

1 **Hydrologic control of carbon cycling and aged carbon**  
2 **discharge in the Congo River basin**

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18 **The age of organic material discharged by rivers provides information about its**  
19 **sources and carbon cycling processes within watersheds. While elevated ages in**  
20 **fluviially-transported organic matter are usually explained by erosion of soils and**

21 **sediments deposits<sup>1,2</sup>, it is commonly assumed that mainly young organic material is**  
22 **discharged from flat tropical watersheds due to their extensive plant cover and rapid**  
23 **carbon turnover<sup>3-7</sup>. Here we present compound-specific radiocarbon data of terrigenous**  
24 **organic fractions from a sedimentary archive offshore the Congo River in conjunction**  
25 **with molecular markers for methane-producing land cover reflecting wetland extent.**  
26 **We find that the Congo River has been discharging aged organic matter for several**  
27 **thousand years with apparently increasing ages from the Mid- to the Late Holocene.**  
28 **This suggests that aged organic matter in modern samples is concealed by radiocarbon**  
29 **from atmospheric nuclear weapons testing. By comparison to indicators for past rainfall**  
30 **changes we detect a systematic control of organic matter sequestration and release by**  
31 **continental hydrology mediating temporary carbon storage in wetlands. As aridification**  
32 **also leads to exposure and rapid remineralization of large amounts of previously stored**  
33 **labile organic matter we infer that this process may cause a profound direct climate**  
34 **feedback currently underestimated in carbon cycle assessments.**

35 Tropical humid ecosystems are hot spots of terrestrial carbon storage<sup>8</sup> and large river  
36 systems in tropical areas form an important conduit in the global carbon cycle by transporting  
37 vast amounts of biosynthetic OM to the ocean<sup>9,10</sup>. Apparent radiocarbon ages of riverine  
38 organic carbon are interpreted as the mean time elapsed since biosynthesis, integrating all  
39 intermediate storage, transport and mixing processes, and thus considered to reflect the speed  
40 of carbon cycling in watersheds. Radiocarbon studies of fluvially-transported OM reveal  
41 relatively young ages in tropical areas<sup>3-7</sup>, suggesting rapid carbon turnover, and greater ages in  
42 temperate regions with larger influence of geomorphology and soil erosion<sup>1,2</sup>. Among the  
43 controlling processes, relative changes in export of contemporary biomass versus erosion of  
44 OM from soils or sedimentary rocks (e.g., refs 1,7) as well as storage in intermediate

45 reservoirs, such as floodplains and wetlands (e.g., refs 11-13), are discussed. The exact factors  
46 controlling the continental residence times of terrestrial OM in tropical watersheds and their  
47 response to climatic changes are, however, not yet fully understood.

48 To provide insight into the response of OM cycling in large tropical watersheds to  
49 climatic changes we investigated a sedimentary archive simultaneously recording continental  
50 palaeo-climatic changes and variations in terrestrial carbon cycling in the Congo basin.  
51 Sediment core GeoB6518-1 (05° 35.30' S, 11° 13.30' E, 962 m water depth, Fig. 1) was  
52 recovered from the Congo deep-sea fan close to the river mouth. The Congo is the second  
53 largest river on Earth in terms of drainage basin size (about  $3.7 \times 10^6$  km<sup>2</sup>), water discharge<sup>14</sup>  
54 and terrestrial organic matter export<sup>15</sup>. Located in equatorial Africa, it is characterized by low  
55 intra- and inter-annual discharge variability<sup>16</sup>. Steep rapids close to its estuary separate the  
56 central Congo basin from sea-level influence. A submarine canyon incises the continental  
57 shelf, extending from the Congo estuary and leading to rapid transport of discharged material  
58 to the deep-sea fan. The ages of terrestrial organic material are therefore considered to reflect  
59 retention processes within the river basin. We measured the <sup>14</sup>C content of various OM  
60 fractions (total organic matter, microscopic wood fragments, leaf-wax *n*-alkanes, and  
61 individual leaf-wax *n*-alcohols) from several depth intervals of core GeoB6518-1 (Table S2).  
62 Using the depositional ages based on radiocarbon dating of planktonic foraminifera (Table  
63 S1), radiocarbon contents of OM fractions were decay-corrected to derive initial radiocarbon  
64 contents. The deviation from the past atmospheric <sup>14</sup>C content ( $\Delta\Delta^{14}\text{C}_{\text{initial}}$ , see Methods) at the  
65 time of deposition can be converted to apparent initial radiocarbon ages. The initial ages of  
66 the OM fractions range from isochronous up to 3,000 <sup>14</sup>C years (Fig. 2a). Notably, initial ages  
67 of wood fragments are contemporaneous to or only slightly older than depositional ages in the  
68 Early to Mid-Holocene. In contrast, the plant-wax fractions are older and show higher but

69 coherent age variability (Fig. 3). This is in accordance with both a rapid transfer of plant  
70 debris through the river system under high discharge conditions and the refractory nature and  
71 persistence of plant waxes in soils<sup>17</sup>. The aged terrestrial organic contributions strongly  
72 influence the age of total organic carbon (TOC) deposited off the Congo River despite its  
73 mixed terrestrial and aquatic origin (Fig. 2a). From about 5,000 years before present (BP) all  
74 organic components show a similar trend to greater apparent initial ages towards the present.  
75 The Congo River has, thus, exported aged OM for the last several thousand years. This  
76 finding is in contrast to <sup>14</sup>C results from modern fluvial OM in the Congo River and other  
77 tropical river systems, where terrestrial components were found to be mainly contemporary in  
78 age<sup>4-7</sup>. We infer that this discrepancy is caused by the influence of radiocarbon from  
79 atmospheric nuclear weapons testing in modern samples, masking their original age. This  
80 influence is also detected for the uppermost sample from GeoB6518-1 which exhibits  
81 reversals in the  $\Delta^{14}\text{C}_{\text{initial}}$  of all OM fractions (Fig. S3). The influence of bomb-derived  
82 radiocarbon on modern samples in carbon cycle studies therefore needs to be considered more  
83 carefully.

84 To explain the Holocene age variations we investigated indicators for OM contributions  
85 from soils, sedimentary rocks and wetlands, and also considered variable carbon turnover due  
86 to changes in river transport, continental temperatures and hydrologic conditions. Previously  
87 we showed that the OM of core GeoB6518-1 is predominantly terrigenous with the majority  
88 derived from soils<sup>18</sup>. The proportion of soil- versus plant-derived OM estimated by the  
89 abundance of membrane lipids from soil-hosted bacteria, however, was relatively invariant  
90 through time<sup>18</sup> (Table S2). While this suggests that relative contribution changes of soil-  
91 derived OM due to variable vegetation cover and soil erosion cannot explain the age  
92 variations, it does not rule out erosion of deep soil layers and intermediate deposition and re-

93 suspension during riverine transport as potential processes leading to elevated ages.  
94 Nevertheless, we regard these effects as minor considering the relatively flat geomorphology  
95 of the Congo basin<sup>14</sup>, the Congo's high discharge even under today's relatively dry conditions  
96 and the observation that similar age variations were also detected for wood fragments (Fig.  
97 2a, 3, 4). Similarly, we rule out an influence of fossil OM contributions from sedimentary  
98 rocks as the molecular composition of the plant-wax fractions does not show any indication of  
99 thermally mature hydrocarbons (Fig. S1). Also, we infer that hydraulic sorting of fine and  
100 coarse particles carrying different radiocarbon contents<sup>5</sup> cannot explain the observed ages as  
101 variations were also detected for the coarse (> 150  $\mu\text{m}$ ) wood fragments. As no large  
102 continental temperature variations in central Africa occurred during the Holocene<sup>19</sup> (Fig. 2b),  
103 we also exclude temperature-driven changes in soil carbon turnover<sup>8,20</sup> as an explanation for  
104 the observed age variations. Instead, we observe a strong relation to changes in continental  
105 hydrology. In particular, the trend towards greater ages from the Mid- to Late Holocene is  
106 paralleled by the aridification trend in central Africa<sup>21</sup> (Fig. 2c). Towards the relatively dry  
107 present-day conditions all terrestrial OM fractions converge to their greatest initial ages.  
108 Comparing the radiocarbon contents of the molecular OM fractions to the hydrogen stable  
109 isotope compositions ( $\delta\text{D}$ ) of the *n*-C<sub>24</sub> alcohol as a measure of rainfall intensity<sup>21</sup>, reveals that  
110 initial ages significantly increased when  $\delta\text{D}$  values exceeded -145 ‰ VSMOW, indicating  
111 more arid conditions (Fig. 4). We thus conclude that the observed age trend was caused by  
112 release of previously stored OM from intermediate reservoirs controlled by changes in  
113 continental hydrology. Despite the high coverage of the Congo basin by tropical rainforest,  
114 even the deposited wood fragments follow this trend, suggesting a massive release of aged  
115 terrestrial OM. Disentangling the sedimentary TOC into pre-aged and fresh portions, i.e.,  
116 directly from plants and aquatic organisms, reveals that about 30 to 70 % of TOC is pre-aged  
117 during the Early to Mid-Holocene while this portion increases to 70 to 90 % in the Late

118 Holocene (Fig. 2d). Accumulation rates of pre-aged OC at GeoB6518-1 (Fig. 2e) are higher  
119 during the latest Holocene than during the wetter Early to Mid-Holocene suggesting strongly  
120 increased export fluxes of pre-aged OM by the Congo River under more arid conditions.

121 In order to identify the source of this large-scale old OM release, we analysed bacterial  
122 signature lipids, i.e., bacteriohopanepolyols (BHPs)<sup>22,23</sup>, in sediments of GeoB6518-1. In  
123 particular, we focused on 35-aminobacteriohopane-30,31,32,33,34-pentol (aminopentol), a  
124 marker for aerobic methanotrophic bacteria predominant in wetlands<sup>22</sup>. Strong similarities of  
125 the BHP signature in the Congo deep-sea fan and in wetland deposits<sup>22,23</sup> (Fig. S2), coupled  
126 with limited <sup>13</sup>C depletion of the BHPs, are consistent with aerobic oxidation of methane in a  
127 terrestrial setting<sup>23</sup> (see supplement). The aminopentol abundance profile in GeoB6518-1  
128 (Fig. 2f) reveals a striking resemblance to the continental hydrologic changes<sup>21</sup> (Fig. 2c). In  
129 the humid Early Holocene, maximum abundance of aminopentol indicates largest wetland  
130 extent in the Congo basin while its decreasing abundance suggests shrinking methane-  
131 producing land cover during the Mid- to Late Holocene concomitant with increasing initial  
132 ages of terrestrial OM (Fig. 2a). The observed threshold-like age trend with decreasing  
133 rainfall intensity (Fig. 4) may point to an environmental tipping point with respect to wetland  
134 extent depending on the regional geomorphology of the basin. The most likely candidate for  
135 such a wetland system is the Cuvette Congolaise in the vast central depression of the Congo  
136 basin at the confluence of several tributaries. It hosts one of the World's largest swamp forests  
137 containing seasonally and permanently flooded wetlands with an estimated area of 360,000  
138 km<sup>2</sup> (ref 24) (Fig. 1). These wetlands receive plant OM from local and upstream sources and  
139 accumulate substantial amounts of OM<sup>25,26</sup>. Having remained largely unnoticed until  
140 recently<sup>27,28</sup>, the modern central Congo basin is estimated to store at least 9 Pg C<sup>28</sup> as a  
141 consequence of water-saturated wetland soils inhibiting aerobic OM decomposition and

142 instead resulting in (slower) anaerobic degradation emitting methane and other greenhouse  
143 gases<sup>29</sup>.

144         These various lines of evidence suggest that areas of OM storage under anoxic  
145 conditions and associated methane production in the central Congo basin were more extended  
146 during the more humid Early Holocene, serving as an important locus of temporary storage of  
147 plant biomass. More rainfall in the basin led to higher transport of plant organic material into  
148 the Cuvette Congolaise where it accumulated in the vast permanently flooded swamp forest  
149 areas. In water-logged wetland soils remineralisation is diminished leading to enhanced  
150 preservation and storage of OM. The elevated ages of refractory plant-wax lipids even under  
151 wet, high discharge conditions point to additional processes, such as intermediate storage  
152 during fluvial transport and /or deep soil erosion, affecting their ages. Upon aridification,  
153 permanently flooded wetland areas with methane-producing land cover contracted and  
154 previously anoxic deposits eroded triggering release of aged terrestrial OM. Additionally,  
155 lower water levels caused erosion of deeper soil layers and previously deposited river beds.  
156 Exposure of OM previously stored under anoxic conditions not only leads to release of  
157 refractory organic components which are discharged but also of labile OM that is rapidly  
158 oxidized. Thus, in addition to decreasing carbon sequestration due to wetland shrinkage, the  
159 release and remineralisation of labile OM introduces a direct climatic feedback under more  
160 arid conditions, the magnitude of which remains uncertain. Given that most tropical  
161 watersheds, such as the Amazon<sup>27</sup>, contain extended wetland areas these findings have  
162 profound global implications for the response of tropical terrestrial carbon inventories and  
163 carbon cycle feedbacks upon hydrological changes. Impacted by natural climatic changes as  
164 well as anthropogenic activities such as land use, deforestation, rising CO<sub>2</sub> levels and  
165 associated effects on climate<sup>30</sup>, any changes in tropical wetland extent may thus exert a direct

166 climatic feedback. Presently, such effects are underestimated in global climate assessments<sup>30</sup>  
167 and must be considered to more accurately assess the response of terrestrial carbon cycle  
168 dynamics to future climatic change.

169



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244

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260 **Author contributions**

261 E.S., T.I.E., J.R., P.M.G., and R.R.S. designed the study. Analytical work was performed by  
262 E.S., C.L.S.-J., H.M.T., J.R., P.M.G., and R.D.P.-H.. E.S. wrote the manuscript approved by  
263 all co-authors.

264

265 **Competing financial interests**

266 The authors declare no competing financial interests.

267

268 **Figure captions**

269

270 **Figure 1: The Congo River basin in central Africa.** Redrawn after ref 14. Light  
271 grey areas are lakes. Dark grey area is the present-day extent of swamp forest in the  
272 Cuvette Congolaise<sup>24,27</sup>. Black star offshore the Congo River mouth is sampling  
273 location of sediment core GeoB6518-1.

274

275 **Figure 2: OM ages offshore the Congo River and central African environmental**  
276 **changes.** a) Offsets in radiocarbon contents versus the past atmosphere and  
277 apparent initial ages at time of deposition (brown: wood pieces, green: *n*-C<sub>24</sub> alcohol,  
278 grey: *n*-alkanes, blue: TOC), error bars show analytical uncertainty propagated with  
279  $\Delta^{14}\text{C}_{\text{atm}}$  uncertainty, b) estimates of past temperatures<sup>19</sup>, c) hydrogen stable isotope  
280 composition of *n*-C<sub>29</sub> alkane<sup>21</sup> reflecting rainfall intensity, green dots: *n*-C<sub>24</sub> alcohol,  
281 error bars show analytical uncertainty, d) TOC disentangled in fresh (green) and pre-  
282 aged (brown) portions, e) accumulation rate of pre-aged OC, f) abundance of  
283 aminopentol reflecting extent of methane-producing landcover<sup>23</sup>.

284

285 **Figure 3: Correlation of age variations between different OM fractions.** Initial  
286 radiocarbon offsets are strongly correlated ( $r = 0.93$ ,  $p < 0.05$ ) for *n*-alkanes (grey  
287 dots) and *n*-C<sub>24</sub> alcohol indicating that both are affected by the same continental  
288 retention processes. Error bars show analytical uncertainty propagated with  $\Delta^{14}\text{C}_{\text{atm}}$   
289 uncertainty. Radiocarbon offsets are more negative for *n*-alkanes than for *n*-C<sub>24</sub>  
290 alcohol indicating that *n*-alkanes are more refractory than *n*-C<sub>24</sub> alcohol. Radiocarbon

291 offsets of wood fragments (brown dots) show no correlation to initial radiocarbon  
292 offsets of  $n\text{-C}_{24}$  alcohol except for the lowest initial radiocarbon offsets, i.e., highest  
293 apparent initial ages.

294

295 **Figure 4: Relation between rainfall intensity and OM ages.** Comparison of initial  
296 radiocarbon offsets of wood pieces (brown dots) and  $n\text{-C}_{24}$  alcohol (green dots) with  
297 hydrogen isotope compositions of  $n\text{-C}_{24}$  alcohol. Error bars show analytical  
298 uncertainty propagated with  $\Delta^{14}\text{C}_{\text{atm}}$  uncertainty. Initial radiocarbon offsets of  $n\text{-}$   
299 alkanes (Fig. 3) and TOC show the same trend but are omitted for clarity. Where the  
300 hydrogen stable isotope composition of the  $n\text{-C}_{24}$  alcohol exceeds  $-145\text{‰}$  VSMOW,  
301 initial radiocarbon offsets of all OM fractions become more negative indicating  
302 release of previously stored, i.e., pre-aged, material.

303

304 **Online Content** Methods are available in the online version of the paper; references unique to  
305 this section appear only in the online paper. Source data and additional display items are in  
306 the Supplementary Information.

307

## 308 **Methods**

309 **Age model of GeoB6518-1.** The age model of GeoB6518-1 is based on AMS dating of mixed  
310 planktonic foraminifera containing *Globigerinoides ruber* (white), *Globigerinoides sacculifer*  
311 and *Orbulina universa* isolated from sediments by wet-sieving (> 150 µm) and picking.  
312 Fractions were cleaned with H<sub>2</sub>O and 15% H<sub>2</sub>O<sub>2</sub>, carbonate was converted to CO<sub>2</sub> with 100%  
313 phosphoric acid and subsequently catalytically reduced to graphite for AMS measurement of  
314 radiocarbon (<sup>14</sup>C) contents. <sup>14</sup>C contents were corrected for blank effects<sup>31</sup> (Table S1). Most  
315 foraminiferal ages were reported earlier<sup>21</sup> and re-calibrated to calendar ages in this study. An  
316 additional age point was added for depth 128-138 cm. A further sample (78-88 cm) was lost  
317 during AMS measurement. All dates were calibrated with Calib7.0 using the Marine13  
318 radiocarbon age calibration and no regional and temporal offset in the reservoir age  
319 correction<sup>32</sup>. We set the mid-point of the sampling interval to the mean age of the calibrated 2-  
320 σ age interval. Because the uppermost sample (5-15 cm) contains radiocarbon from  
321 atmospheric nuclear weapons testing (post-1950 age), we set the core-top to zero age and did  
322 not regard the uppermost sample as an age tie-point. Ages of individual samples between tie-  
323 points were linearly interpolated.

324 **Radiocarbon dating of total organic carbon and wood fragments.** Total organic carbon  
325 (TOC) contents (Tables S2, S3, S4) were determined by combustion of ground and de-  
326 carbonated sediment samples at 1050°C using a Leco CS230 Carbon-Sulphur analyser. The  
327 relative precision of the measurements, based on triplicate analyses was better than 1.8%  
328 relative standard deviation. For <sup>14</sup>C analyses of TOC, ground sediments were treated with 1%



329 hydrochloric acid to remove carbonates and subsequently freeze-dried. Samples were  
330 combusted with copper oxide and silver wool in quartz tubes and the CO<sub>2</sub> released converted  
331 into graphite for AMS measurement. <sup>14</sup>C contents were corrected for blank contributions<sup>31</sup>.  
332 Several microscopic wood fragments (> 150 μm) were isolated from each sediment sample  
333 under a binocular microscope. After acid-base-acid treatment to remove humic materials they  
334 were combusted and the resulting CO<sub>2</sub> catalytically converted to graphite for <sup>14</sup>C  
335 measurement by AMS. <sup>14</sup>C contents were corrected for blank contributions and small sample  
336 size<sup>33</sup>. Two samples (253-258 cm, 453-458 cm) yielded ages of wood pieces younger than  
337 depositional ages. This may be due to slight variations in the marine reservoir age. Therefore,  
338 their corresponding <sup>14</sup>C data were omitted from further calculations. As these data derive from  
339 deglacial and early Holocene samples, omitting them from discussion has no influence on the  
340 observation of increasing wood ages towards the Late Holocene. Data are listed in  
341 supplementary Table S2.

342 **Radiocarbon dating of plant-waxes.** Sediments were Soxhlet-extracted with a 93:7 mixture  
343 of dichloromethane and methanol and afterwards saponified with 0.5 M KOH in methanol.  
344 After re-extraction with hexane, neutral fractions were separated by liquid chromatography  
345 over silica-gel (SiO<sub>2</sub>) columns into apolar, ketone and polar fractions by elution with hexane,  
346 hexane/dichloromethane and methanol, respectively. Elemental sulphur was removed from  
347 apolar fractions using activated copper before branched and cyclic lipids were removed by  
348 urea adduction. Unsaturated compounds were removed by liquid chromatography over  
349 AgNO<sub>3</sub>-impregnated SiO<sub>2</sub> columns. *n*-Alkane fractions were quantified against external  
350 alkane standards via gas chromatography-flame ionisation detection (GC-FID) and  
351 quantitatively transferred into quartz tubes, combusted and the produced CO<sub>2</sub> catalytically  
352 converted into graphite before AMS measurement. Alcohol fractions were acetylated with  
353 acetic anhydride with known isotopic composition and treated by urea adduction and AgNO<sub>3</sub>-  
354 SiO<sub>2</sub> chromatography. After GC-FID quantification, the *n*-C<sub>24</sub> alcohol was isolated by  
355 preparative gas chromatography using a gas chromatograph coupled to a preparative fraction  
356 collector<sup>34</sup>. After cleaning the isolated compounds by silica-gel column chromatography,

357 aliquots were checked for purity by GC-FID and samples were transferred into quartz tubes,  
358 combusted and the produced CO<sub>2</sub> catalytically converted into graphite for AMS measurement.  
359 <sup>14</sup>C contents were corrected for modern and fossil blank contributions to small samples by  
360 error propagation. *n*-Alcohol radiocarbon contents were corrected for carbon contribution  
361 from the added acetate group by mass balance calculation. The hydrogen isotope ratio of the  
362 *n*-C<sub>24</sub> alcohol was measured using a mass spectrometer connected to a gas chromatograph via  
363 a pyrolysis interface against H<sub>2</sub> reference gas. The H<sub>3</sub>-factor was measured daily and was < 6  
364 ppm mV<sup>-1</sup> with variability from day to day of less than 0.2 ppm mV<sup>-1</sup>. Analyses of an external  
365 alkane standard (“Arndt B”, Arndt Schimmelmann, Indiana State University) revealed a mean  
366 absolute precision of 3 ‰ and an accuracy of 0 ‰. Precision of δD composition of the *n*-C<sub>24</sub>  
367 alcohol is based on replicate analyses. The δD value of the *n*-C<sub>24</sub> alcohol was corrected for the  
368 added acetate group by mass-balance calculation. Data are listed in supplementary Table S2.

369 **Calculation of initial ΔΔ<sup>14</sup>C and apparent initial ages.** If the depositional age is known, i.e.,  
370 the calendar age derived from the planktonic foraminifera, it is possible to calculate the initial  
371 radiocarbon content from the measured fraction modern (Fm) of all OM AMS results (Table  
372 S2) using the following equation<sup>35</sup>:

$$373 \quad \Delta^{14}\text{C}_{\text{initial}} = (\text{Fm} e^{(\lambda t)} - 1) \times 1000 \text{ ‰}$$

374 Fm is the measured fraction modern, λ is the decay constant (1/8267 years<sup>-1</sup>) of <sup>14</sup>C, and  
375 t is time since deposition in years. For the sampling depth for which the foraminiferal <sup>14</sup>C  
376 sample was lost (78-88 cm), we assumed the depth-integrated age from the linear  
377 interpolation (2492 ± 354 calendar years) as depositional age in order to be able to calculate  
378 initial radiocarbon contents of different OM fractions.

379 The offset of the initial radiocarbon contents of OM fractions to that of the past  
380 atmosphere (Δ<sup>14</sup>C<sub>atm</sub>) is calculated as:

381  $\Delta\Delta^{14}\text{C}_{\text{initial}} = \Delta^{14}\text{C}_{\text{initial}} - \Delta^{14}\text{C}_{\text{atm}}$   
382  $\Delta^{14}\text{C}$  values for the past atmosphere are based on time-integrated values derived from the  
383 Intcal13 southern Hemisphere atmospheric data<sup>36</sup>. For the uppermost sample (5-15 cm),  
384 which contains nuclear bomb-derived radiocarbon, we obtained the atmospheric  $^{14}\text{C}$  content  
385 from the atmospheric measurements<sup>37</sup> at the year of core retrieval (year 2000 CE). The  
386 associated error for this sample was obtained from the corresponding ages of the sample depth  
387 interval<sup>37</sup>.  $\Delta^{14}\text{C}_{\text{atm}}$  values are given in Table S2.

388 In order to provide ages instead of only radiocarbon contents, the apparent initial  
389 (conventional)  $^{14}\text{C}$  age is calculated from the initial radiocarbon content<sup>35</sup>:

390  $^{14}\text{C}$  age =  $-8033 \times \ln [(1 + \Delta^{14}\text{C}_{\text{initial}}/1000)/(1 + \Delta^{14}\text{C}_{\text{atm}}/1000)]$   $^{14}\text{C}$  years  
391 with  $\Delta^{14}\text{C}_{\text{initial}}$  the initial radiocarbon content of each OM fraction and  $\Delta^{14}\text{C}_{\text{atm}}$  the atmospheric  
392 radiocarbon content at the time of deposition.

393 **Estimates of pre-aged OC fractions and accumulation rates.** To provide estimates of the  
394 relative and absolute release of previously deposited, i.e., aged, organic matter, we conducted  
395 a mass-balance calculation using the amount and initial  $^{14}\text{C}$  contents of TOC and the initial  
396  $^{14}\text{C}$  contents of plant-wax *n*-alkanes and of the past atmosphere (Table S2) to disentangle  
397 fresh from pre-aged portions within TOC.

398  $\text{Pre-aged OC \%} = \text{TOC \%} \times (\Delta^{14}\text{C}_{\text{TOC\_initial}} - \Delta^{14}\text{C}_{\text{atm}}) / (\Delta^{14}\text{C}_{\text{alkanes\_initial}} - \Delta^{14}\text{C}_{\text{atm}})$   
399 with TOC = TOC content of sample,  $\Delta^{14}\text{C}_{\text{TOC\_initial}}$  = decay-corrected past  $^{14}\text{C}$  contents of  
400 TOC,  $\Delta^{14}\text{C}_{\text{atm}}$  = past atmospheric  $^{14}\text{C}$  contents,  $\Delta^{14}\text{C}_{\text{alkanes\_initial}}$  = decay-corrected past  $^{14}\text{C}$   
401 contents of *n*-alkanes (all data in Table S2).

402 The *n*-alkanes as oldest dated fractions in all sediment samples were taken as representing the  
403 age of released organic material acknowledging that also these compounds contain fresh  
404 portions, i.e., directly derived from plants. As TOC also contains aquatic OM of modern  
405 origin albeit in small amounts<sup>18</sup> which adds to the estimated fresh portion of TOC this results  
406 in a slight over-estimation of the fresh, directly plant-derived OM. Additionally, it must be

407 considered that the labile OM, which is released from wetland deposits, is rapidly oxidised  
408 (see main text) and will not be preserved in sedimentary archives. The estimates of pre-aged  
409 sedimentary TOC portions therefore reflect minimum estimates of released organic matter.

410 To evaluate if not only the relative portion of pre-aged OC in the sedimentary archive  
411 increased but also the absolute flux of pre-aged material, we calculated the accumulation rate  
412 of pre-aged OC in the sediment given by the percentage of pre-aged OC multiplied by the  
413 bulk sediment accumulation rate (bulk accumulation rate = sedimentation rate x dry bulk  
414 density). While we acknowledge that the accumulation rates of all sedimentary components  
415 are strongly dominated by the sedimentation rate (see supplementary Fig. S3d) it is clear that  
416 the accumulation rate of pre-aged OC in the latest Holocene exceeds its values during the  
417 Early and Mid-Holocene suggesting that also the export flux of pre-aged OC by the Congo  
418 River is higher under most arid conditions.

419 **Influence of fossil plant-wax contributions.** In order to evaluate if the higher plant-wax ages  
420 were caused by variable admixture of fossil, i.e., petrogenic, contributions, we calculated the  
421 Carbon Preference Index (CPI)<sup>38</sup>:

$$422 \text{ CPI} = 0.5 \times (\Sigma(C_i + C_{i+2} + \dots + C_n) / \Sigma(C_{i-1} + C_{i+1} + \dots + C_{n-1}) + \Sigma(C_i + C_{i+2} + \dots + C_n) / \Sigma(C_{i+1} +$$

423  $C_{i+3} + \dots + C_{n+1}))$

424 where *i* is the number of carbon atoms. CPI was calculated for *n*-alkanes ranging from *i* = 27  
425 to *n* = 33 and for *n*-alcohols from *i* = 22 to *n* = 28. Terrestrial higher plants produce long-chain  
426 *n*-alkanes with elevated CPI values<sup>38</sup> whereas thermally altered and extensively degraded  
427 organic matter contains *n*-alkanes with a CPI around 1 (ref 39). CPI indices of *n*-alkanes and  
428 *n*-alcohols do not correlate with their initial radiocarbon content (see supplementary Fig. S1).  
429 Therefore, we rule out that the observed age variations reflect contributions of petrogenic  
430 material from eroded sedimentary rocks.

431 **Bacteriohopanepolyols.** Full details of the BHP methodology were published previously<sup>23,40</sup>.  
432 Briefly, total lipids were extracted from freeze-dried sediments using a modified Bligh and

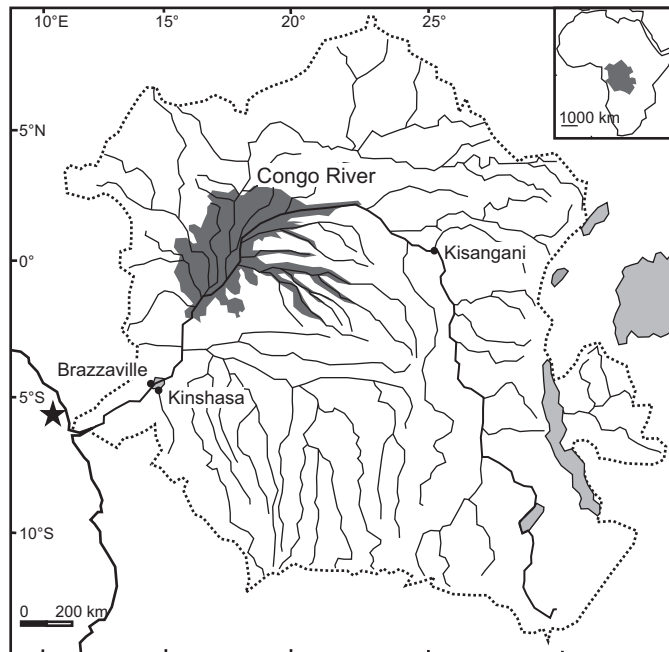
433 Dyer technique. One third of the extract was then acetylated to yield acetylated BHPs, which  
434 were analysed by reversed-phase high performance liquid chromatography-atmospheric  
435 pressure chemical ionisation-mass spectrometry (HPLC-APCI-MS<sup>n</sup>). Semi-quantification of  
436 BHP contents was achieved employing the characteristic base peak areas of individual BHPs  
437 in mass chromatograms relative to the *m/z* 345 mass chromatogram base peak area of the  
438 acetylated 5 $\alpha$ -pregnane-3 $\beta$ ,20 $\beta$ -diol internal standard. Averaged relative response factors  
439 relative to the internal standard, determined from a suite of acetylated BHP standards, were  
440 used to adjust the BHP peak areas. Typical error in absolute quantification was  $\pm$  20%, based  
441 on selected replicate analyses and BHP standards of known concentration<sup>23,40</sup>. BHP data are  
442 in supplementary tables S3, S4 and supplementary figure S2.

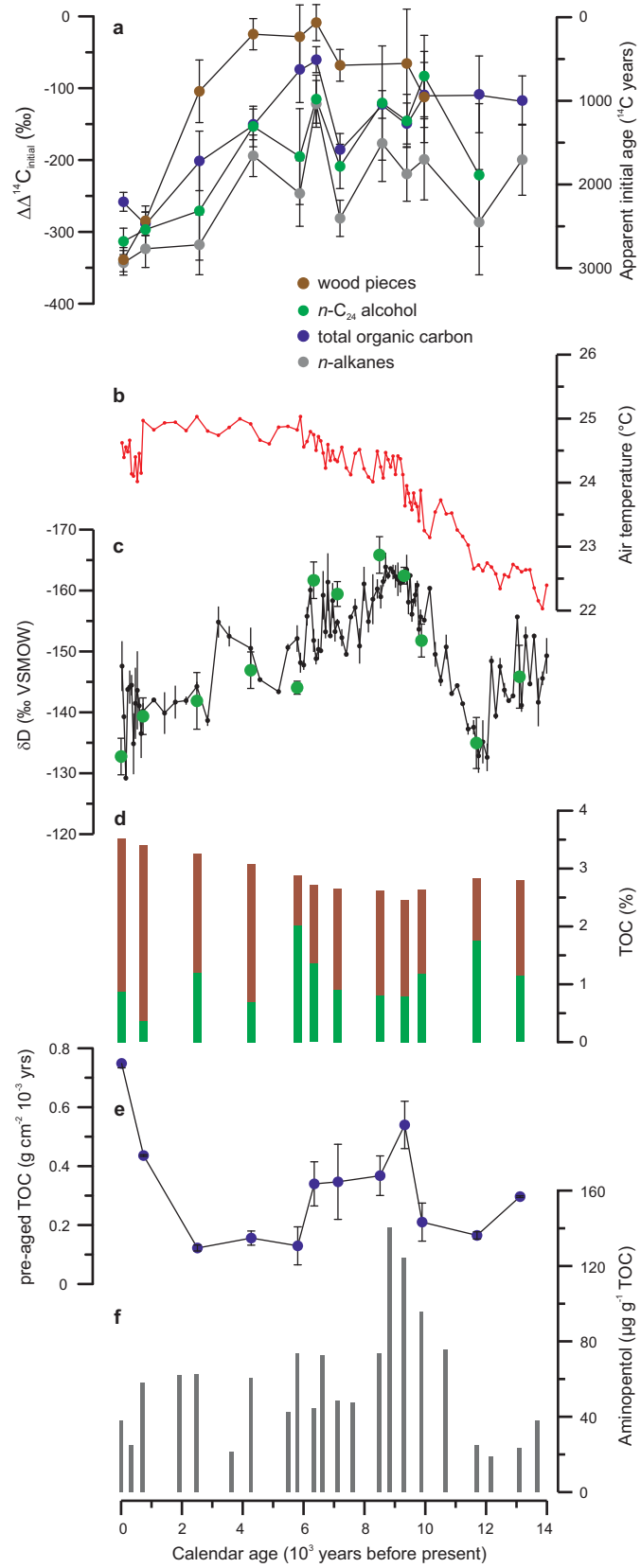
443 **Data availability.** Data generated in this study are available from the PANGAEA database  
444 (<https://doi.pangaea.de/10.1594/PANGAEA.862021>).

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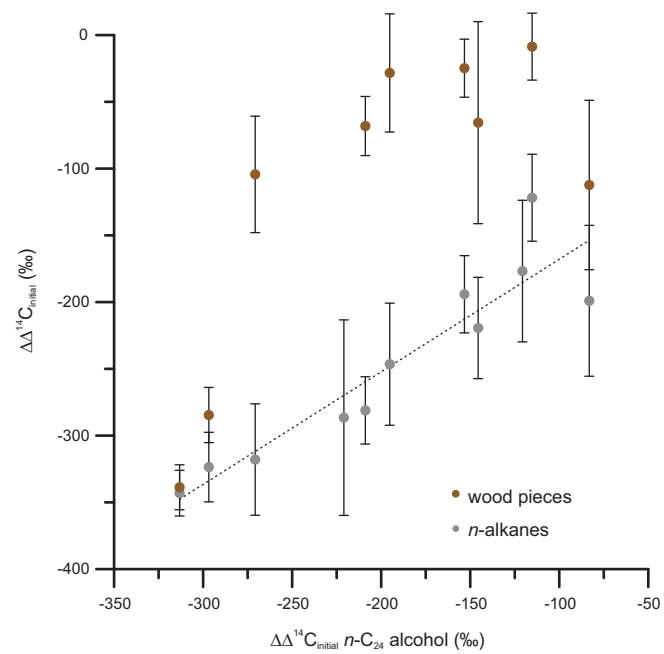
446 **References only in Methods**

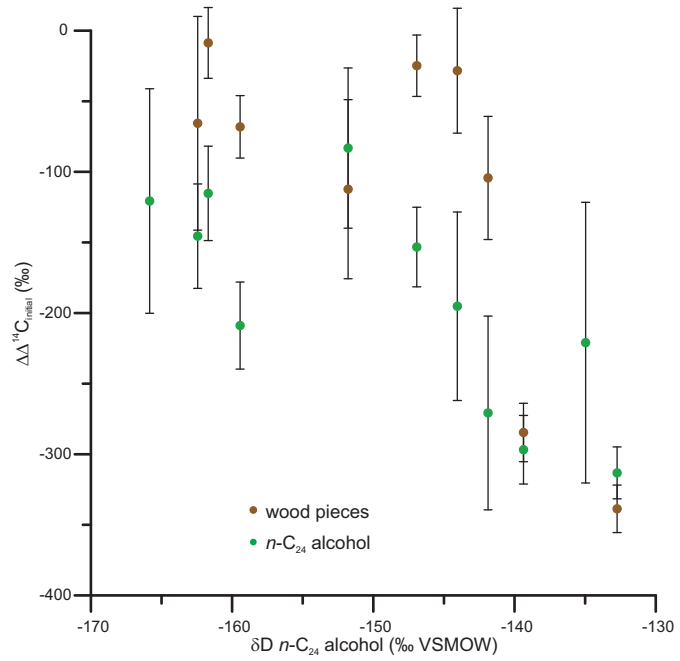
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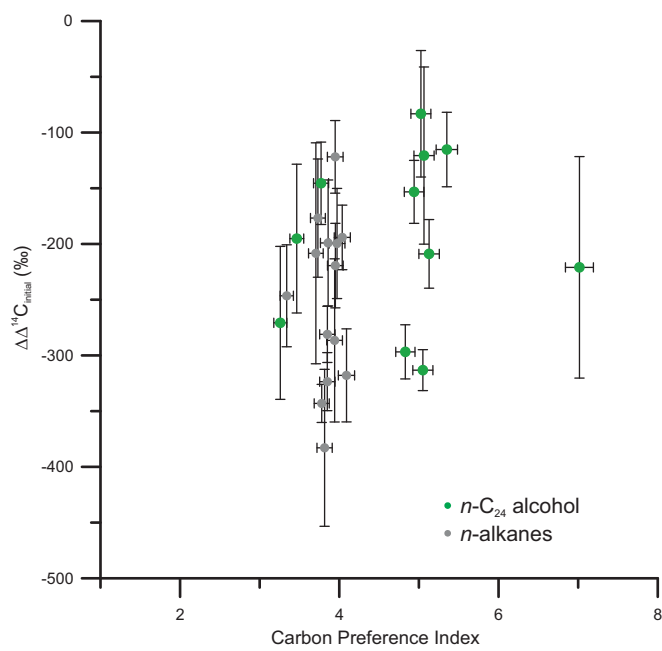




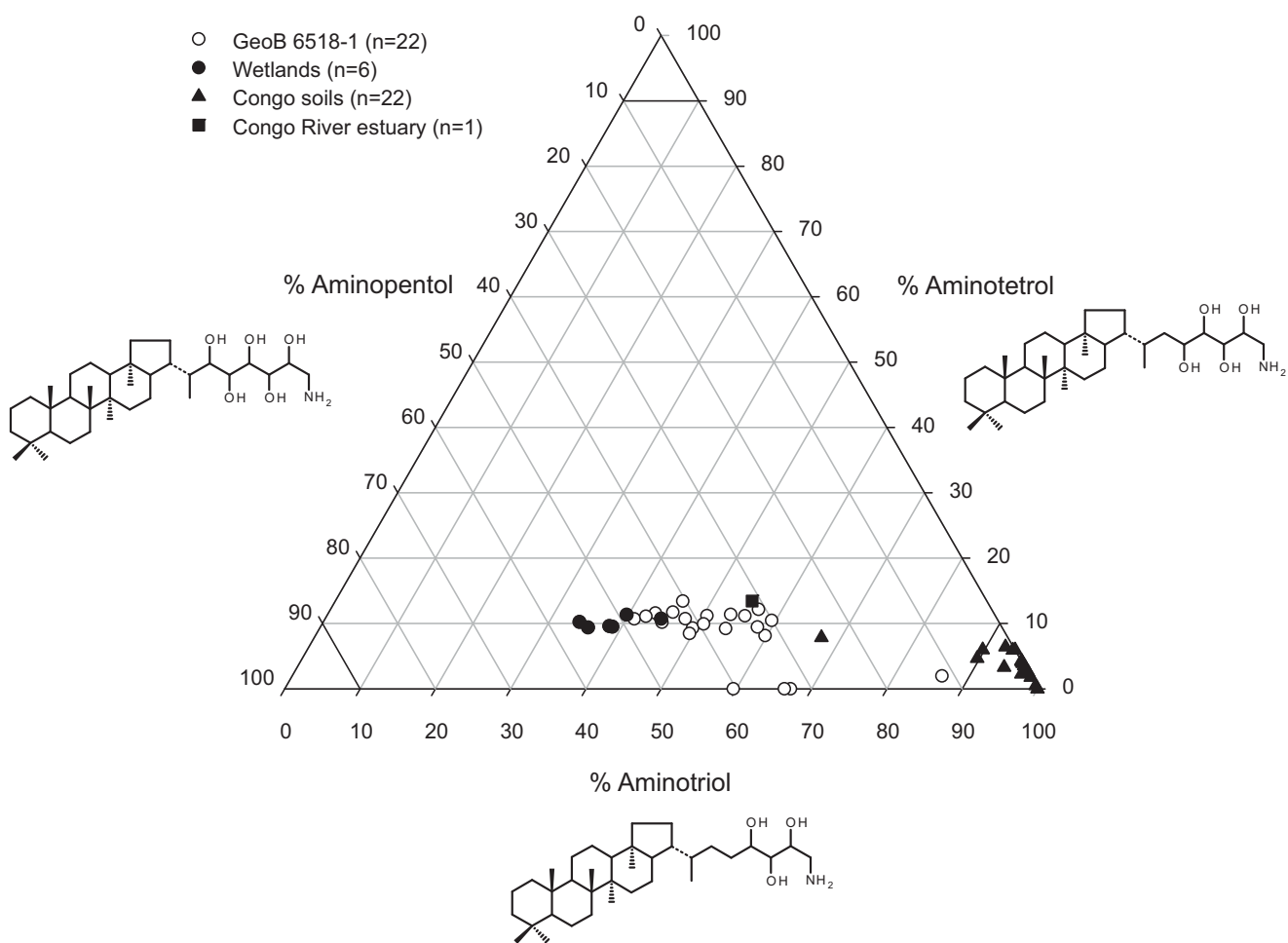




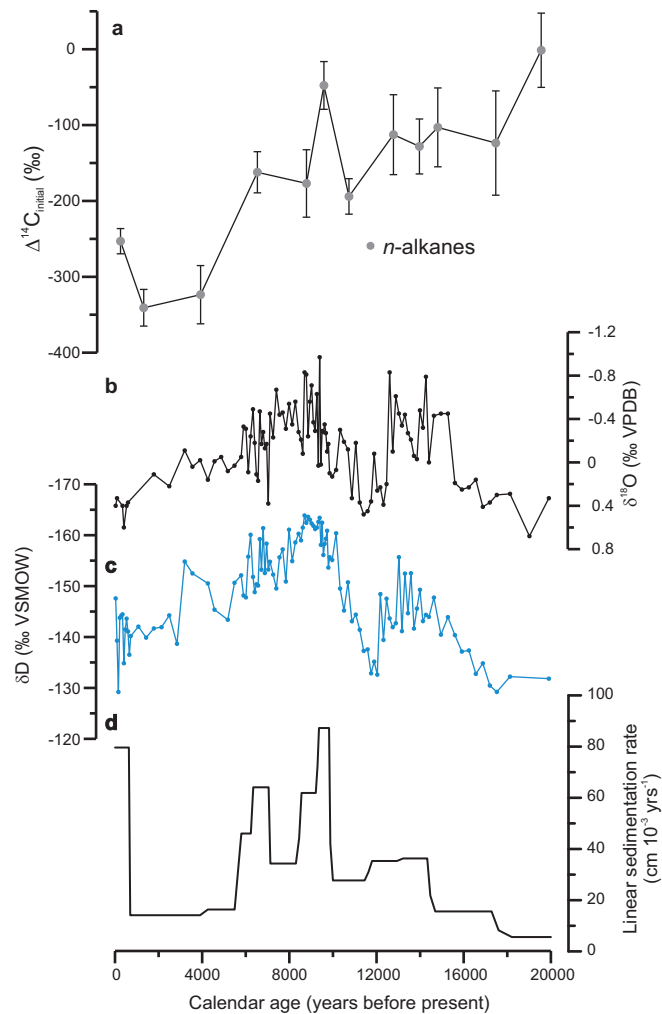




**Figure S1: Absence of fossil OM influences on OM ages.** Initial radiocarbon offsets of *n*-alkanes (grey dots) and *n*-C<sub>24</sub> alcohol (green dots) versus their respective Carbon-Preference-Indices (CPI), error bars show analytical uncertainty propagated with  $\Delta^{14}\text{C}_{\text{atm}}$  uncertainty.



**Figure S2: BHP compositions of Congo wetland deposits, soils, and sediments.** Ternary plot of the relative abundance of aminoBHP compounds (aminotriol, aminotetrol and aminopentol) present in core GeoB6518-1 (22 samples; this study), the Congo estuarine sediment, 6 wetland sediments and 22 soils from the Congo (data from ref 23).



**Figure S3: Independence of OM ages, proxy records and sedimentation.** Comparison of initial radiocarbon contents of *n*-alkanes in GeoB6518-1 (a) with Congo River runoff reconstructions based on oxygen isotope compositions of planktonic foraminifera (b, black), compound-specific plant-wax based reconstruction of rainfall intensity in the Congo basin<sup>21</sup> (c, blue) and linear sedimentation rate of GeoB6518-1 (d). Error bars in a) reflect analytical uncertainty.