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Quality not quantity: organic matter composition controls of CO_2 and CH_4 fluxes in Neotropical peat profiles

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Abstract

Tropical peatlands represent an important source of carbon dioxide (CO_2) and methane (CH_4) to the atmosphere. However, we do not know where in the peat profile these gases are produced and how controlling factors, such as substrate quality, which can vary substantially with peat age, and anoxic-oxic conditions, interact to determine production rates. To address this knowledge gap, this study investigated if substrate limitation of CO_2 and CH_4 production differs under anoxic-oxic peat conditions using entire peat profiles, from tropical peatlands in Panama. We determined the variation in peat organic chemistry through stratigraphic profiles using tetramethylammonium-pyrolysis-gas chromatography-mass spectrometry (TMAH-Py-GC/MS). To explore how variation in peat organic chemistry through the depth profile impacted on CO_2 and CH_4 production rates under anoxic-oxic conditions we carried out a series of incubation experiments. The TMAH-Py-GC/MS analysis showed high concentrations of long chain fatty acids ($> C_{20}$) in surface peat, and variation in the distribution of the lignin monomers through the peat profile. Both anoxic CH_4 and CO_2 production was greatest from the surface of the peat profile with surface peat accounting for 92 ± 1.7 and 54 ± 2.9 % of the cumulative CH_4 and CO_2 production, respectively. The high CO_2 and CH_4 production rate under anoxic conditions, in surface peat, was strongly related to greater concentrations of lignin, but also long chain fatty acids and polysaccharides, in this section of the peat profile. As expected, CH_4 production decreased, and became decoupled from peat organic chemistry, following peat aeration. In contrast, aeration dramatically increased CO_2 emissions throughout the entire peat profile. This demonstrates that the recalcitrance of buried peat does not protect C stocks in tropical peatlands, if their water tables are lowered in response to drainage or prolonged drought. In conclusion, our

work highlight that information on both labile substrate availability and water table fluctuation are needed to predict CO_2 and CH_4 fluxes from tropical peatlands.

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

1. Introduction

Recent work suggests that peatlands of considerable depth exist within the Amazon basin as well as in Central America (Hoyos-Santillan, 2014; Lähteenoja et al., 2012). They act simultaneously as carbon (C) sinks and sources, exchanging large amounts of greenhouse gases (*e.g.*, CO_2 and CH_4) with the atmosphere (Sjögersten et al., 2014). Given their potential for large C storage and greenhouse gas emissions, it is important to quantify their role within the global C cycle (Kirschke et al., 2013), and how they may respond to environmental change (Lähteenoja et al., 2009; Sjögersten et al., 2014). Tropical peatlands currently store 40-90 GtC as peat (Kurnianto et al., 2015) and tropical wetlands contribute with at least two thirds of the global CH_4 emissions from wetlands (Melton et al., 2013). Drainage, land use change, and climate change (*e.g.* prolonged droughts) threatens C sequestration of tropical peatlands (Turetsky et al., 2014), by subjecting peatlands to aeration leading to higher decomposition rates. This can turn tropical peatlands into net carbon sources (Couwenberg et al., 2010; Hoyos-Santillan et al., 2016; Page et al., 2011). However, current knowledge of CO_2 and CH_4 emissions from tropical peatlands is mainly represented by surface gas fluxes measurements (Couwenberg et al., 2010; E. L. Wright et al., 2013), while the controls and contribution of subsurface emissions remain poorly understood despite their potentially large contribution of net surface emissions (Wright et al., 2011). This lack of understanding on the controls of peat CO_2 and CH_4 emissions and information on gas production through the peat profile, severely limits predictions of how tropical peatlands CO_2 and CH_4 emissions will respond to environmental and land use change.

In high latitude peatlands, the degree of decomposition has been recognized as one of the primary factors controlling the variation of C effluxes through the peat profile (Moore and Dalva, 1997); where deeper, more decomposed, peat layers have been found to be more resistant to decomposition than recently formed peat (Hogg et al., 1992). This may also apply to tropical peatlands, in which distinct decomposition environments over time (*e.g.*, anoxic-oxic) drive variation in peat chemistry with depth (Hoyos-Santillan et al., 2015; E. Wright et al., 2013). Indeed, a strong relationship between CO_2 and CH_4 emissions and the organic matter composition of the peat in the upper 2 m of the stratigraphic profile has been observed in tropical peatlands in Panama (Wright et al., 2011). However, the influence of peat organic chemistry on CO_2 and CH_4 emissions is currently not resolved.

Peat decomposability also varies significantly depending on its botanical origin (*e.g.*, Moore and Dalva, 1997; Nilsson and Bohlin, 1993). Peat deposits in the lowland tropics are formed principally by succession of forest communities (Anderson, 1964; Phillips et al., 1997). Thus, it is plausible that the influence of peat chemistry on CO_2 and CH_4 production differs between the well-studied high latitude peatlands and tropical peatlands. Molecular chemical analyses can be used to determine the botanical origin of peat (Hoyos-Santillan et al., 2015; McClymont et al., 2011), its degree of decomposition (Hoyos-Santillan et al., 2015; Schellekens et al., 2015), and provide insight into the environmental conditions under which decomposition has occurred (Schellekens, 2013). Pyrolysis gas chromatography mass spectrometry (Py-GC/MS) has been used to characterize the molecular composition of peat (Schellekens et al., 2009) and through peat depth profiles (Hoyos-Santillan et al., 2015).

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

The aims of this study were to (1) use Py-GC/MS to quantify variation in organic matter chemistry through the peat profile within palm and mixed forest communities, and (2) determine the relationship between peat chemistry and C mineralization under anoxic-oxic conditions. We tested the hypothesis that CO_2 and CH_4 production rates are greatest from the surface peat under anoxic-oxic conditions due to the availability of labile C substrate from decomposing litter and root exudates (here we use labile to denote organic molecules that are easily degradable by decomposer microorganisms).

2. Materials and methods

2.1. Study area

Study sites were lowland located within the Bocas del Toro province in the north-western Caribbean coast of Panama. Sites included the Changuinola peat deposit (CPD, ≈ 80 km^2) in the

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

2.2.1. Study sites

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

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

136 *eliptica,* and *Euterpe precatoria* 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 HNO_3 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 it's 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 µg μL^{-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 × 0.25 mm (0.25µm film thickness)). Samples were introduced into a preheated interface (310
199 °C) and pyrolyzed at 610 °C for 15 seconds. The GC injector temperature was set to 280 °C and
200 the GC oven temperature was held at 40 °C for 2 minutes and was heated at a rate of 4 °C min^{-1}

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

Compound concentrations were estimated by integrating the areas obtained in the pyrogram and calculating its corresponding concentration using the 5-α-cholestane as an internal standard; concentrations were expressed in relation to the total C content in the peat sample as $\mu g_{compound}$ mg C^{-1}. TMAH pyrolysis produces methyl esters and ethers (Challinor, 1989) consequently methyl ester derivatives of fatty acid and methylated lignin monomers are obtained. Taking this into consideration, each TMAH-Py-GC/MS product was assigned a chemical class based on their molecular similarity to its probable source molecule (Hoyos-Santillan et al., 2015; Schellekens, 2013). Seven main classes were defined: FA = fatty acids; AL = aliphatic; Lg = lignin, subdivided in the three monolignols (*p* – Coumaryl alcohol, Coniferyl alcohol, and Sinapyl alcohol); Ar = Aromatic; Ph = phenol, PA = poly-aromatic hydrocarbons; and PS = poly-saccharides. Prist-1-ene, which has been reported as a product of chlorophyll pyrolysis (Ishiwatari et al., 1991), was given its own category. The short and long chain methylated fatty acids (Short < C_{20} and Long > C_{20}) were further grouped into separate categories to aid data interpretation. The separation of the three lignol-monomers (*p* – Coumaryl alcohol, Coniferyl alcohol, and Sinapyl alcohol) can be used to differentiate types of lignin.

2.4. Respirometric assays

222 *2.4.1. Anoxic assays*

223 The production rate of CO_2 and CH_4 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 CO_2 and CH_4 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 N_2 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,

emulating *in situ* soil temperature (24.6 ± 0.05 °C) (Hoyos-Santillan, 2014). Following two months acclimatization, to allow the establishment of the microbial community, and the depletion of alternative electron acceptors, each serum bottle was re-flushed with N_2 and resealed. Afterwards, a single anoxic incubation (390 days) was conducted, during which all bottles were shaken on a daily basis. The headspace gas of each bottle was analysed by gas chromatography (GC) at the end of the assays (GC-2014, Shimadzu UK LTD, Milton Keynes, UK). CO_2 and CH_4 concentrations were determined using a single injection system with a 1 mL sample loop that passed the gas sample using N_2 as carrier through a non-polar methyl silicone capillary column (CBP1-W12-100, 0.53 mm I.D., 12 m, 5 mm; Shimadzu UK LTD, Milton Keynes, UK). Thermal conductivity (TCD) and H_2 flame ionization (FID) detectors were used to measure CO_2 and CH_4, respectively (Wright et al., 2011). Gas concentrations were adjusted for temperature (25 °C constant) and pressure within the serum bottles according to the ideal gas law. The rate of gas production from the samples expressed as mg g C^{-1} h^{-1} was calculated as the difference between the initial and final concentration of gas in the headspace of the serum bottles at the end of the assay (Hogg et al., 1992). The gas production rate was then expressed in terms of total C content in the sample.

2.4.2. Oxic assays

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

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

2.5. Statistical analysis

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

For the gas production rates under anoxic-oxic conditions (mg g C^{-1} h^{-1}; CO_2 and CH_4), the specific depth of the peat sample within the peat profile and the current forest community in the 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 ± SE. Statistical analyses were performed in
303 GenStat (VSN International, 2011).

304

305 **3. Results**

306

307 *3.1. Peat stratigraphy and physicochemical properties*

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

1, Table S2). The first principal component 1 (PC-1) separates the stratigraphic profile of the peat cores according to depth; presenting, in most of the cases, a strong segregation between the top layer of the peat cores (0 – 0.1 m) and the underlying strata. The segregation of the upper layer of the peat core along PC-1 was primarily driven by the presence of long chain fatty acids (*e.g.*, C_{26}, C_{29}, $C_{30,}$ and C_{31}) and lignin moieties related to coniferyl alcohol (Fig. 1, Table S2). By contrast, the separation along the second principal component (PC-2) was mainly due to the influence of both short (*e.g.*, C_{16}, C_{18}) and long chain fatty acids (*e.g.* C_{27}), as well as lignin moieties related to *p*-coumaryl and sinapyl alcohols. Polysaccharides included pentamethoxy heptanoic acid and methylated glucose, and were not evenly scattered over the plots but were in most cases related to upper peat layers, contributing to both the distribution of scores along PC-1 and PC-2. The scores plots indicate a variation in the composition of peat layers through the stratigraphic profile. Surface peat chemistry differed between the two forest types. The differences in surface peat chemistry were primarily related to the proportions the distinct lignin moieties, specifically those associated to *p*-coumaryl and sinapyl alcohols, and long chain fatty acids.

3.3. Gas production rates through the peat profile

The CO_2 and the CH_4 production rates varied significantly depending on whether the assays were conducted under anoxic or oxic conditions. CO_2 production rates were one order of magnitude higher under oxic conditions in comparison with anoxic conditions (Anoxic-Oxic: CO_2, $F_{1,140}$ = 719, $P < 0.001$) (Fig. 2); whereas, CH_4 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 CH_4, $F_{1,140} = 24$, $P < 0.001$) (Fig. 3).

376

377 In both anoxic and oxic assays, CO_2 production varied significantly with depth across four orders
378 of magnitude (Table 2). In the anoxic assays, the highest CO_2 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 CO_2 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 CO_2, CH_4 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 CO_2 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 CH_4 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 CO_2, CH_4
391 production did no vary between the forest communities (Table 2). Although CH_4 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 CO_2 and CH_4 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 CO_2 nor CH_4 production varied between the forest communities (Anoxic: CO_2, $F_{1,14} = 0.08$, $P >$

397 0.05; CH_4, $F_{1,14} = 0.11$, $P > 0.05$; Oxic: CO_2, $F_{1,4} = 6.15$, $P > 0.05$; CH_4, $F_{1,4} = 4.81$, $P > 0.05$).

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 CO_2 and CH_4 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 CO_2 and CH_4 production rates (Fig. 4 and Fig.5; Table S3-S4).

407 Under anoxic conditions, CO_2 and CH_4 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 CO_2 production was strongly

411 related to the coniferyl and sinapyl alcohol monolignols, CH_4 production was related more

412 strongly to *p*-coumaryl alcohol monolignol (Table S4).

413 In contrast with anoxic conditions, under oxic conditions, CH_4 production was only weakly

414 related to lignin moieties (Fig. 5; Table S3). For both the CO_2 and CH_4 production rates, the

415 strongest relationships were observed with coniferyl and sinapyl alcohol monolignols, long chain

416 fatty acids, and polysaccharides (Table S3).

For both anoxic and oxic conditions, the best model to explore the relation between CO_2 production and lignin moieties was the exponential regression; however, linear regression offered a better fit for the relation between CH_4 production and lignin moieties (Table S3-S4).

4. Discussion

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

The distribution of the pyrolysis products through the stratigraphic profile of the peat cores reflected a selective preservation of the most recalcitrant vegetation tissues and biomacromolecules through time (Briggs, 1999; Hoyos-Santillan et al., 2015). The selective preservation is not necessarily the result of a complete halt in the decomposition process (Cotrufo et al., 2015), but suggests a substantial difference in the decomposition rates of the different peat layers, with lower decomposition rates in deeper layers. The higher abundance of pyrolysis products derived from polysaccharides, long chain fatty acids, and chlorophyll in the upper layers of the peat profile are indicators of the presence of organic matter derived from recently deposited litter in early stages of decomposition (Schellekens, 2013). The relatively high concentrations of long chain fatty acids and n-alkanes in the surface peat layer can be attributed to the presence of foliar litter (Eglinton and Hamilton, 1967; Vancampenhout et al., 2008), specifically epicuticular leaf waxes (Nip et al., 1986). The increase in short chain fatty acids ($< C_{20}$) in deeper strata of the Almirante, PS2, PS1, and Cricamola cores suggests more decomposed organic matter, as decomposition of long chain fatty acids produces shorter chain fatty acids (Hajje and Jaffé, 2006).

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

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

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

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

4.2. Peat composition and anoxic CO_2 and CH_4 production

The greater production of CH_4 and CO_2 in surface peat under anoxic conditions (Fig. 2 c,d and Fig. 3 c,d), together with the relationship between gas production rates and concentrations of lignin, long chain fatty acids, and polysaccharides (Fig. 4; Table S4), suggests that the abundance of labile substrates strongly controls the production of CH_4 and CO_2 under anoxic conditions. The lignin, long chain fatty acids, and polysaccharides found in decomposing leaf litter in the 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 CH_4 production (Yavitt and Williams, 2015). Furthermore, lignins rich in *p*-
486 coumaryl alcohol are also used by methanogenic bacteria to produce CH_4 (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 CH_4 and CO_2; in temperate peatlands,
491 surface peat layers produce up to 12 times more CO_2 than deeper peat layers (Hogg et al., 1992).
492 However, despite having a lower CO_2 and CH_4 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 CH_4
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 CO_2
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 CO_2 and CH_4
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 CO_2 and CH_4 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 CO_2 and CH_4 production under oxic conditions*

509 CO_2 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 CO_2 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, CO_2
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 CO_2 to the atmosphere
524 (Couwenberg et al., 2010; Hooijer et al., 2012).

525

As expected, the shift from anoxic to oxic conditions substantially decreased the CH_4 production rates (Fig. 3), as oxygen is toxic to methanogens (Whitman et al., 2006). Similar reductions in CH_4 fluxes due to peat aeration associated to low water tables in drained peatlands has been previously reported (Couwenberg et al., 2010). However, the reduction in CH_4 emission derived from peat drainage has to be considered in the context of the dramatic increases in CO_2 losses following peat aeration. Indeed, lowering of water tables for long periods can cause irreversible degradation of the tropical peatland ecosystem and its transformation into a net C source to the atmosphere (Couwenberg et al., 2010; Jauhiainen et al., 2005; Page et al., 2011). Our study demonstrates strong substrate controls of CH_4 production through the peat profile, but importantly, CO_2 emissions, even from old, highly degraded peat material, are not limited by such substrate control if peat is aerated. The strong substrate controls of the anoxic decomposition pathway shown here, may both explain the high emissions CH_4 from peat swamp forests, which tend to have high litter inputs providing a continuous supply of fresh substrates and the high rates of peat accumulation in undisturbed tropical peatlands (Sjögersten et al., 2014).

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Figure captions

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

Fig. 2 CO_2 production rates (mg g C^{-1} h^{-1}) through the peat profile from each site under anoxic and oxic conditions; open and closed symbols correspond to palm swamp and mixed forest communities respectively. Grey symbols indicate mineral soil samples. Legends correspond to Al=Almirante; Ch=Chiriquí Grande; Cr=Cricamola; Da=Damani-Guariviara; PS1= San San Pond Sak 1; and PS2= San San Pond Sak 2. Symbols represent mean ± SE (n = 3 cores per site for anoxic assays; n = 1 core two repetitions for oxic assays). REML outputs are summarized in Table 2.

Fig. 3 CH_4 production rates (mg g C^{-1} h^{-1}) through the peat profile from each site under anoxic and oxic conditions; open and closed symbols correspond to palm swamp and mixed forest communities respectively. Grey symbols indicate mineral soil samples. Legends correspond to Al=Almirante; Ch=Chiriquí Grande; Cr=Cricamola; Da=Damani-Guariviara; PS1= San San Pond Sak 1; and PS2= San San Pond Sak 2. Symbols represent mean ± SE (n = 3 cores per site

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

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

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

Table 1 Location and characteristics of study sites

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

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

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

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

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

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

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