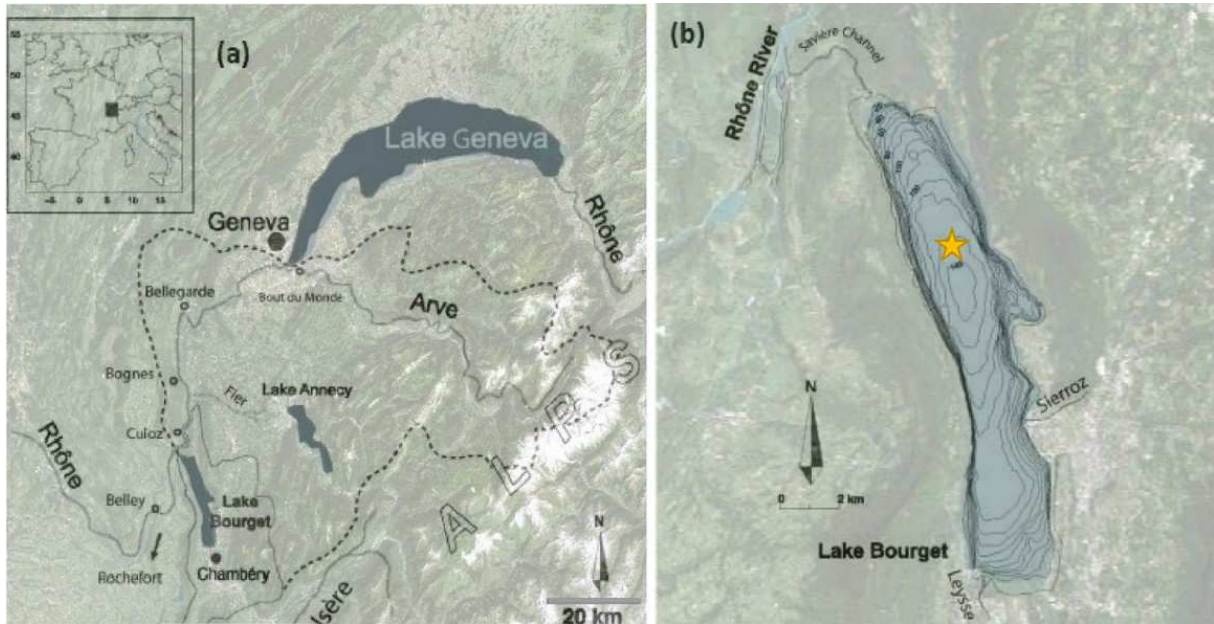
592 *Table 1: Performance of complete and reduced PLSR models for the LOI550 prediction without removing water bands in blue*  
 593 *and after removing them in green.*

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
<b>27</b>	<b>6</b>	<b>0.98</b>	<b>0.95</b>	<b>0.77</b>

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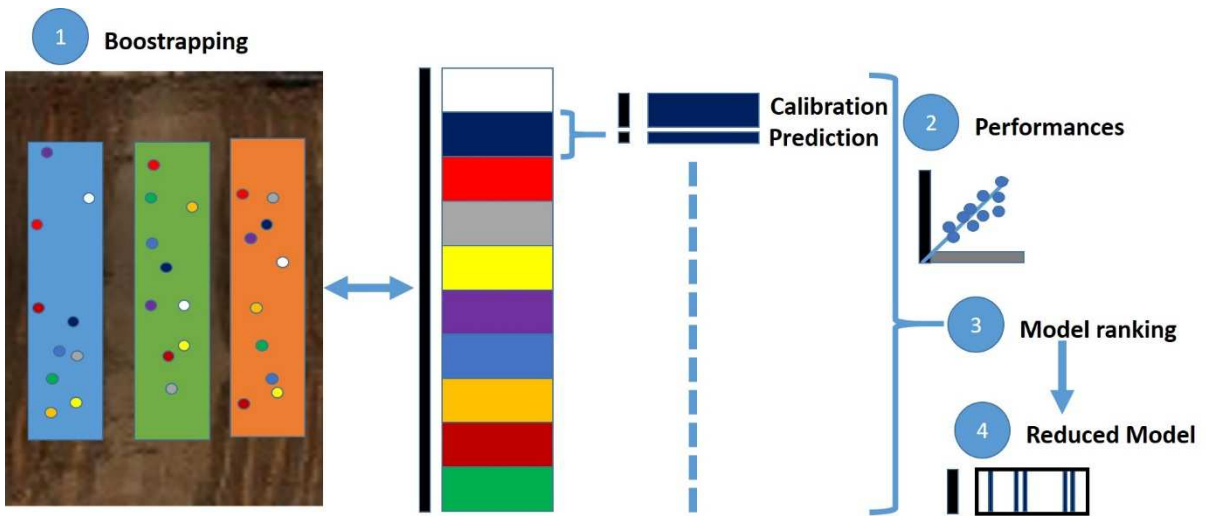
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596 **Figure captions**



597

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



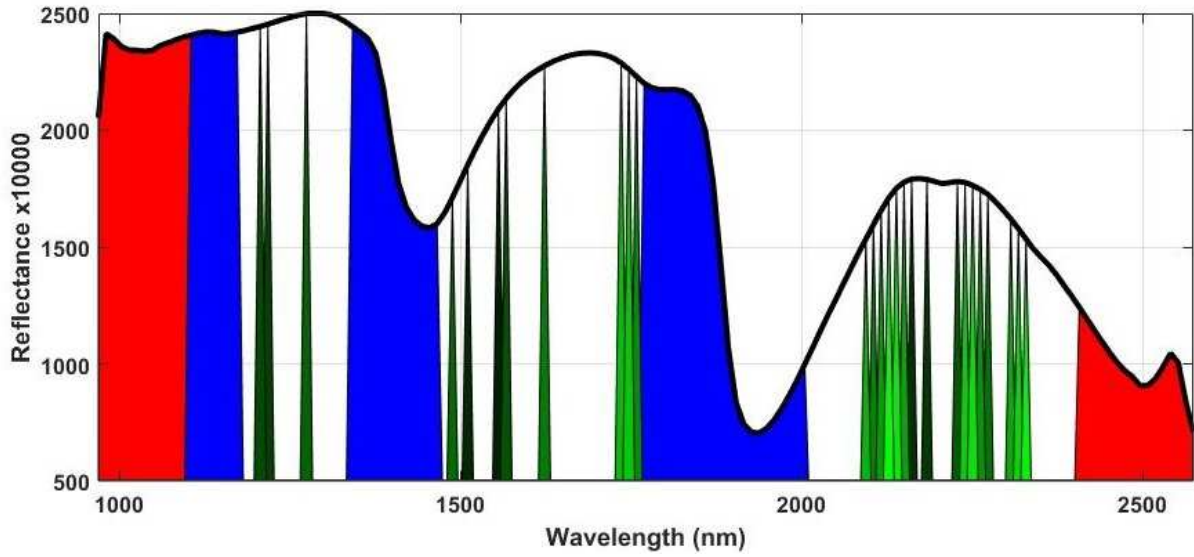
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600 *Figure 2: The four principal steps followed to create a model: (1) dataset creations with bootstrapping in the sampling area*

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.*



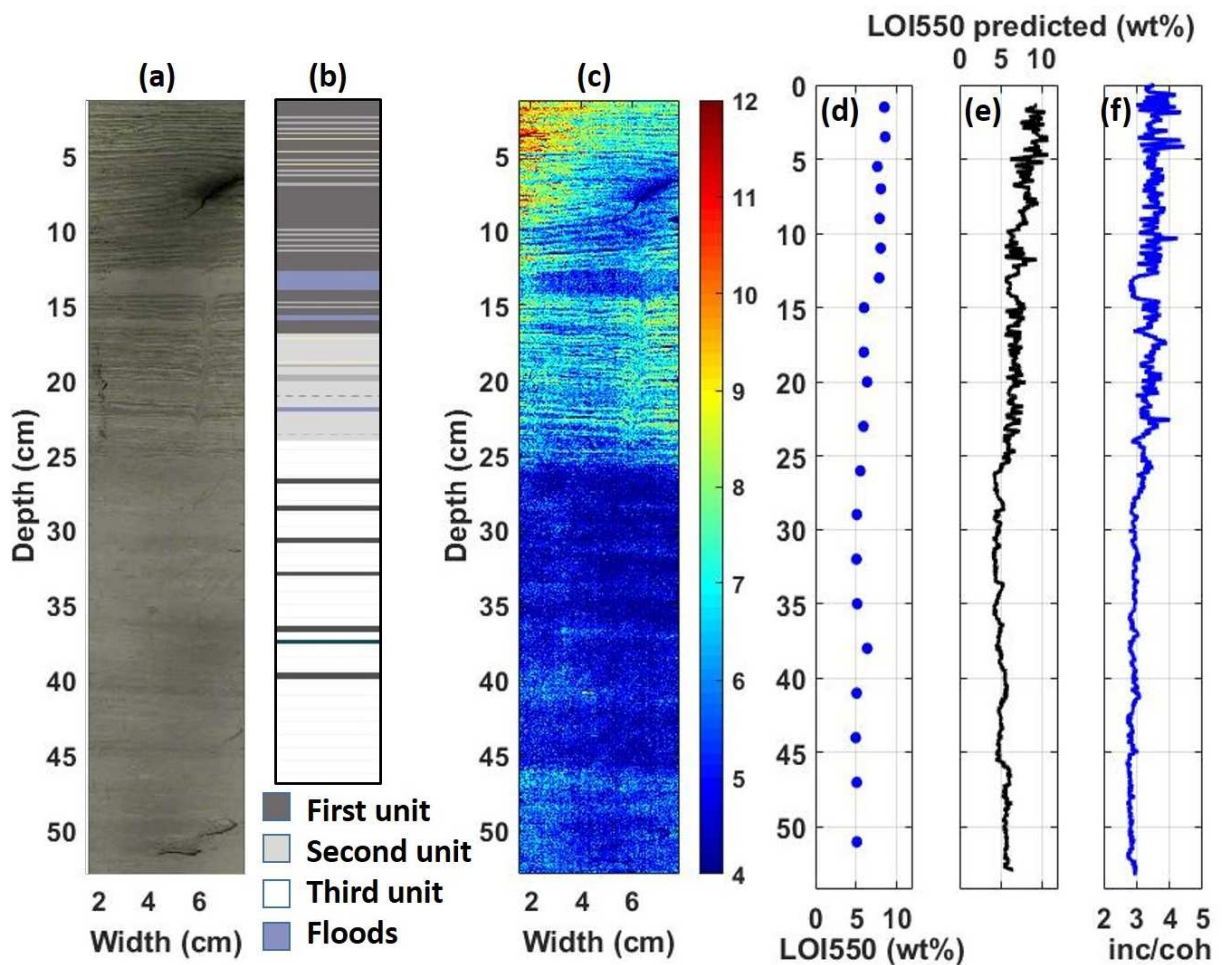
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Figure 3: 27 most correlated wavelengths to LOI550 are highlighted with a green gradient (light green: most), the water bands are in blue, and the noise bands are in red on the mean spectrum in black.

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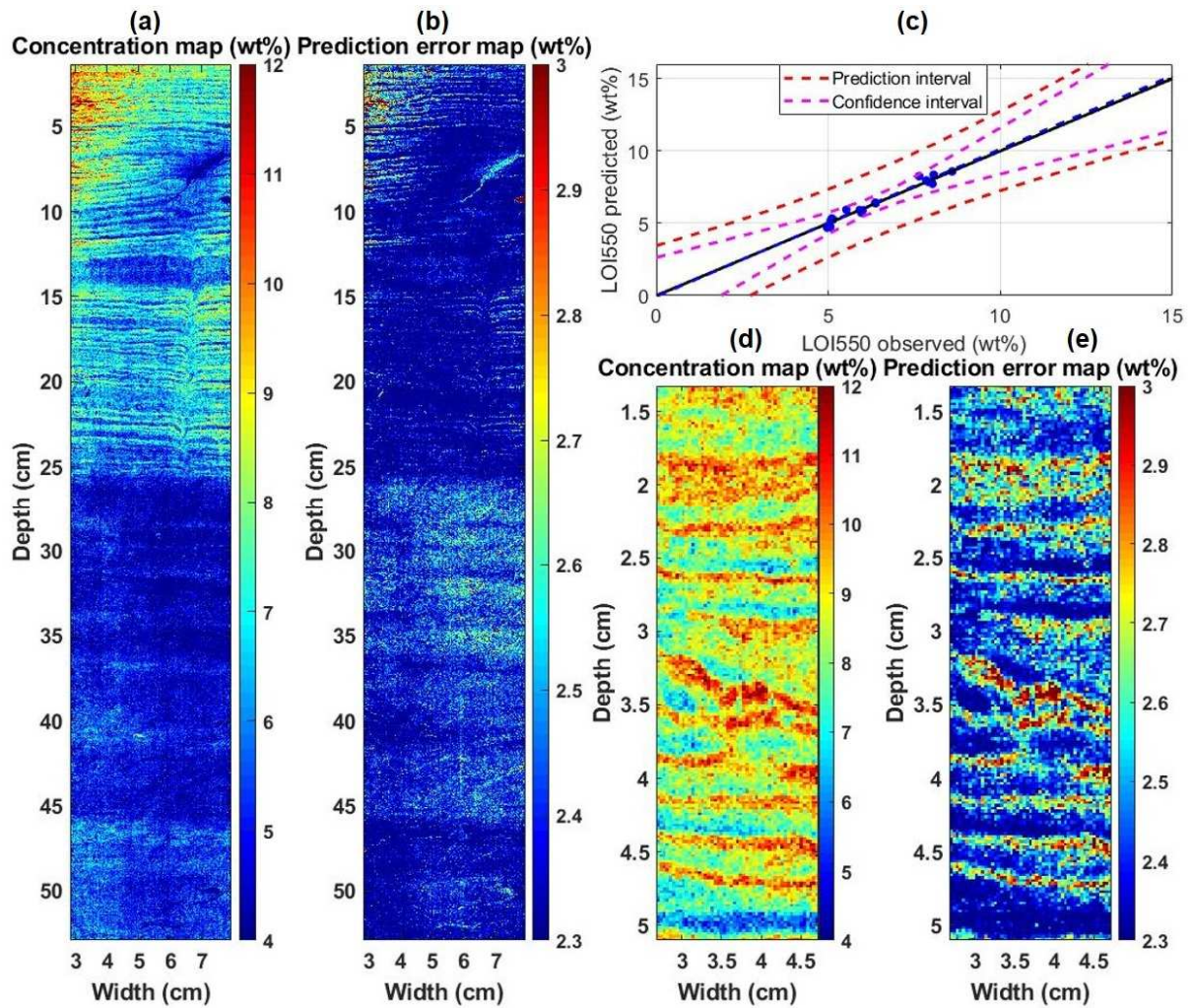
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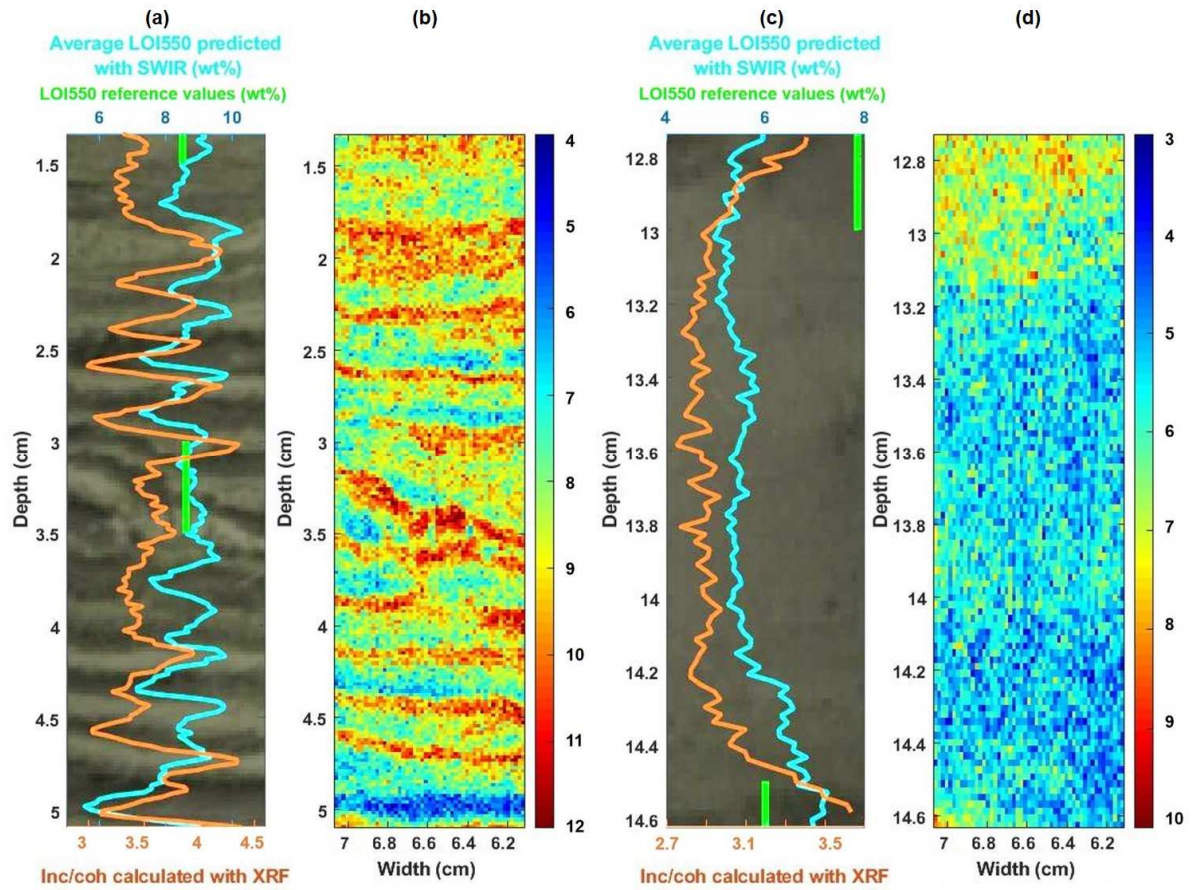
609 Figure 4: Lake Bourget (a) RGB image, (b) lithology units, (c) LOI550 predicted concentration map with the reduce model, (d)  
 610 LOI550 reference values, (e) average LOI550 predicted values, and (f) inc/coh ratios.



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).

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

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