

Modeling the Decomposition Signal and Correcting Bulk Organic Data From a Peat Deposit, a Case Study at Low Latitudes (Cameroon)

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1	Modeling the decomposition signal and correcting bulk organic data from a
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34 Abstract

Organic compounds are widely used for paleoclimatic and paleoenvironmental reconstructions. Bulk organic proxies, however, are more complicated to interpret due to the multiple causes of variation in climatic and environmental conditions and the degree of diagenetic alteration. As labile compounds, rich in easily degradable function and generally richer in heteroatoms such as oxygen and nitrogen, decompose, the remaining organic matter becomes progressively richer in refractory carbon and its carbon content increases. Thus, in a peat deposit composed almost entirely of organic matter, total organic carbon (TOC) is expected to increase with time and depth, which could mask the paleoclimatic signal. We propose a simple model for peat sediments to remove the decomposition signal based on a logarithmic function fitted with a partial dataset where decomposition is the main parameter. The subtraction of the obtained logarithmic function to the raw data (i.e., measured data) leads to "residual" data. We discuss the influence of different parameters (water table depth, vegetation, microbial community) on the "residual" data and their possible link to paleoclimatic and paleoenvironmental variations. This method is tested on bulk elemental and isotopic data obtained from a new peatcore from the Adamawa Plateau (North-East Cameroon) covering nearly 10 ka cal BP. Comparison with Rock-Eval® parameters highlights similar variations between the Hydrogen Index and residual TOC variations, supporting the interpretation based on residual TOC. Our approach allows to extract paleoenvironmental information from decomposition-prone bulk organic proxies and can be generalized to peat deposits where decomposition plays a major role in controlling bulk data. Key words: Peat deposit, Decomposition model, Bulk organic data

71 Introduction

Paleoclimatic proxies based on organic compounds rely on the assumption that these compounds are resistant to diagenesis. Many organic compounds can record pre-depositional and syn-depositional information such as climatic conditions (e.g., temperature, hydrology) or environmental conditions (e.g., major vegetation types, pH, methanogenesis) (Sachse et al., 2012; Diefendorf and Freimuth, 2017; Inglis et al., 2019; Naafs et al., 2019). This signal can, however, be overprinted by postdepositional processes such as decomposition (Gupta and Kawahata, 2006) or contamination by other reservoirs (Makou et al., 2018).

79 Peat deposits have been successfully used to reconstruct past climatic variations at all latitudes using 80 diverse proxies such as pollen, plant macrofossils or biomarkers (e.g., Pancost et al., 2003; Booth et 81 al., 2004; Baker et al., 2014). Bulk analysis of organic matter such as Rock-Eval® or elemental analysis 82 are routine techniques in paleoenvironmental studies. These non-specific analyses give first insights 83 into the sources, nature and decomposition stage of organic matter (e.g., Talbot and Johannessen, 84 1992; Kuhry and Vitt, 1996; Baker et al., 2014). However, in bulk organic data, the paleoclimatic or 85 paleoenvironmental signal is often hidden by the signal of decomposition (Kuhry and Vitt, 1996; 86 Drollinger et al., 2019). Some proxies were specifically developed to reconstruct the peat 87 decomposition stage such as colorimetric determination (Chambers et al., 2011; Biester et al., 2014) 88 or thermal analyses (Upton et al., 2018; Cooper et al., 2019), while others such as the C/N ratio are 89 sometimes used as an indicator of organic matter decomposition (Kuhry and Vitt, 1996) or of organic 90 matter sources (Baker et al., 2014). In intertropical regions, peat deposits have a large paleoclimatic 91 potential especially when applying organic geochemistry techniques (e.g., Sukumar et al., 1993; 92 Bonnefille et al., 1995; Aucour et al., 1996, 1999; Behling and Safford, 2010). Until now, no study has 93 specifically focus on correcting bulk organic data in tropical peat.

94 Peatlands are highly impacted by organic matter decay (Clymo, 1984). Peats are usually divided in two 95 distinct layers: the upper layer (the acrotelm), above the mean water table depth and exposed to oxic 96 conditions, and the lower layer (the catotelm) situated under the mean water table depth and 97 dominated by anoxic conditions (Ingram, 1978; Clymo, 1984). Clymo (1984) and Clymo et al. (1998) 98 focused on models of peat mass accumulation and decay rules and indicated that about 90% of the 99 original biomass is lost in the upper oxic part of the peat within an indicative period of 10 to 100 years 100 but selective decay continues in the anoxic layer.

101 Peat organic matter is often mainly composed of different pools of organic compounds with different sensitivities to decomposition (Dodla et al., 2012) and different δ^{13} C composition (Benner et al., 1987). 102 103 The labile organic compounds such as carbohydrates and proteins composed of easily hydrolyzable 104 functions rich in oxygen and nitrogen rapidly decompose after deposition while recalcitrant organic 105 compounds such as lignin and lipids, having long carbon chains and aromatic structures rich in carbon, 106 can be selectively preserved (Dodla et al., 2012; Wang et al., 2015). Thus, despite global mass loss and 107 carbon loss during organic matter decomposition (Clymo, 1984), the remaining organic matter, mainly 108 composed of recalcitrant compounds, becomes more and more concentrated in carbon with 109 increasing time and depth (Fig. 1). In the oxic layer, aerobic decomposers preferentially use ¹²C, resulting in an increase in ¹³C content (Ågren et al., 1996; Drollinger et al., 2019). The mineral fraction 110 in the peat is a key point to understand the variations in TOC. If the mineral component is very low, 111 112 the TOC will follow the trend of the organic matter and increase with depth and time (e.g., Upton et 113 al., 2018). In mineral-rich peat, or when mineral fraction supply varies, the increasing trend will no 114 longer be visible because the increasing proportion of the mineral fraction due to the decomposition 115 of the organic matter will mask the evolution of the carbon in the organic matter (e.g., Baker et al., 116 2014; Njagi et al., 2021).

While the effects of early diagenesis on δ^{13} C, δ^{18} O or Mg/Ca of foraminifera and carbonate sediments 117 118 have been studied for decades (Berner, 2020), and several corrections of these proxies from 119 diagenetic overprint have been proposed (e.g., Schrag et al., 1995; Rosenthal and Lohmann, 2002), 120 only a few studies exist on the diagenetic effects of organic matter decomposition on bulk parameters 121 used for paleoenvironmental studies. The importance of TOC corrections for petroleum studies is well 122 known and several corrections specific to source rocks are available but they have not been applied 123 to paleoenvironmental reconstructions until recently (Hart and Hofmann, 2022). In a marine core from the Timor Sea, Gupta and Kawahata (2006) observed a high impact of diagenesis on labile components 124 125 (amino acids) and proposed a correction of the measured total organic carbon (TOC) using a linear 126 equation. They suggest that corrected organic carbon more accurately reflects the original organic 127 carbon deposited on the sea floor and thus is more appropriate for primary productivity estimates. 128 In this paper, we focus on bulk organic data from a peatcore situated on the Adamawa Plateau in 129 Cameroon. Several maar lakes from the Adamawa Plateau have been studied for paleoclimatic and 130 paleoenvironmental reconstruction (e.g., Ngos III et al., 2003; Vincens et al., 2010; Nguetsop et al., 131 2011; Lebamba et al., 2016; N'nanga et al., 2021) but until now no peat deposit has been investigated. 132 We propose a method to deconvoluate the diagenetic signal from the climatic signal in peat. We 133 develop a model that allows subtraction of a mean decomposition signal from bulk parameters such 134 as TOC, δ^{13} C and C/N. Residual data provide a robust means of interpreting palaeoclimatic and 135 palaeoenvironmental variations in parameters for which the decomposition signal is the main mode 136 of variability (in particular TOC).

137

1381. Study site and materials1391.1.Study site

The NGaoundaba peat deposit (N7.13542° E13.69009°, 1175m above sea level) is located in North Cameroon near the city of NGaoundéré on the Adamawa Plateau, occupying a volcanic crater situated next to Lake Tabéré. Its current surface area covers ~18 000 m², and the maximum depth is still unknown. According to Letouzey (1958), the peat deposit is situated in the soudano-guinean shrubs savannas from the Adamawa Plateau. Nowadays, the peat is covered by sedges (Cyperaceae), that are annually burned. Tropical peatlands of Africa from similar settings are largely sedge-dominated and peat composition is a mix of sedges and woody remains from the surrounding forests (Dargie, 2015).

147 **1.2. Sampling**

A 6-meter-long core was collected on February 2019 using a Russian peat corer. The core is composed of twelve consecutive 50-cm sections and consists of dark brown peat containing plant debris. The color is consistently dark brown over the whole core. The NGaoundaba peat deposit is continuous and essentially composed of peat without sandy or clayey zones. The core was subsampled at 2.5-cm intervals corresponding to a resolution of around 40yr. Samples were freeze-dried prior to analysis.

153

154 **2.** Analytical methods

155 **2.1. Dating**

The chronological framework of NGaoundaba sequence is based on 30 radiocarbon dates carried out
at the LMC14 Laboratory (Saclay, France) following the procedure from Dumoulin et al. (2017) and
Moreau et al. (2013). Measurements were performed on bulk peat sediment. Data were compiled

using the R-software Bacon v2.5 (Blaauw and Christen, 2011) and calibrated using the SHCal20 calibration curve (Hogg et al., 2020) and postbomb calibration curve NH3 (Hua et al., 2013).

161

162 **2.2. Rock-Eval® thermal analysis**

163 Rock-Eval® analyses were performed on 69 samples using 10 mg of ground peat and a Rock-Eval® 6 164 (Vinci Technologies, France). The Rock-Eval® thermal analysis is based on continuous measurement of effluents, i.e., hydrocarbons (HC), carbon monoxide (CO), and carbon dioxide (CO₂), released during 165 166 the thermal cracking of organic compounds under pyrolytic conditions (from 200 to 650°C at 25°C min⁻ 167 ¹ in an inert atmosphere), followed by the combustion of residual organic compounds (from 200 to 168 850°C in an oxidative atmosphere). The resulting thermograms were used to calculate the standard 169 parameters by integrating the amounts of HC, CO, and CO₂ within the defined temperature limits 170 (Lafargue et al., 1998; Behar et al., 2001). The Total Organic Carbon (TOC parameter) is calculated as 171 the sum of all C effluents (i.e., HC, CO, and CO₂) under a temperature limit (Lafargue et al., 1998) and 172 usually represents the amount of organic C. When inorganic carbon forms are negligible, the percent 173 C is calculated as the sum of organic carbon (TOC) and MinC parameter. The Hydrogen Index (HI) 174 corresponds to the amount of HC released during pyrolysis relative to percent C. In organic samples 175 with the same source of organic inputs, a decrease in HI is usually related to the decomposition of H-176 rich organic compounds (dehydrogenation), leading to an enrichment of aromatic compounds during 177 diagenesis in lake deposits (Meyers and Lallier-Vergès, 1999) or pedogenesis in soils (Disnar et al., 178 2003; Barré et al., 2016). In addition to the above standard parameters, Disnar et al. (2003) proposed 179 using the shape of thermograms to obtain additional information about OM quality. In the present 180 study, we used the I index to quantify the preservation of the thermolabile C pool (Sebag et al., 2016). 181 This index is derived from the integrated S2 areas in specific temperature ranges (200--400 °C, 400--182 460 °C, and > 460 °C), and is usually interpreted in terms of specific thresholds of the thermal stability 183 of organic compounds, separating the thermolabile, thermoresistant, and thermorefractory C pools 184 (Disnar et al., 2003; Sebag et al., 2006; Saenger et al., 2013). The I-index has recently been used to 185 measure the degree of decomposition of a tropical peat to identify an event of increased 186 decomposition of organic matter after deposit (Garcin et al., 2022).

187 While it is well calibrated for sedimentary organic matter (i.e., kerogens), Rock-Eval[®] percent C needs 188 to be corrected in soils and litters (Disnar et al., 2003). The correction factor calculation depends on 189 an estimation of the decomposition state of the sediment. As decomposition state is a focus of this 190 study, we chose to use elemental and stable isotope analyses rather than Rock-Eval[®] analyses for data 191 processing to avoid the use of any pre-processing assumption of decomposition state.

192

193

2.3. Elemental and stable isotope analyses

194 A total of 66 samples was ground and homogenized, then measured for TOC, total nitrogen, and δ^{13} C 195 composition of TOC. Between 2 and 4 mg of non-acidified sediment were combusted in tin capsules 196 using an elemental analyser (Vario Micro Cube Elementar) coupled to a thermal conductivity detector 197 and an isotope ratio mass spectrometer IRMS (Elementar Vision). The carrier gas was helium. 198 Samples were first passed through a combustion furnace at 950°C under an excess of oxygen with 199 copper oxide as an oxidation catalyst, producing CO₂, N_xO_x, and H₂O. Then, a reduction furnace at 200 550°C reduced NxOx to N2 and removed excess O2 using reduced copper. H2O was trapped and 201 removed using a phosphorous pentoxide chemical trap. N₂ and CO₂ were separated using a purge and 202 trap desorption column. The C/N ratio was calculated as the ratio between TOC and wt%N.

A working standard (IVA sediment) was analysed every 10 samples and used to normalize the mass spectrometer signals. Triplicates were analysed every 3 samples and standard deviations were calculated. The absence of carbonates in the samples was confirmed by acid-treating 6 samples (1 every meter) using vapour of 12N hydrochloric acid for 72 hours and then performing a comparative analysis.

208

209 3. Data processing 210 3.1.General information

The method proposed in this study is divided into 4 steps (Fig. 2) and described in detail below. 211 212 Kinetics of organic compound degradation follow a simple first order equation (Westrich and Berner, 213 1984; Grossi et al., 2003) with different reactivity depending on the compounds. The increase in the 214 proportion of recalcitrant compounds leads to a progressive increase in carbon concentration despite 215 the total mass loss (Fig. 1). Using a different approach, Clymo (1984) and Clymo et al. (1998) developed 216 models of peat accumulation. Based on equation 1, α denotes the manner of decay and constant, 217 linear and quadratic rules were tested by Clymo et al. (1998). Using a linear decay rule α_{L}^* , the plot of 218 peat growth (cumulative carbon M_t) follows the logarithmic equation (2) with p* the rate of addition 219 of dry mass at the top of the peat deposit (Clymo et al., 1998).

220
$$\frac{d\mu}{dt} = -\alpha \times \mu \, \text{with} \, \mu = \frac{m_t}{m_0} \qquad (1)$$

227
$$M_t = \frac{p^*}{\alpha_L^*} \times \ln(1 + \alpha_L^* \times t) \quad (2)$$

Based on these observations and on the logarithmic trend followed by TOC with age and depth in our dataset and in several others (e.g., Upton et al., 2018; Wei et al., 2012; Garcin et al., 2022), we chose to use a natural logarithmic function (noted "In") in two possible forms presented in equations 3 and 4 using age as the variable. The parameter c can be linked to the initial C content in freshly deposited organic matter, while a and b are related to the kinetic constants and the proportion of labile versus recalcitrant organic matter.

228

$$f(x) = a \times \ln(b \times t) + c \quad \forall t \in \Re^{+*}$$
(3)

236

$$f(x) = a \times \ln(b \times t + d) + c \quad \forall t \in] - d/b, +\infty[.$$
(4)

Data processing was performed using the Python software. The different parameters a, b, c and d of each function are optimized using the curve.fit() function of the SciPy Python library. The difference between the two forms is slight; equation 4 allows an offset on the t axis of the data and the domains of the function defined as the set of *t*-values accepted by the function are slightly different for the two functions. By definition, the In function is only defined for strictly positive values, equation 3 is defined for strictly positive values \Re^{+*} , while equation 4 is defined for t above the ratio of d and b parameters -d/b (i.e. for *t c*]-d/b; +∞[).

The choice of the function for each parameter was determined by comparing the determination coefficient r^2 between the raw data and the curve-fit for each form. We called "raw data" the initial data prior to any data treatment.

240 **3.2. Data normalization**

- As logarithmic functions can only be used for positive and non-zero values, raw data were normalized
- 242 (scaling of all values in the range of 0 and 1) prior to any analysis (Fig. 2 Step1). Practically, all values

were normalized using the MinMaxscaler transforms from Python library sklearn.preprocessing basedon the following equation 5:

247

 $x_{scaled} = \frac{x - x_{min}}{x_{max} - x_{min}} \tag{5}$

245 We add 0.001 to all normalized ages to avoid having a zero *t*-value that cannot be used in a

246 logarithmic function.

248

249 **3.3. Total curve fitting and derivative calculation**

The method is based on two successive curve fittings, which are presented in the next two subsections.
The objective is to find a curve fit based only on a part of the initial dataset where the decomposition
is predominant.

253 A first option would use the upper oxic layer thickness (acrotelm) as most of the decomposition occurs 254 in this layer (Clymo, 1984). However, no measurement of this parameter is available for the 255 NGaoundaba peat deposit. Based on the mean water table depth, upper oxic layer thicknesses 256 between 5 and 35 cm were estimated for several temperate peat deposits (Kuhry and Vitt, 1996; Evans 257 et al., 1999; Weijers et al., 2004, 2006; Liu et al., 2010; Drollinger et al., 2019). In a tropical peat swamp 258 forest, Jauhiainen et al. (2005) reported a water table varying between 80 cm under and 20 cm above 259 the peat sediment surface throughout the year with maximum occurrences of values between 10 and 260 30 cm under the peat sediment surface. The upper oxic layer thickness is usually on the order of tens 261 of centimeters. In the case of the NGaoundaba dataset, neither measurement of the upper layer 262 thickness nor estimation based on literature can be used for the modeling as it would involve only a 263 few points and would lead to poorly constrained results.

To determine the age where the decomposition is the main parameter controlling bulk organic data, we first fit the logarithmic function *f* using all x-values, then we calculate the derivative of this function *f* and determine the range of x-values where f'(x)>1, thus finding the inflection point of the curve (Fig.2 - Step 2 and Fig.3 - Light colored curves). The value f'(x)>1 was fixed arbitrarily. This choice avoids using the whole dataset for the modeling and avoids purely circular reasoning.

269

270 **3.4. Partial curve fitting**

271 A new function *g* is then fitted based only on the reduced range of x-values (Fig. 2 - Step 3 and Fig. 3). 272 In other words, only a part of the original data is selected for the final curve fitting *g*. For each 273 parameter, the selected x-values are indicated in dark color on Figure 3. A total of 13, 17 and 11 x-274 values were selected for TOC, $\delta^{13}C_{\text{bulk}}$ and C/N, respectively.

275

276 **3.5. Curve fit subtraction**

The last step is the subtraction of the function *g* (i.e., the modeled data) to the raw data. The resulting data are named the residual data. Thus, positive residual values indicate that the raw data values are superior to those of the modeled data, indicating an excess of this parameter compared to the modeled data. Residual data are smoothed (Fig. 2 - Step 4) using a moving average method.

282 **4. Results**

283 **4.1. Age model**

Calibrated ages range from -39 a cal BP at 10 cm depth to 9642 a cal BP at the bottom (590 cm) (Fig.
4, Tab. 1). The age-depth model presents a quite uniform sediment accumulation rate except around
150 cm-depth (2.5 ka cal BP) and 200 cm-depth (4.0 ka cal BP). These two periods are not situated at
the limit between two core sections, as indicated on figure 4.

288

289 4.2. Elemental raw data

TOC increases with increasing depth and age ranging from 26.76 to 53.5 % for elemental and stableisotope analyses (Fig. 5(A)).

The C/N ratio roughly increases with depth and age. Until 4.5 ka cal BP, values increase nearly linearly (Fig. 5(C)). From 4.5 to around 5 ka cal BP, the C/N ratio decreases and then stabilizes until 7.1 ka cal BP. The bottom of the core is marked by a general increase of the C/N ratio with small-scale variations.

The range of values of elemental raw data is consistent with data reported for other African peat deposits (e.g., Aucour et al., 1999; Baker et al., 2014; Strobel et al., 2019).

297

298 4.3. Rock-Eval® I-index and HI

299 The I-index ranges from 0.06 to 0.37. The I-index variations can be divided into two periods (Fig. 5(D)).

The first period from the present to 6.4 ka cal BP is characterized by a regular decrease in I-index from 0.37 to 0.08. The second period from 6.4 ka cal BP to the bottom of the core presents more variations,

but with a narrower amplitude between 0.2 and 0.06 (Fig. 5(D)).

The HI ranges from 195 to 427 (Fig. 6(G)). The HI is between 250 and 300 from 5.8 ka cal BP until present except between 4 and 3 ka cal BP where values are around 225. The highest HI values are found from 7.9 to 5.8 ka cal BP and at the bottom of the core. From 9.4 to 7.9 ka cal BP, HI values are under 300 (Fig. 6(G)).

307

3084.4. Isotopic raw data

309 The $\delta^{13}C_{bulk}$ presents a general decrease with increasing depth and age ranging from -15.6 to 310 -26.3‰ (Fig. 5(B)). The $\delta^{13}C_{bulk}$ decreases from the top of the core to 3 ka cal BP from values around -311 16‰ to values around -22‰. Between 3 and 4 ka cal BP, $\delta^{13}C_{bulk}$ is close to -25‰. The $\delta^{13}C_{bulk}$ increases 312 between 4 ka cal BP and 5.8 ka with most values between -23 and -20.4‰ compared to values around 313 -25 between 5.8 and 9.4 ka cal BP. The $\delta^{13}C_{bulk}$ also increases from 9.4 ka to the bottom of the core 314 ranging from -21.4 to -20.4‰ during this period.

315

316 4.5. Processed residual data

317 Processed residual data range from -0.126 to 0.181, -0.189 to 0.815 and -0.090 to 0.782 for TOC,

 $\delta^{13}C_{\text{bulk}}$ and C/N respectively. Both residual TOC, residual $\delta^{13}C_{\text{bulk}}$ and residual C/N are mostly positive (Fig. 6(C), (D) and (E) respectively).

- Residual TOC values are decreasing from the bottom of the core until 8 ka cal BP with values close zero between 9 and 8 ka cal BP (Fig. 6(D)). From 8 to 4 ka cal BP, residual TOC are between 0.1 and 0.2 except around 5.5 ka cal BP where values are slightly lower. From 2.5 ka cal BP until present, TOC
- 323 values present rapid variations between -0.13 and 0.12.

324 The residual $\delta^{13}C_{bulk}$ presents a general decreasing trend and positive values from the bottom of the 325 core to around 4 ka cal BP (Fig. 6(E)). The period of less depleted values from 5.8 to around 4 ka cal BP 326 observed in the raw $\delta^{13}C_{bulk}$ data (Fig. 5(B)) is still visible in the residual $\delta^{13}C_{bulk}$ with positive residual 327 data ranging from 0.2 to 0.5.

The residual C/N presents similar variations as the raw C/N data with a globally increasing trend with depth and age (Fig. 6(F)). Values are close to zero until 2.5 ka cal BP and between 5 and 7.5 ka cal BP. The highest values occur between 8.5 and 9 ka cal BP.

331

333

5. Discussion

5.1. Interpreting the residual data

The log-generated data represent the part of the signal due to decomposition. Residual values close to 0 indicate a good correspondence between the original data and the log-generated data (Fig. 6). Higher values (both positively and negatively) indicate a greater difference between raw data and the model and suggest either a change in the decomposition compared to the model or the influence of other parameters that will be discussed in the next paragraphs.

In a simple approach, the carbon accumulation in peatlands can be described as a balance between vegetation inputs and decomposition (Frolking et al., 2001; Kurnianto et al., 2015). Even if microbial organic matter is generally not considered in the mass balance, microbial activity is a key point of decomposition processes (Moore, 1989). The TOC excess is thus linked to either reduced decomposition or an increase in deposition compared to the mean decomposition signal (and viceversa). Changes in paleo -climate and -environment exert a strong influence on these parameters.

345

346 5.2

5.2. Influence of water table depth

347 An increase in wetness leads to changes in peatland surface structure and an increase in carbon 348 sequestration by increasing litter production and decreasing litter decay losses (Belyea and Malmer, 349 2004). These changes are driven by an increase in acrotelm thickness due to a rise of the water table 350 (Belyea and Malmer, 2004). Moisture content, redox potential and pH control the microbial 351 community structure and can limit or enhance the presence of key decomposers (Girkin et al., 2020), 352 even in deep peat deposits (Kluber et al., 2020). Furthermore, Ise et al. (2008) demonstrate the 353 existence of a positive feedback between accumulation of soil organic carbon, water table depth and 354 decomposition rates, highlighting the high sensitivity of peatland to climate variations. Hodgkins et al. 355 (2018) demonstrated that the recalcitrance of tropical peat deposits is higher than that of boreal peat 356 deposits which allows them to persist despite warmer and sometimes drier conditions. Tropical peat 357 also accumulates because of the low decomposition of roots and woods under anoxic conditions when 358 the water table is high (Chimner and Ewel, 2005).

The positive values of residual TOC before ca 4 ka cal BP (Fig. 6(D)) could indicate a period of increased wetness leading to a rise of the water table favouring preservation of the organic matter. This period is consistent with the timing of the African Humid Period (AHP), beginning around 14.5 ka cal BP and ending between 6 and 4 ka cal BP (among others, Demenocal et al., 2000; Kröpelin et al., 2008; Amaral
et al., 2013). The period between 9 and 8 ka cal BP that presents residual TOC close to zero could
correspond to a relatively drier intermission during the AHP.

365

366 **5.3. Influence of changes in vegetation**

367 Major shifts in vegetation also have a strong influence on both decomposition and deposition of organic matter (Belyea and Malmer, 2004). Tropical peat deposits may be visually uniform despite 368 369 considerable changes in vegetation inputs (Page et al., 1999). The visual homogeneity of the 370 NGaoundaba peat deposit does not exclude changes in the vegetation. A reciprocal relation between 371 carbon storage and plant species diversity has been identified in a tropical peat deposit from Sumatra 372 (Shimamura and Momose, 2007). Changes in the sources of organic matter have an influence on the 373 initial proportion of thermo-labile vs thermo-stable organic matter (Wang et al., 2015) and, thus, on 374 the evolution of this organic matter during decomposition. Major changes in vegetation are reported 375 at the end of the African humid period (AHP) (Maley and Brenac, 1998; Vincens et al., 2010) and could 376 explain part of the observed variations in residual TOC by changing the type and amount of vegetation 377 inputs to the peatland.

To identify the period where the signal is most influenced by vegetation changes at the NGaoundaba peat deposit, we use $\delta^{13}C_{\text{bulk}}$, both raw and residual (Fig. 5(B) and fig. 6(E)). Skrzypek et al. (2010) demonstrated that the primary $\delta^{13}C$ signal of peat-forming plants is preserved and that decomposition has only a secondary influence on the $\delta^{13}C_{\text{bulk}}$ signal. The latter has been directly used to describe changes in C3/C4 vegetation (Baker et al., 2014).

383 The two main periods observed in the residual $\delta^{13}C_{bulk}$ data before and after around 4 ka cal BP are 384 roughly consistent with the timing of the AHP (Fig. 6(E)). The raw $\delta^{13}C_{bulk}$ values close to -25‰ until 385 5.8 ka cal BP are consistent with a C3-dominated environment suggesting predominance of forest taxa 386 (Fig. 5(B)). The period from 5.8 to around 4 ka cal BP highlighted in both residual and raw $\delta^{13}C_{\text{bulk}}$ 387 presents less depleted values. It may suggest a short transition to C4-dominated savanna taxa 388 followed by a short return of the C3-dominated environment between 4 and 3 ka cal BP, with raw 389 $\delta^{13}C_{bulk}$ around -25‰. After 3 ka cal BP, the signal is consistent with an increasing influence of C4-type 390 plants.

Human activities such as turning peatland into cultured field also can have an impact on the accumulation of carbon (Wang et al., 2017) and, consequently, on the $\delta^{13}C_{\text{bulk}}$ signature (Lane et al., 2008). The influence of human occupation on sedimentary archives is reported in several studies from West Africa during late Holocene such as around 2.6 ka cal BP at lake Barombi MBo (Cameroon) (Garcin et al., 2018) or after 2.2 ka cal BP in the Congo River Basin (Bayon et al., 2019). It cannot be excluded that the recent history of the NGaoundaba peat deposit was influenced by human occupation.

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5.4. Influence of C-cycling and microbial organic matter

400 Peat deposits can shift from a sink to a source of CO_2 and CH_4 gases reflecting changes in the microbial 401 communities and associated biogeochemical processes such as methanotrophy and methanogenesis 402 (Jauhiainen et al., 2005; Roehm, 2005). Even if the proportion, in terms of the mass of the microbial 403 organic matter, is not large, the specific $\delta^{13}C$ signature of some microbial compounds may not be 404 negligible. Indeed, some carbon sources such as methane can present important variations of their 405 carbon isotopic composition and values as depleted as -110‰ for direct reduction of CO₂ to CH₄ 406 (Whiticar, 1999). The δ^{13} C of methanotrophs' biomass is generally close to the carbon source signature 407 even if depletion or enrichment of cellular components can be observed depending on metabolic 408 pathway or environmental parameters (Jahnke et al., 1999). Thus, even a small proportion of highly 409 ¹³C-depleted microbial biomass could significantly modify the δ^{13} C_{bulk}.

Mosses such as Sphagnum spp. can use recycled carbon in wet environments (Price et al., 1997; 410 411 Nichols et al., 2009). By extension, $\delta^{13}C_{\text{bulk}}$ has also been proposed to reflect variations in the uptake of C recycled from methanogenesis with enriched values corresponding to periods of high 412 413 methanogenesis (Jones et al., 2010). However, Sphagnum are not present at the NGaoundaba 414 peatland, which is dominated by sedges, so $\delta^{13}C_{\text{bulk}}$ cannot be interpreted this way. 415 As an example, if we consider CH₄ with a δ^{13} C signature close to -60‰, taking into account both direct 416 reduction of CO₂ to CH₄ and acetotrophic methanogenesis (Whiticar, 1999). In a first approximation, 417 we can consider that bulk organic matter produced by consumption of this methane will have a similar 418 δ^{13} C signature as the source CH₄. Even a 1% input of this microbial organic matter in the bulk will lead 419 to a decrease of more than 0.5‰ of the $\delta^{13}C_{\text{bulk}}$. Present bulk data don't give us much information 420 about microbial activity. However, it is important to keep in mind that a microbial signal can superimpose on the primary $\delta^{13}C_{bulk}$ signal and either increase or mask pre-existing variations. Kuhry 421 422 and Vitt (1996) compared the evolution of bulk C/N in both the acrotelm and catotelm in a Sphagnum 423 peat, suggesting a predominant impact of peat decomposition on C/N values. The increase in acrotelm 424 is interpreted as a preferential N loss in oxic conditions while the decrease in catotelm is consistent 425 with a predominance of methanogenesis affecting C content while N is no longer affected by 426 decomposition and is much less mobile in the sediment under anoxic conditions. These observations 427 are not consistent with the general increase observed in C/N in the NGaoundaba peat deposit (Fig. 428 6(G)). This increase follows the general increase observed in TOC and is interrupted by a short interval 429 from 9 to 8 ka cal BP when the C/N increases and might suggest a change in the origin of the organic 430 matter (Talbot and Johannessen, 1992).

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5.5. Validation and limits of the approach

433 The decreasing I-index observed in the NGaoundaba peat deposit from 6.4 ka cal BP to the surface 434 reflects the decrease of thermolabile compounds and the relative increase in thermostable 435 compounds, reflecting the progressive decomposition of labile organic matter and the increase in 436 thermal stability of organic matter from 6.4 ka cal BP until present (Sebag et al., 2016) (Fig. 5(D)). 437 During this period, raw TOC increases, indicating an enrichment in thermostable C-rich compounds 438 relatively to thermolabile compounds more rich in heteroatoms. Between the bottom of the core and 439 6.4 ka cal BP, the I-index remains rather stable; it is likely that most thermolabile compounds are 440 decomposed and it is consistent with a raw TOC around 50% with limited variations during this period.

441 Our method is based on the observation that for this particular peat deposit, the TOC increases 442 progressively with depth and follows nearly exactly a logarithmic curve. The function used for the 443 modelling will depend on the dynamics of the system (Clymo et al., 1998). Thus, this method is 444 undoubtedly not applicable to all peat deposits. This increasing trend is expected for peats composed 445 almost entirely of organic matter. The presence of mineral-rich intervals such as clayey or sandy 446 intervals or a steady input of a large amount of mineral matter will affect this trend (Baker et al., 2014; 447 Njagi et al., 2021). Such records are therefore not ideal for the modeling presented in this study. The 448 method gives a lot of weight to the top values of the core and slight analytical errors in these values 449 could have a strong impact on the model.

As vegetation may be the primary factor controlling $\delta^{13}C_{\text{bulk}}$ (Skrzypek et al., 2010), the curve fitting might be distorted by the primary impact of vegetation changes. It may explain why the curve fitting for $\delta^{13}C$ is not as good as for TOC with the modeling function rapidly diverging from the data (Fig. 3).

453 The residual $\delta^{13}C_{bulk}$ (Fig. 6(E)) erases two periods of relatively enriched $\delta^{13}C_{bulk}$ from 5.8 to 4 ka cal BP 454 and from the bottom of the core to 9 ka cal BP visible in the raw $\delta^{13}C_{bulk}$ record (Fig. 5(B)).

The comparison between residual TOC and HI from the same peatcore shows striking similarities (Fig. 6(D) & (G)). The HI can be controlled by the degree of decomposition but can also reflect changes in the origin of the organic matter (Sebag et al., 2016). The higher values observed between 8 and 6 ka cal BP and at the bottom of the core tend to indicate well preserved terrestrial organic matter that is consistent with the TOC data and the wettest period of the African Humid Period. The decrease in HI

- 460 between 9 and 8 ka cal BP suggests a change in the origin of the organic matter or in its decomposition
- 461 and is consistent with the increase in the C/N ratio observed at the same period.
- 462

463 Conclusions

464 The present case study based on a West-African peat deposit presents several interesting characteristics: it is nearly continuous, macroscopically homogeneous without clayey passages, and 465 466 some bulk parameters such as TOC present a strong logarithmic trend with age. Thus, it is possible to 467 propose a method to isolate and subtract the part of the variation only due to the decomposition of 468 organic matter and interpret the residual variations as modifications of the environmental conditions. The residual TOC obtained with our method highlights well-known climatic transitions and variations 469 470 such as the African Humid Period and presents similar variations as other parameters such as HI. 471 Results obtained from residual C/N and $\delta^{13}C_{bulk}$ are more questionable, suggesting a greater impact of 472 parameters other than decomposition on the variations, such as vegetation shifts (Skrzypek et al., 473 2010; Baker et al., 2014), changes in microbial processes (Moore, 1989; Girkin et al., 2020) or detrital 474 input (Amorim et al., 2022) associated with differences in the way the decomposition processes affect 475 these parameters (Ågren et al., 1996). Based only on bulk organic parameters, it is difficult to precisely 476 constrain the origin and timing of the proposed environmental and climatic changes, thus the use of 477 other proxies such as pollen data and biomarkers will help to confirm or infirm the climatic and 478 environmental interpretation proposed here.

479 This method is certainly not applicable to all peat deposits and we recommend a careful analysis of 480 the data and testing before applying it. We recommend applying this method to records composed 481 almost entirely of organic matter and without significant variation in the mineral fraction. This method 482 is a quick and straightforward way to obtain a first overview of the paleoclimatic and 483 paleoenvironmental variations from a new sediment core based on bulk analytical methods 484 (Elemental Analysis and Rock-Eval®). It can help to identify periods of great interest for more intensive 485 investigations (e.g., pollen, biomarkers), by highlighting the main transitions visible in bulk organic 486 data.

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Figure captions 771 772 773 Fig. 1: Evolution of carbon mass and carbon concentration with time in OM-dominated sediment 774 reflecting the progressive mineralization of organic matter. Labile compounds are richer in 775 heteroatoms than resistant compounds, leading to an increase in C concentration as labile 776 compounds decompose while the global mass of carbon decreases. 777 778 Fig. 2: Description of the different steps of the procedure from raw to residual data. 779 780 Fig. 3: Normalized data of the NGaoundaba peat deposit plotted against age (ka cal BP & normalized): (A) TOC, (B) $\delta^{13}C_{bulk}$ and (C) C/N. The light colored curves represent the curve fitting 781 782

hormalized). (A) FOC, (b) or Clauk and (c) C/N. The light colored curves represent the curve fitting based on the
 based on the whole dataset and the dark colored curves represent the curve fitting based on the
 partial dataset using only depth with a positive derivative. The function selected for each parameter
 is indicated on the left of each panel, the constants a, b, c and d are fitted for each parameter and
 x-range. The selected x-range for each parameter is indicated in dark color (encircled points). The x-

range limit is indicated in both age and depth for each parameter.

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Fig. 4: Age-depth model of NGaoundaba peatland core. The corresponding section number is
 indicated for each ¹⁴C sample.

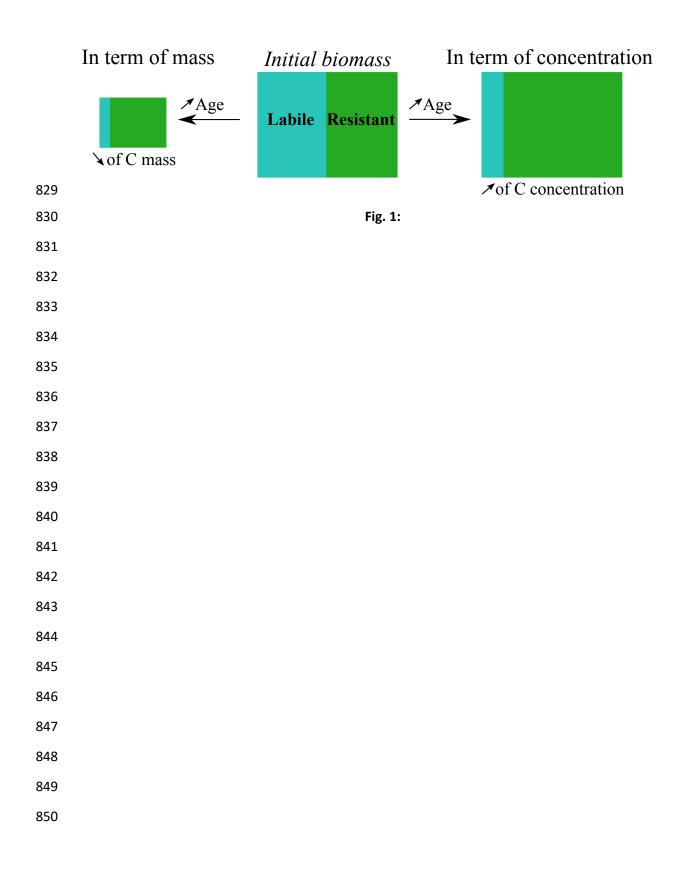
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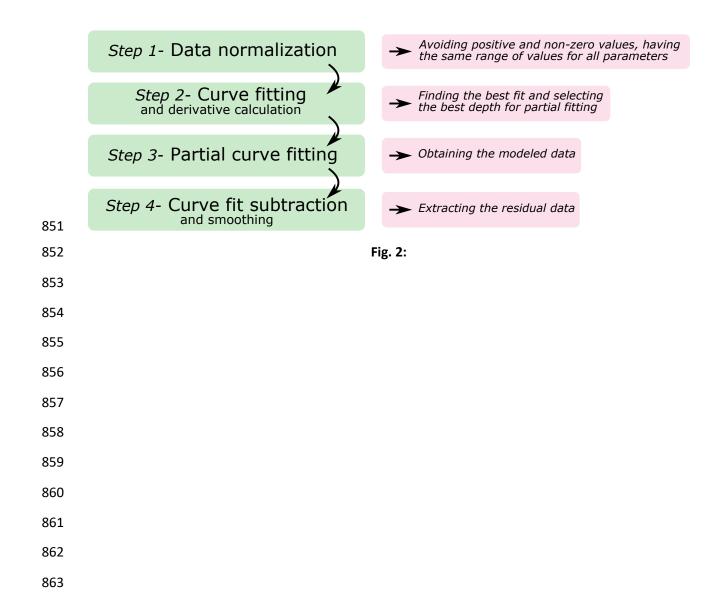
791Fig. 5: Raw data (i.e., before data processing) from the NGaoundaba peat deposit: (A) TOC (%), (B)792 $\delta^{13}C_{bulk}$ (‰), (C) C/N from Elemental and stable isotope analysis and the I-index from Rock-Eval®793analysis. Visible transitions are indicated with vertical red dashed lines.

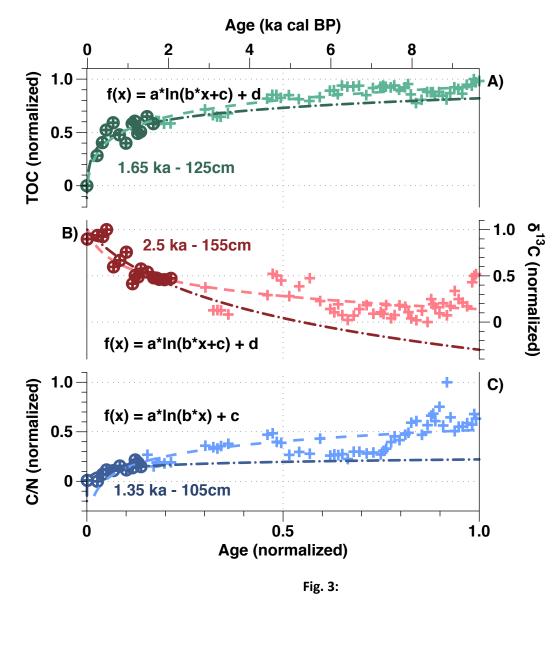
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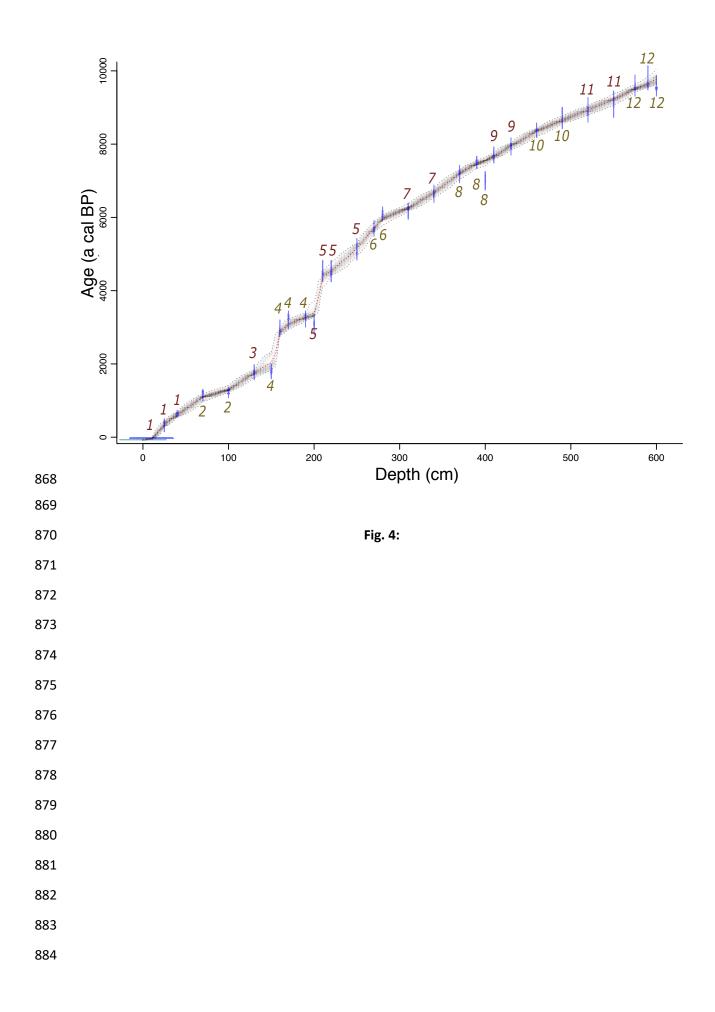
Fig. 6: Retreated NGaoundaba peat deposit data and regional climatic and environmental settings: (A) Insolation 0°N (W.m⁻²) from Berger et al. (1981), (B) $\delta D_{n-alkC31}$ corrected for vegetation changes in Lake Barombi (Southwest Cameroon) (Garcin et al., 2018), (C) Simplified pollen data from Lake MBalang (about 25 km from the NGaoundaba peat deposit) (Vincens et al., 2010) (D) TOC (%), (E) $\delta^{13}C_{bulk}$ (‰) and (F) C/N as well as (G) Hydrogen Index (HI) from Rock-Eval® analysis. The African Humid Period is highlighted in green, the termination of this period has been represented as a color gradient to illustrate the uncertainties and different possible timings of the termination. The mean

802 803	value of HI is indicated as a dashed line. Visible transitions are indicated with vertical red dashed lines.
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Sample code	Depth (cm)	Uncalibrated Age	Calibrated age (a cal BP)
58976	10	120 pMC	-39
62587	25	330 ± 30 BP	343
58977	40	725 ± 30 BP	614
58978	70	1310 ± 30 BP	1093
58979	100	1390 ± 30 BP	1290
58980	130	1870 ± 30 BP	1741
62588	150	1910 ± 30 BP	1981
64844	160	2840 ± 30 BP	2871
58981	170	3090 ± 30 BP	3082
58982	190	3130 ± 30 BP	3274
62589	200	2975 ± 30 BP	3345
64845	210	4070 ± 30 BP	4417
58983	220	4070 ± 30 BP	4531
58984	250	4475 ± 30 BP	5180
62590	270	5000 ± 35 BP	5690
58985	280	5335 ± 30 BP	5960
58986	310	5460 ± 30 BP	6255
58987	340	5875 ± 30 BP	6668
58988	370	6335 ± 35 BP	7201
64846	390	6660 ± 30 BP	7465
58989	400	6170 ± 30 BP	7547
62591	410	6870 ± 40 BP	7665
58990	430	7180 ± 40 BP	7955
58991	460	7600 ± 35 BP	8361
58992	490	7925 ± 40 BP	8653
58993	520	8080 ± 35 BP	8926
58994	550	8210 ± 40 BP	9223
62592	575	8605 ± 45 BP	9511
64847	590	8700 ± 40 BP	9642
58995	600	8590 ± 40 BP	9759

Table 1: Chronology of NGaoundaba peatland with uncalibrated AMS ¹⁴C ages (BP : before present)
 and calibrated median ¹⁴C age (a cal BP).

