

1 **Quality not quantity: organic matter composition controls of CO₂ and CH₄**
2 **fluxes in Neotropical peat profiles**

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21 **Abstract**

22 Tropical peatlands represent an important source of carbon dioxide (CO₂) and methane (CH₄) to
23 the atmosphere. However, we do not know where in the peat profile these gases are produced
24 and how controlling factors, such as substrate quality, which can vary substantially with peat
25 age, and anoxic-oxic conditions, interact to determine production rates. To address this
26 knowledge gap, this study investigated if substrate limitation of CO₂ and CH₄ production differs
27 under anoxic-oxic peat conditions using entire peat profiles, from tropical peatlands in Panama.
28 We determined the variation in peat organic chemistry through stratigraphic profiles using
29 tetramethylammonium-pyrolysis-gas chromatography-mass spectrometry (TMAH-Py-GC/MS).
30 To explore how variation in peat organic chemistry through the depth profile impacted on CO₂
31 and CH₄ production rates under anoxic-oxic conditions we carried out a series of incubation
32 experiments. The TMAH-Py-GC/MS analysis showed high concentrations of long chain fatty
33 acids (> C₂₀) in surface peat, and variation in the distribution of the lignin monomers through the
34 peat profile. Both anoxic CH₄ and CO₂ production was greatest from the surface of the peat
35 profile with surface peat accounting for 92 ± 1.7 and 54 ± 2.9 % of the cumulative CH₄ and CO₂
36 production, respectively. The high CO₂ and CH₄ production rate under anoxic conditions, in
37 surface peat, was strongly related to greater concentrations of lignin, but also long chain fatty
38 acids and polysaccharides, in this section of the peat profile. As expected, CH₄ production
39 decreased, and became decoupled from peat organic chemistry, following peat aeration. In
40 contrast, aeration dramatically increased CO₂ emissions throughout the entire peat profile. This
41 demonstrates that the recalcitrance of buried peat does not protect C stocks in tropical peatlands,
42 if their water tables are lowered in response to drainage or prolonged drought. In conclusion, our

43 work highlight that information on both labile substrate availability and water table fluctuation
44 are needed to predict CO₂ and CH₄ fluxes from tropical peatlands.

45

46 Keywords: *Neotropical peatland; pyrolysis; greenhouse gases; methane; carbon dioxide, palm*
47 *and mixed forest swamp*

48

49 **1. Introduction**

50

51 Recent work suggests that peatlands of considerable depth exist within the Amazon basin as well
52 as in Central America (Hoyos-Santillan, 2014; Lahteenoja et al., 2012). They act simultaneously
53 as carbon (C) sinks and sources, exchanging large amounts of greenhouse gases (*e.g.*, CO₂ and
54 CH₄) with the atmosphere (Sjogersten et al., 2014). Given their potential for large C storage and
55 greenhouse gas emissions, it is important to quantify their role within the global C cycle
56 (Kirschke et al., 2013), and how they may respond to environmental change (Lahteenoja et al.,
57 2009; Sjogersten et al., 2014). Tropical peatlands currently store 40-90 GtC as peat (Kurnianto et
58 al., 2015) and tropical wetlands contribute with at least two thirds of the global CH₄ emissions
59 from wetlands (Melton et al., 2013). Drainage, land use change, and climate change (*e.g.*
60 prolonged droughts) threatens C sequestration of tropical peatlands (Turetsky et al., 2014), by
61 subjecting peatlands to aeration leading to higher decomposition rates. This can turn tropical
62 peatlands into net carbon sources (Couwenberg et al., 2010; Hoyos-Santillan et al., 2016; Page et
63 al., 2011). However, current knowledge of CO₂ and CH₄ emissions from tropical peatlands is
64 mainly represented by surface gas fluxes measurements (Couwenberg et al., 2010; E. L. Wright
65 et al., 2013), while the controls and contribution of subsurface emissions remain poorly
66 understood despite their potentially large contribution of net surface emissions (Wright et al.,
67 2011). This lack of understanding on the controls of peat CO₂ and CH₄ emissions and
68 information on gas production through the peat profile, severely limits predictions of how
69 tropical peatlands CO₂ and CH₄ emissions will respond to environmental and land use change.

70

71 In high latitude peatlands, the degree of decomposition has been recognized as one of the
72 primary factors controlling the variation of C effluxes through the peat profile (Moore and
73 Dalva, 1997); where deeper, more decomposed, peat layers have been found to be more resistant
74 to decomposition than recently formed peat (Hogg et al., 1992). This may also apply to tropical
75 peatlands, in which distinct decomposition environments over time (*e.g.*, anoxic-oxic) drive
76 variation in peat chemistry with depth (Hoyos-Santillan et al., 2015; E. Wright et al., 2013).
77 Indeed, a strong relationship between CO₂ and CH₄ emissions and the organic matter
78 composition of the peat in the upper 2 m of the stratigraphic profile has been observed in tropical
79 peatlands in Panama (Wright et al., 2011). However, the influence of peat organic chemistry on
80 CO₂ and CH₄ emissions is currently not resolved.

81
82 Peat decomposability also varies significantly depending on its botanical origin (*e.g.*, Moore and
83 Dalva, 1997; Nilsson and Bohlin, 1993). Peat deposits in the lowland tropics are formed
84 principally by succession of forest communities (Anderson, 1964; Phillips et al., 1997). Thus, it
85 is plausible that the influence of peat chemistry on CO₂ and CH₄ production differs between the
86 well-studied high latitude peatlands and tropical peatlands. Molecular chemical analyses can be
87 used to determine the botanical origin of peat (Hoyos-Santillan et al., 2015; McClymont et al.,
88 2011), its degree of decomposition (Hoyos-Santillan et al., 2015; Schellekens et al., 2015), and
89 provide insight into the environmental conditions under which decomposition has occurred
90 (Schellekens, 2013). Pyrolysis gas chromatography mass spectrometry (Py-GC/MS) has been
91 used to characterize the molecular composition of peat (Schellekens et al., 2009) and through
92 peat depth profiles (Hoyos-Santillan et al., 2015).

93 Neotropical peatlands are often forested by palms or evergreen broadleaved trees, forming
94 distinct phasic communities (Draper et al., 2014; Sjögersten et al., 2011). For instance, peat
95 swamp forests in the Caribbean coast of Panama and Costa Rica typically support
96 monodominant stands of the canopy forming evergreen palm *Raphia taedigera* (Mart.) (Hoyos-
97 Santillan et al., 2016; Myers, 1981; Phillips et al., 1997), or mixed forests composed of palms
98 and evergreen broadleaved hardwood trees (e.g. *Camptosperma panamensis* (Standl.) (Phillips
99 et al., 1997; Urquhart, 1999); the peat layer in area has been reported to be up to 8 m thick
100 (Cohen et al., 1989).

101 The aims of this study were to (1) use Py-GC/MS to quantify variation in organic matter
102 chemistry through the peat profile within palm and mixed forest communities, and (2) determine
103 the relationship between peat chemistry and C mineralization under anoxic-oxic conditions. We
104 tested the hypothesis that CO₂ and CH₄ production rates are greatest from the surface peat under
105 anoxic-oxic conditions due to the availability of labile C substrate from decomposing litter and
106 root exudates (here we use labile to denote organic molecules that are easily degradable by
107 decomposer microorganisms).

108

109 **2. Materials and methods**

110

111 *2.1. Study area*

112 Study sites were lowland located within the Bocas del Toro province in the north-western
113 Caribbean coast of Panama. Sites included the Changuinola peat deposit (CPD, $\approx 80 \text{ km}^2$) in the

114 San San Pond Sak wetland (Ramsar site No. 611), the Damani-Guariviara wetland (Ramsar site
115 No. 1907), and peatlands along the Cricamola River shore (Table 1). Extensive palm swamps
116 and mixed forests are among the main forest types that can be found in the region (Hoyos-
117 Santillan, 2014; Myers, 1981; Phillips and Bustin, 1996; Phillips et al., 1997). The region
118 receives 3092 ± 181 mm of annual rainfall and the mean annual air temperature is 26.4 ± 0.1 °C
119 (2003 to 2011, Smithsonian Tropical Research Institute Physical Monitoring Program); there is
120 no pronounced seasonality with respect to either rainfall (dry-wet season) or temperature
121 (Hoyos-Santillan, 2014; Wright et al., 2011).

122

123 2.2.1. Study sites

124 Three palm swamp peatlands dominated by *R. taedigera* and three mixed forest peatlands
125 dominated by *C. panamensis* were selected for this study (Table 1); all sites were freshwater with
126 pore water conductivity $< 200 \mu\text{S cm}^{-1}$. The water table remains close to the peat surface
127 throughout most of the year, but during periods of high or low rainfall it can range from + 0.15 to
128 -0.4 m relative to the peat surface, respectively (Hoyos-Santillan, 2014; Wright, 2011).

129

130 Palm sites were monodominant (>80 % of basal area; Table S1), with large standing biomass
131 (basal area of $110 \pm 7 \text{ m}^2 \text{ ha}^{-1}$), large amounts of palm leaf litter at the surface (*R. taedigera* is
132 highly productive and its pinnate leaves are up to 10 m long at the sites), and a dense (200 g m^{-2} of
133 root in the top 10 cm of the peat profile) but shallow fibrous root system extending to
134 approximately 1.1 m depth (Sjögersten et al., 2011; Wright et al., 2011). The tree basal area at
135 mixed forest sites was $25 \pm 6 \text{ m}^2 \text{ ha}^{-1}$, with *C. panamensis*, *Sympohonia globulifera*, *Cassipourea*

136 *eliptica*, and *Euterpe precatorea* comprising most of the biomass (Table S1). The mixed forest
137 sites had large amounts of *C. panamensis* surface leaf litter (but relatively less surface litter
138 compared to the very high litter inputs at the palm sites) at the surface, but also had leaf litter
139 from other species. The *C. panamensis* root system was characterized by woody lignified
140 structural roots reaching at least 1 m depth, abundant surface knee roots, and thinner lateral roots
141 in the litter layer and surface peat (Wright et al., 2011). The density of the thinner lateral roots
142 was *ca.* 50 g m⁻² in the top 10 cm of the peat profile (Wright et al., 2011). Microtopography
143 within all sites consisted of shallow ponds and raised areas (close to trees associated with root
144 structures). At each site, permanent vegetation census plots (0.1 ha; 20 × 50 m) were established,
145 peat samples and peat cores were collected within these plots.

146

147 2.2.2. Peat core collection

148 Peat cores for the respirometric assays and physiochemical characterisation (4 peat cores per site,
149 n = 24) were collected from the plots installed in the study sites (Table 1). The collection was
150 done using a Russian peat corer, which extracted semi cylindrical peat samples of 0.5 m length
151 and 48 mm diameter. We sampled the entire peat profile in 0.5 m increments, from the surface to
152 the underlying mineral material. To differentiate between peat and mineral soil, peat was defined
153 as soil containing ≥ 30 % dry weight organic matter (Joosten and Clarke, 2002). The presence of
154 coarse root material in the top layers of the peat profile made it difficult to collect intact peat
155 samples from the surface layer (top 0.1 m) using the Russian corer. For this reason, additional
156 peat samples (0.1 × 0.1 × 0.1 m) were collected with a knife from the surface adjacent to the
157 location where each peat core was collected. Surface samples were placed in sealed plastic bags,

158 while the 0.5 m core segments were tagged, wrapped in aluminium foil, and placed in plastic
159 boxes for transportation (< 3 h) to the laboratory at the Smithsonian Tropical Research Institute
160 (STRI) Bocas del Toro Research Station (BDT). Three of the peat cores and the surface samples
161 from each site were refrigerated at 2 °C and shipped to the University of Nottingham, UK. The
162 remaining core was used to determine bulk density following Chambers et al. (2011) at the
163 Bocas del Toro Research Station.

164

165 *2.3. Peat chemistry*

166

167 *2.3.1. General characterisation*

168 Three of the peat cores from each site were split into 0.1 m sections for determination of the
169 following. Moisture content was determined by gravimetric analysis of the water mass loss of 10
170 g fresh peat samples after oven drying peat samples at 70 °C for 70 h (Wright et al., 2011). Loss
171 on ignition (LOI), as an indirect measurement of soil organic matter content (SOM), was
172 measured by gravimetric analysis of mass loss from dry peat samples placed in the muffle
173 furnace for 7 h at 550 °C. Peat pH and conductivity were determined in a 1:2.5 peat fresh weight
174 (fw)-deionized water solution. Total C, nitrogen (N), and sulphur (S) were measured from 0.5 g
175 homogenised peat samples (homogenization was carried out in a Planetary Ball Mill, Retsch-
176 PM400, Castleford, UK) using a total element analyzer (Thermo Flash EA 1112, CE
177 Instruments, Wigan, UK). Peat ash from loss on ignition analysis was dissolved in 6 M HNO₃ to
178 estimate the peat phosphorus (P) concentration by molybdate colorimetry (Andersen, 1976). For
179 detailed methods see Hoyos-Santillan (2014).

180

181 2.3.2. Tetramethylammonium-pyrolysis-gas chromatography-mass spectrometry (TMAH-Py-
182 GC/MS)

183 Treating the peat samples with tetramethylammonium prior to Py-GC/MS analysis (*i.e.* TMAH-
184 Py-GC/MS or thermochemolysis) prevents thermal degradation of lignin-derived monomers
185 (monolignols) found in peat, as well as large fatty acids derived from plants epicuticular waxes
186 or microorganisms (Steward et al., 2009). TMAH protects molecules containing carboxyl (*e.g.*
187 avoiding decarboxylation of aromatic acids) and hydroxyl groups from thermal reactions,
188 preserving important structural information (*e.g.* del Rio and Hatcher, 1996). Consequently,
189 TMAH-Py-GC/MS provides a powerful tool to gain insights into peat composition, sources of
190 organic material, and its degradation through time.

191

192 For TMAH-Py-GC/MS analyses, dry samples (0.5 mg) were individually placed in quartz tubes
193 and secured in place using quartz wool plugs. Prior to pyrolysis, each sample was soaked with 10
194 μL tetramethylammonium hydroxide (TMAH). In addition, 10 μL of a 0.25 $\mu\text{g } \mu\text{L}^{-1}$ solution of
195 5- α -cholestane in hexane was added to each sample to enable quantification. Py-GC/MS analyses
196 were carried out using a CDS 1000 pyroprobe coupled with a gas chromatograph and mass
197 spectrometer (Perkin Elmer Clarus 500 GC/MS) equipped with a CP Sil 5CB-MS column (30 m
198 \times 0.25 mm (0.25 μm film thickness)). Samples were introduced into a preheated interface (310
199 $^{\circ}\text{C}$) and pyrolyzed at 610 $^{\circ}\text{C}$ for 15 seconds. The GC injector temperature was set to 280 $^{\circ}\text{C}$ and
200 the GC oven temperature was held at 40 $^{\circ}\text{C}$ for 2 minutes and was heated at a rate of 4 $^{\circ}\text{C } \text{min}^{-1}$

201 and was held at 320 °C for 20 minutes. A total of 40 major TMAH-Py products were identified
202 based on retention time and MS spectra.

203

204 Compound concentrations were estimated by integrating the areas obtained in the pyrogram and
205 calculating its corresponding concentration using the 5- α -cholestane as an internal standard;
206 concentrations were expressed in relation to the total C content in the peat sample as $\mu\text{g}_{\text{compound}}$
207 mg C^{-1} . TMAH pyrolysis produces methyl esters and ethers (Challinor, 1989) consequently
208 methyl ester derivatives of fatty acid and methylated lignin monomers are obtained. Taking this
209 into consideration, each TMAH-Py-GC/MS product was assigned a chemical class based on their
210 molecular similarity to its probable source molecule (Hoyos-Santillan et al., 2015; Schellekens,
211 2013). Seven main classes were defined: FA = fatty acids; AL = aliphatic; Lg = lignin,
212 subdivided in the three monolignols (*p* – Coumaryl alcohol, Coniferyl alcohol, and Sinapyl
213 alcohol); Ar = Aromatic; Ph = phenol, PA = poly-aromatic hydrocarbons; and PS = poly-
214 saccharides. Prist-1-ene, which has been reported as a product of chlorophyll pyrolysis
215 (Ishiwatari et al., 1991), was given its own category. The short and long chain methylated fatty
216 acids (Short < C₂₀ and Long > C₂₀) were further grouped into separate categories to aid data
217 interpretation. The separation of the three lignol-monomers (*p* – Coumaryl alcohol, Coniferyl
218 alcohol, and Sinapyl alcohol) can be used to differentiate types of lignin.

219

220 *2.4. Respirometric assays*

221

222 2.4.1. Anoxic assays

223 The production rate of CO₂ and CH₄ through the peat profile (mg g C⁻¹ h⁻¹) was measured using
224 respirometric assays at 0.5 m intervals. This entailed incubation of peat samples in serum bottles
225 under anoxic conditions. The assays were conducted using samples from different depths of each
226 of the 18 cores, where the three cores per site were repetitions (total number of assays = 107),
227 whereas the replication was derived from the use of three sites for each forest community. The
228 underlying processes investigated in this study aim to improve our understanding of the
229 mechanisms that controls of CO₂ and CH₄ production *in situ*. However, it is important to note
230 that the production rates obtained from the incubations do not reflect *in situ* production rates.
231 This is due to disturbance of the peat samples caused by the sampling process and the
232 experimental set up (*e.g.*, agitation and addition of deionized water) (*e.g.* Moore and Dalva,
233 1997). Therefore, production rates presented here should not be used to estimate *in situ*
234 emissions nor be extrapolated to large peatland areas; instead they should be used to identify
235 trends in the variation of the production rates through the peat profile.

236

237 For the incubations, each sample (10 g fresh weight) was placed into 120 mL glass serum
238 bottles; then anoxic deionized water was added until 70 mL volume within the bottles was
239 occupied by the peat-deionized water solution (leaving 50 mL headspace). Six additional bottles,
240 with 70 mL deionized water each were used as controls. Each bottle was flushed with N₂ for 10
241 min to displace the dissolved oxygen thus creating anoxic conditions. Bottles were sealed with
242 custom made rubber septa (13 × 19 × H12 mm; Rubber B.V., Hilversum, NL) and aluminium
243 crimp tops. Incubations were conducted at 25 ° C in the dark in temperature controlled chambers,

244 emulating *in situ* soil temperature (24.6 ± 0.05 °C) (Hoyos-Santillan, 2014). Following two
245 months acclimatization, to allow the establishment of the microbial community, and the
246 depletion of alternative electron acceptors, each serum bottle was re-flushed with N₂ and
247 resealed. Afterwards, a single anoxic incubation (390 days) was conducted, during which all
248 bottles were shaken on a daily basis. The headspace gas of each bottle was analysed by gas
249 chromatography (GC) at the end of the assays (GC-2014, Shimadzu UK LTD, Milton Keynes,
250 UK). CO₂ and CH₄ concentrations were determined using a single injection system with a 1 mL
251 sample loop that passed the gas sample using N₂ as carrier through a non-polar methyl silicone
252 capillary column (CBP1-W12-100, 0.53 mm I.D., 12 m, 5 mm; Shimadzu UK LTD, Milton
253 Keynes, UK). Thermal conductivity (TCD) and H₂ flame ionization (FID) detectors were used to
254 measure CO₂ and CH₄, respectively (Wright et al., 2011). Gas concentrations were adjusted for
255 temperature (25 °C constant) and pressure within the serum bottles according to the ideal gas
256 law. The rate of gas production from the samples expressed as mg g C⁻¹ h⁻¹ was calculated as the
257 difference between the initial and final concentration of gas in the headspace of the serum bottles
258 at the end of the assay (Hogg et al., 1992). The gas production rate was then expressed in terms
259 of total C content in the sample.

260

261 2.4.2. *Oxic assays*

262 Once the anoxic assay was completed, a subset of samples corresponding to a single core from
263 each site, were selected to conduct oxic assays (32 bottles). Supernatant water was filtered out
264 from each serum bottle, simulating peat drainage until peat was water-saturated. Each bottle was
265 then covered with Parafilm. To aerate the peat, bottles were shaken twice a day over a two weeks

266 acclimatization period. Bottles were then sealed with custom made rubber septums (13 × 19 ×
267 H12 mm; Rubber B.V., Hilversum, NL) and aluminium crimp tops, and 30 mL of laboratory air
268 were injected to each bottle; this allowed the subsequent collection of gas samples for GC
269 analysis. Incubations were conducted at 25 °C in temperature controlled chambers for 4 days.
270 During the incubation period, bottles were shaken twice a day. Gas samples from the headspace
271 (10 mL) were taken with plastic syringes at 0, 50, and 96 h for immediate GC analysis (as
272 previously described). Gas concentrations obtained from the gases chromatography analyses
273 were adjusted for temperature (25°C constant) and pressure within the serum bottles. The assay
274 was repeated in two occasions with a 2 days interval between repetitions (total number of assays
275 = 64).

276

277 *2.5. Statistical analysis*

278 Linear mixed models were used to analyse the gas production rates through the peat profile, and
279 were fitted by using Residual Maximum Likelihood (REML). REML analysis was undertaken
280 due to the unbalanced nature of the data, a consequence of the differences in depth of the peat
281 cores. The gas production rates were \log_{10} transformed to fulfil the normality condition of the
282 REML. Level of significance of the differences between the fixed effects was estimated by Wald
283 tests using an F distribution. Significance was attributed at $P < 0.05$.

284

285 For the gas production rates under anoxic-oxic conditions ($\text{mg g C}^{-1} \text{ h}^{-1}$; CO_2 and CH_4), the
286 specific depth of the peat sample within the peat profile and the current forest community in the
287 site (*R. taedigera*-palms swamp and *C. panamensis*-mixed forest) were used as fixed factors;

288 whereas the core (three from each site for the anoxic assay) or temporal repeats (one core
289 measured twice for the oxic assay), and the specific site (six sites in total) were introduced into
290 the model as random factors.

291

292 Relationships between gas production rates (\log_{10} transformed) and covariates (*e.g.*, pH,
293 conductivity, TMAH-Py-GC/MS products) were explored by linear and exponential regression
294 analyses. The data used for the linear and exponential regression analyses included only the
295 information corresponding to one of the cores from each of the six sites.

296

297 Similarities in the molecular composition of the peat samples from different depths were
298 explored by Principal Component Analysis (PCA) (Vancampenhout et al., 2008), based on
299 correlation matrices including the 40 products identified through the TMAH-Py-GC/MS
300 analyses, which were used as molecular fingerprints. The % of variance accounted (adjusted R^2)
301 by regression statistical models is referred to as R^2 in text and figures. Results throughout the
302 text, figures and tables are presented as mean \pm SE. Statistical analyses were performed in
303 GenStat (VSN International, 2011).

304

305 **3. Results**

306

307 *3.1. Peat stratigraphy and physicochemical properties*

308 Peat cores from both phasic communities contained abundant fresh vascular plants roots within
309 the upper 2 m. However, roots were considerably more fibrous and compact in the palm swamp
310 cores. Below 2 m, peat ranged from fibrous, with identifiable plant tissues, to heavily
311 decomposed in deeper layers. Bulk density increased with depth in all sites, varying from $0.09 \pm$
312 0.006 g cm^{-3} in the surface layers to $0.61 \pm 0.09 \text{ g cm}^{-3}$ in the underlying mineral soil (Fig. S1).
313 The peat section of the cores had a relatively homogeneous low bulk density, but in the
314 Cricamola site, the river contiguous to the peatlands seasonally deposited mineral sediments
315 increasing the variability of bulk density with depth (Fig. S1). The pH throughout the peat
316 section of the cores was acidic (Schoeneberger et al., 2012), with mean values of 5.07 ± 0.03 and
317 4.85 ± 0.05 for the mixed forest and palm swamp respectively (Fig. S1). However, peat pH in the
318 Damani-Guariviara site was up to 6.5 in the mineral section of the cores; by contrast, pH at the
319 Chiriquí Grande site declined markedly below 60 cm (Fig. S1). Conductivity increased with
320 depth in the peat cores at most sites, from values $< 200 \mu\text{S cm}^{-1}$ in the upper layers, to maximum
321 values of $2400 \mu\text{S cm}^{-1}$ in the underlying mineral layers of marine origin. For both phasic
322 communities, C and N concentrations were variable and did not show clear trends, but values
323 were consistent with a high content of organic matter. The overall concentration of carbon and
324 nitrogen in the cores were $39 \pm 0.8 \%$ and $1.4 \pm 0.04 \%$, respectively. Carbon did not
325 significantly vary with depth ($F_{58, 347} = 1.36$, $P > 0.05$), but nitrogen did ($F_{58, 347} = 2.22$, $P <$
326 0.001). Phosphorus concentrations varied through depth ($F_{12, 17} = 6.01$, $P < 0.001$; Fig. S1),
327 increasing sharply in the mineral section of the cores from Almirante and San San Pond Sak 1.
328 The highest concentrations of phosphorus were observed in the upper and deeper layers of the
329 cores, reaching concentrations of 476 and $511 \mu\text{g g}^{-1}$ for the upper and deeper layers,
330 respectively.

331

332 3.2.2. TMAH-Py-GC/MS

333 The abundance of long chain fatty acids ($> C_{20}$) was higher in the upper peat layers and declined
334 with depth (Fig. S2). However, in the Cricamola core long chain fatty acids increased with depth
335 and declined once reaching the mineral soil. The short chain fatty acids were dominated by C_{16}
336 and C_{18} chain lengths and did not present a clear trend. Their concentrations varied widely
337 throughout the peat profile and high concentrations were not restricted to the upper layers (Fig.
338 S2). The pyrolysis products related to lignin moieties were highest in the upper layers of the peat
339 cores (Fig. S2). However, each lignin monomer presented a distinct distribution through the peat
340 stratigraphic profile. The products related to *p*-coumaryl alcohol were highest in the top 0.5 m of
341 the peat cores rapidly declining with depth (Fig. S2). Similarly, the coniferyl related compounds
342 declined with depth, with the exception of the Cricamola core, where these compounds increased
343 with depth through the peat profile and abruptly decreased in the mineral layer (Fig S2). Sinapyl
344 related products had the lowest concentrations in the peat cores and did not follow a consistent
345 trend with depth. Parallel with lignin monomers, polysaccharide products were higher in upper
346 layers and declined with depth, but the Cricamola core presented a different distribution. Finally,
347 prist-1-ene distribution with depth was similar to that of the long chain fatty acids, being
348 particularly abundant in the upper peat layers and declining with depth (Fig. S2).

349

350 3.2.3. Multivariate analysis

351 The scores and loadings of principal components 1 (horizontal axis) and 2 (vertical axis)
352 explained most of the observed variation, with the first factor contributing with up to 87 % (Fig.

353 1, Table S2). The first principal component 1 (PC-1) separates the stratigraphic profile of the
354 peat cores according to depth; presenting, in most of the cases, a strong segregation between the
355 top layer of the peat cores (0 – 0.1 m) and the underlying strata. The segregation of the upper
356 layer of the peat core along PC-1 was primarily driven by the presence of long chain fatty acids
357 (*e.g.*, C₂₆, C₂₉, C₃₀, and C₃₁) and lignin moieties related to coniferyl alcohol (Fig. 1, Table S2). By
358 contrast, the separation along the second principal component (PC-2) was mainly due to the
359 influence of both short (*e.g.*, C₁₆, C₁₈) and long chain fatty acids (*e.g.* C₂₇), as well as lignin
360 moieties related to *p*-coumaryl and sinapyl alcohols. Polysaccharides included pentamethoxy
361 heptanoic acid and methylated glucose, and were not evenly scattered over the plots but were in
362 most cases related to upper peat layers, contributing to both the distribution of scores along PC-1
363 and PC-2. The scores plots indicate a variation in the composition of peat layers through the
364 stratigraphic profile. Surface peat chemistry differed between the two forest types. The
365 differences in surface peat chemistry were primarily related to the proportions the distinct lignin
366 moieties, specifically those associated to *p*-coumaryl and sinapyl alcohols, and long chain fatty
367 acids.

368

369 *3.3. Gas production rates through the peat profile*

370 The CO₂ and the CH₄ production rates varied significantly depending on whether the assays were
371 conducted under anoxic or oxic conditions. CO₂ production rates were one order of magnitude
372 higher under oxic conditions in comparison with anoxic conditions (Anoxic-Oxic: CO₂, F_{1,140} =
373 719, *P* < 0.001) (Fig. 2); whereas, CH₄ production rates were up to two orders of magnitude

374 higher under anoxic conditions when compared to those where peat was aerated (Anoxic-Oxic:
375 CH₄, $F_{1,140} = 24$, $P < 0.001$) (Fig. 3).

376

377 In both anoxic and oxic assays, CO₂ production varied significantly with depth across four orders
378 of magnitude (Table 2). In the anoxic assays, the highest CO₂ production was located in the top
379 layers, contributing with 54 ± 3 % of the cumulative production through the peat profile and
380 declining with depth (Fig. 2c,d). However, under oxic conditions, the declining trend was no
381 longer evident (Fig. 2a,b). The CO₂ production rates did not vary significantly between the forest
382 communities and the different forest communities displayed similar trends through the peat
383 profile in both the anoxic and oxic assays (Fig. 2; Table 2).

384

385 Parallel to CO₂, CH₄ production rates varied significantly with depth (Fig.3; Table 2). Under
386 anoxic conditions, the decline with depth was steeper (particularly below 1 m depth) than that of
387 CO₂ production, and ranged across five orders of magnitude (Fig. 3c,d). Under anoxic
388 conditions, the surface peat layer contributed with 92 ± 1.7 % of the cumulative CH₄ production
389 through the peat profile, whereas once peat was aerated, the contribution of surface peat was
390 highly variable (36 ± 14 % of the profile cumulative production). Similar to CO₂, CH₄
391 production did not vary between the forest communities (Table 2). Although CH₄ production
392 rates followed the same declining trend with depth at all sites under anoxic conditions (Fig.
393 3c,d); after aerating the peat, the depth trend varied between forest communities (Fig. 3a,b; Table
394 2). For both the CO₂ and CH₄ production, the underlying mineral soil had the lowest production
395 rates (Fig. 2,3). A separate analysis, including only the surface peat layer, indicated that neither

396 CO₂ nor CH₄ production varied between the forest communities (Anoxic: CO₂, $F_{1,14} = 0.08$, $P >$
397 0.05 ; CH₄, $F_{1,14} = 0.11$, $P > 0.05$; Oxic: CO₂, $F_{1,4} = 6.15$, $P > 0.05$; CH₄, $F_{1,4} = 4.81$, $P > 0.05$).

398

399 *3.4. Gas production and peat's physicochemical characteristics*

400 Among the peat physicochemical variables that were explored by linear and exponential
401 regression analyses (*i.e.*, pH, conductivity, bulk density, total C, total N, and C:N), only bulk
402 density showed a significant inverse linear relationship with both the CO₂ and CH₄ production
403 under anoxic and oxic conditions (Fig. 4 and Fig.5; Table S3-S4).

404

405 Some of the products obtained from the TMAH-Py-GC/MS showed positive linear relationship
406 and exponential relationship with CO₂ and CH₄ production rates (Fig. 4 and Fig.5; Table S3-S4).
407 Under anoxic conditions, CO₂ and CH₄ production rates were related to lignin, long chain fatty
408 acids, polysaccharides, and prist-1-ene (related to chlorophyll) (Fig. 4; Table S4), but not to short
409 chain fatty acids or polyaromatic compounds. The relationship between gas production and
410 lignin varied among the three main lignin monomers. Whereas CO₂ production was strongly
411 related to the coniferyl and sinapyl alcohol monolignols, CH₄ production was related more
412 strongly to *p*-coumaryl alcohol monolignol (Table S4).

413 In contrast with anoxic conditions, under oxic conditions, CH₄ production was only weakly
414 related to lignin moieties (Fig. 5; Table S3). For both the CO₂ and CH₄ production rates, the
415 strongest relationships were observed with coniferyl and sinapyl alcohol monolignols, long chain
416 fatty acids, and polysaccharides (Table S3).

417 For both anoxic and oxic conditions, the best model to explore the relation between CO₂
418 production and lignin moieties was the exponential regression; however, linear regression
419 offered a better fit for the relation between CH₄ production and lignin moieties (Table S3-S4).

420

421 **4. Discussion**

422

423 *4.1. Variation in organic matter composition with depth and forest type*

424 The distribution of the pyrolysis products through the stratigraphic profile of the peat cores
425 reflected a selective preservation of the most recalcitrant vegetation tissues and
426 biomacromolecules through time (Briggs, 1999; Hoyos-Santillan et al., 2015). The selective
427 preservation is not necessarily the result of a complete halt in the decomposition process
428 (Cotrufo et al., 2015), but suggests a substantial difference in the decomposition rates of the
429 different peat layers, with lower decomposition rates in deeper layers. The higher abundance of
430 pyrolysis products derived from polysaccharides, long chain fatty acids, and chlorophyll in the
431 upper layers of the peat profile are indicators of the presence of organic matter derived from
432 recently deposited litter in early stages of decomposition (Schellekens, 2013). The relatively high
433 concentrations of long chain fatty acids and n-alkanes in the surface peat layer can be attributed
434 to the presence of foliar litter (Eglinton and Hamilton, 1967; Vancampenhout et al., 2008),
435 specifically epicuticular leaf waxes (Nip et al., 1986). The increase in short chain fatty acids (<
436 C₂₀) in deeper strata of the Almirante, PS2, PS1, and Cricamola cores suggests more
437 decomposed organic matter, as decomposition of long chain fatty acids produces shorter chain
438 fatty acids (Hajje and Jaffé, 2006).

439

440 The variability in the distribution of monolignols (*i.e.*, *p*-coumaryl, coniferyl, and syringyl)
441 through the stratigraphic profile is likely the result of different resistance to decomposition of
442 each monolignol (Buurman et al., 2007). Hardwood lignin (*i.e.* syringyl-guaiacyl lignin), rich in
443 coniferyl alcohol, is most resistant to decomposition (Vancampenhout et al., 2008), which is
444 reflected by coniferyl alcohol being present throughout the peat profile in all the cores. Coniferyl
445 alcohol is also associated with suberin from the epidermis and hypodermis of roots (Graça and
446 Santos, 2007), which have been recognized as major constituents of tropical peat (Hoyos-
447 Santillan et al., 2015). By contrast, *p*-coumaryl alcohol is primarily found in the upper layers,
448 reflecting palm leaf and reproductive litter inputs (Bu'Lock and Harbone, 1980), and leaf
449 cuticles (Kolattukudy, 1980).

450

451 The lack of a declining trend in long chain fatty acids with depth in the upper layers of the
452 Cricamola site, suggests that this peatland has been affected by different decomposition regimes
453 compared to the other study sites. The decomposition of organic matter under oxic conditions
454 due to a seasonal water table draw down close to the river may have resulted in a reduction in the
455 length of fatty acid chains (Couwenberg et al., 2010; Schellekens et al., 2009). In addition,
456 relatively high abundance of long chain fatty acids, *p*-coumaryl monolignols, polysaccharides,
457 and prist-1-ene in deeper strata, indicates an enhanced preservation of organic matter. Such
458 preservation of organic material could be due to the high amounts of mineral material (*e.g.* clay)
459 found in different layers of the peat core. Clay particles are known to create organo-mineral
460 complexes that protects organic matter from microbial decomposition (Six et al., 2002; Zech et

461 al., 1997). Furthermore, clay can influence the distribution of fatty acids pyrolyzates in samples
462 with high content of mineral material (Nierop and van Bergen, 2002).

463

464 The difference in macromolecular composition of the surface peat chemistry between the two
465 forest types reflects the differences in litter chemistry between the dominant litter forming
466 species at the two sites. *R. taedigera* palm has higher content of *p*-coumaryl alcohol than *C.*
467 *panamensis* in leaves, stems, and roots; whereas in the same tissues, *C. panamensis* has higher
468 content of coniferyl and sinapyl alcohols (Hoyos-Santillan et al., 2015). Such differences in litter
469 chemistry are linked to differences in the plant physiology between monocotyledonous (*e.g.*
470 palms) and dicotyledonous angiosperms. Monocotyledonous angiosperms, develop hydroxyl
471 phenol-guaicyl-syringyl lignin (HGS-lignin), containing higher amounts of lignin moieties
472 related to *p*-coumaryl and sinapyl (Ek et al., 2009). By contrast, dicotyledonous trees, such as *C.*
473 *panamensis*, develop hardwood lignin, which contains higher amounts of coniferyl alcohol (Ek et
474 al., 2009).

475

476 4.2. Peat composition and anoxic CO₂ and CH₄ production

477 The greater production of CH₄ and CO₂ in surface peat under anoxic conditions (Fig. 2 c,d and
478 Fig. 3 c,d), together with the relationship between gas production rates and concentrations of
479 lignin, long chain fatty acids, and polysaccharides (Fig. 4; Table S4), suggests that the abundance
480 of labile substrates strongly controls the production of CH₄ and CO₂ under anoxic conditions.
481 The lignin, long chain fatty acids, and polysaccharides found in decomposing leaf litter in the
482 surface peat layer (Fig. S2) can be used by fermenters to produce the substrates required by

483 methanogens (Nilsson and Bohlin, 1993). Similarly, in temperate peatlands, the primary source
484 of fresh C used by soil microorganisms is foliar litter (Coles and Yavitt, 2004), which can supply
485 substrates for CH₄ production (Yavitt and Williams, 2015). Furthermore, lignins rich in *p*-
486 coumaryl alcohol are also used by methanogenic bacteria to produce CH₄ (Williams and Yavitt,
487 2003). As labile lignin is decomposed (*i.e.* rich in *p*-coumaryl alcohol), deeper strata become
488 relatively enriched with more recalcitrant molecules (Briggs, 1999), such as hardwood lignin (*i.e.*
489 coniferyl alcohol moieties) (Fig. S2). The variation in resistance to microbial decomposition
490 through different strata is reflected in the production of CH₄ and CO₂; in temperate peatlands,
491 surface peat layers produce up to 12 times more CO₂ than deeper peat layers (Hogg et al., 1992).
492 However, despite having a lower CO₂ and CH₄ production, subsurface peat has been recognized
493 as significant contributor to greenhouse gas production in Neotropical peatlands possibly due to
494 root inputs of labile C substrates (Wright et al., 2011). The lack of correlation between CH₄
495 production and C content in the different peat layers suggests that it is the quality (*i.e.*
496 recalcitrance associated to structural characteristics of molecules), rather than the quantity of
497 organic matter what controls methanogenesis (Nilsson and Bohlin, 1993; Valentine et al., 1994).
498
499 In temperate peatlands, peat botanical origin is a main driver of subsurface C mineralization (*e.g.*
500 Moore and Dalva, 1997). For example, Nilsson and Bohlin (1993) observed different CO₂
501 production rates between peat originating from bryophytes (rich in cellulose and hemicellulose)
502 and peat with herbaceous origins (rich in lignin). By contrast, in our study the CO₂ and CH₄
503 production rates in the surface layer did not differ between palm and mixed forest peat (Fig. 2
504 and 3; Table 2). The fact that the contrasting lignin composition between the two plant functional

505 types is not reflected in CO₂ and CH₄ production rates may suggest that polysaccharides and
506 fatty acids from foliar litter are more important substrates under anoxic conditions.

507

508 *4.3. Peat composition and CO₂ and CH₄ production under oxic conditions*

509 CO₂ production rates under oxic conditions throughout the peat profile were up to 40 times
510 higher than those under anoxic conditions (Fig. 2; Table 2), demonstrating strong control of
511 oxygen over decomposition rates. The high oxic CO₂ production rates also in deeper strata
512 despite the substantial variation in peat organic chemistry through the stratigraphic profile (Fig.
513 2a,b; Fig. S2), indicate that peat organic chemistry does not limit decomposition under oxic
514 conditions. Indeed, improved oxygenation of the peat will stimulate activity of ligninolytic
515 microorganisms, which require oxygen for an efficient lignin depolymerization and
516 solubilization (Zeikus, 1981). Additionally, oxygen is required for phenoloxidase activity, which
517 is critical for the decomposition of more complex organic molecules, *e.g.* phenolic compounds,
518 associated with lignin moieties (Fenner and Freeman, 2011). Thus, under oxic conditions, CO₂
519 production was no longer limited to certain substrates and the microbial community was able to
520 decompose substrates that were inaccessible under anoxic conditions. Our data highlight the
521 potential consequences of drainage or extended drought on peatlands, where lowering of the
522 water table occurs making buried C deposits available to fast microbial decomposition,
523 contributing to trigger accelerated peat subsidence and rapid losses of CO₂ to the atmosphere
524 (Couwenberg et al., 2010; Hooijer et al., 2012).

525

526 As expected, the shift from anoxic to oxic conditions substantially decreased the CH₄ production
527 rates (Fig. 3), as oxygen is toxic to methanogens (Whitman et al., 2006). Similar reductions in
528 CH₄ fluxes due to peat aeration associated to low water tables in drained peatlands has been
529 previously reported (Couwenberg et al., 2010). However, the reduction in CH₄ emission derived
530 from peat drainage has to be considered in the context of the dramatic increases in CO₂ losses
531 following peat aeration. Indeed, lowering of water tables for long periods can cause irreversible
532 degradation of the tropical peatland ecosystem and its transformation into a net C source to the
533 atmosphere (Couwenberg et al., 2010; Jauhiainen et al., 2005; Page et al., 2011). Our study
534 demonstrates strong substrate controls of CH₄ production through the peat profile, but
535 importantly, CO₂ emissions, even from old, highly degraded peat material, are not limited by
536 such substrate control if peat is aerated. The strong substrate controls of the anoxic
537 decomposition pathway shown here, may both explain the high emissions CH₄ from peat swamp
538 forests, which tend to have high litter inputs providing a continuous supply of fresh substrates
539 and the high rates of peat accumulation in undisturbed tropical peatlands (Sjögersten et al.,
540 2014).

541

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545

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553

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751

752 **Figure captions**

753

754 **Fig. 1** Scores and loadings from Principal Component Analyses (PCA) in all sites. Legends
755 adjacent to scores correspond to each site (Al=Almirante; Ch=Chiriquí Grande; Cr=Cricamola;
756 Da=Damani-Guariviara; P1= San San Pond Sak 1; and P2= San San Pond Sak 2). Subscripts
757 indicate the depth (cm) at which each peat sample was located within the stratigraphic profile.

758

759 **Fig. 2** CO₂ production rates (mg g C⁻¹ h⁻¹) through the peat profile from each site under anoxic
760 and oxic conditions; open and closed symbols correspond to palm swamp and mixed forest
761 communities respectively. Grey symbols indicate mineral soil samples. Legends correspond to
762 Al=Almirante; Ch=Chiriquí Grande; Cr=Cricamola; Da=Damani-Guariviara; PS1= San San
763 Pond Sak 1; and PS2= San San Pond Sak 2. Symbols represent mean ± SE (n = 3 cores per site
764 for anoxic assays; n = 1 core two repetitions for oxic assays). REML outputs are summarized in
765 Table 2.

766

767 **Fig. 3** CH₄ production rates (mg g C⁻¹ h⁻¹) through the peat profile from each site under anoxic
768 and oxic conditions; open and closed symbols correspond to palm swamp and mixed forest
769 communities respectively. Grey symbols indicate mineral soil samples. Legends correspond to
770 Al=Almirante; Ch=Chiriquí Grande; Cr=Cricamola; Da=Damani-Guariviara; PS1= San San
771 Pond Sak 1; and PS2= San San Pond Sak 2. Symbols represent mean ± SE (n = 3 cores per site

772 for anoxic assays; n = 1 core two repetitions for oxic assays). REML outputs are summarized in
773 Table 2.

774

775 **Fig. 4** Linear regression analyses of gas production rates under anoxic conditions ($\log_{10} \text{ mg g C}^{-1}$
776 h^{-1}) and physicochemical characteristics and TMAH-Py-GC/MS products. Data correspond to
777 the all the data from one core in all sites (6 sites). Variance accounted by the model is presented
778 as adjusted r^2 within the figures; a summary of the statistical information regarding the
779 regression analysis is presented in Table S4.

780

781 **Fig. 5** Linear regression analyses of gas production rates under oxic conditions ($\log_{10} \text{ mg g C}^{-1} \text{ h}^{-1}$)
782 and physicochemical characteristics and TMAH-Py-GC/MS products. Data correspond to the
783 all the data from one core in all sites (6 sites). Variance accounted by the model is presented as
784 adjusted r^2 within the figures; a summary of the statistical information regarding the regression
785 analysis is presented in Table S3.

786

787 **Table 1** Location and characteristics of study sites

788

789 **Table 2** Summary of REML outputs for oxic and anoxic assays: CO_2 and CH_4 production rates
790 ($\log_{10} \text{ mg g C}^{-1} \text{ h}^{-1}$)

791

792 **Fig. S1** Physicochemical characterization of peat profiles from the six study sites showing data
793 from individual cores.

794

795 **Fig. S2** Pyrolyzates concentration through the peat profiles from the six study sites. Symbols
796 correspond to single measurements.

797

798 **Table S1** List of dominant species in the study sites by growth form and their contribution to the
799 % basal area ($\text{m}^2 \text{ha}^{-1}$) per plot (0.1 ha). The total number of species for each of the plots is
800 given in parenthesis.

801

802 **Table S2** Factor loadings of principal component analyses (PCA) from the six study sites.

803

804 **Table S3** Linear and exponential regression models for CO_2 and CH_4 production rates ($\log_{10} \text{mg}$
805 $\text{g C}^{-1} \text{h}^{-1}$) under oxic conditions: physicochemical characteristics of peat and TMAH-Py-GC/MS
806 classes

807

808 **Table S4** Linear and exponential regression models for CO_2 and CH_4 production rates ($\log_{10} \text{mg}$
809 $\text{g C}^{-1} \text{h}^{-1}$) under anoxic conditions: physicochemical characteristics of peat and TMAH-Py-
810 GC/MS classes

811