ORIGIN, COMPOSITION, AND TRANSFORMATION OF DISSOLVED ORGANIC MATTER IN TROPICAL PEATLANDS

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Abstract

Solid and Dissolved Organic Matter (DOM) compositions were investigated in a pristine and a deforested tropical peat forest in Brunei Darussalam. A combination of elemental (%C, %N, C/N), isotopic ($\delta^{15}N$, $\delta^{13}C$, $\Delta^{14}C$), molecular (lignin phenol biomarkers) and optical (Specific UV Absorbance at 280 nm ($SUVA_{280}$), Fluorescence Index (FI)) analyses were performed to characterize DOM in porewater and river water. The DOM composition was compared to vegetation and peat to assess DOM origin and transformations in the ecosystem. Significant relationships were observed between optical properties ($SUVA_{280}$, FI) and bulk ($\Delta^{14}C$) and molecular (ratio of cynnamyl to vanillyl phenols, C:V) composition of DOM.

The radiocarbon content of DOM shows that it is modern at both sites for both surface and deep (to 4.5 m) samples ($\Delta^{14}C$= 74.58±8.53‰ at the pristine site and $\Delta^{14}C$= 87.84±4.5‰ at the deforested site), indicating transport of young DOM to deeper layers. Stable carbon-13 content of vegetation, peat and DOM showed only slight fractionation and ranged from -32.2‰ to -28.3‰. Nitrogen showed a greater shift between ecosystem pools. Nitrogen-15 content was higher in the solid peat ($\delta^{15}N$ = -0.9±0.4‰ in the pristine site, $\delta^{15}N$ = -1.2±1.4‰ in the deforested site) than in DOM ($\delta^{15}N$ = -4.3±2.5‰ in the pristine site, $\delta^{15}N$ = -4.1±2.3‰ in the deforested site). This difference in $\delta^{15}N$ is significantly correlated with the C/N values of peat and DOM and attributable to higher microbial degradation in the peat compared to DOM. Pore water DOM contains less lignin ($\lambda 8$ =1.16±0.35 mg.100mg dw^{-1} in the pristine site and $\lambda 8$ =1.51±0.51 mg.100mg dw^{-1} in the deforested site) than does the solid peat ($\lambda 8$ =5.40±2.11 mg.100mg dw^{-1} in the pristine site and $\lambda 8$ =9.55±4.7 mg.100mg dw^{-1} in the deforested site). All indicators of lignin degradation (P:(V+S), 3.5Bd/V, (Ad/Al)V, (Ad/Al)S) are significantly higher in

DOM than in the solid peat. This shows that lignin can be processed rapidly in the porewater of upper layers of tropical peatlands.

Logging activity affected the composition of organic matter at the deforested site. Higher lignin content (λ8) was observed in the solid peat, and the composition of DOM differed greatly in the deforested site: $\Delta^{14}C$, FI, 3.5Bd/V, (Ad/Al)V are significantly different from the pristine site. Thus it appears that the composition of DOM is more sensitive than the solid phase to the effects of land use change on organic matter dynamic in tropical peatlands.

Key-Words: Dissolved organic matter, Tropical peatland, Stable isotopes, Radiocarbon dating, Lignin biomarkers, Absorbance, Fluorescence

1. Introduction

Dissolved organic matter (DOM) constitutes a small but important fraction of soil carbon stocks because it is both reactive and mobile. Within porewater, DOM performs several ecological functions: provision of carbon and energy for microorganisms, production of CO_2 and CH_4 that may be released to the atmosphere, and control of porewater pH and speciation of diverse nutrients (N and P) and metallic elements (Neff et Asner 2001; Limpens et al. 2008). In peatlands, dissolved organic matter (DOM) is also a key component of the carbon cycle. Transfer of young DOM from surface to deep layers can induce methanogenesis and/or microbial decomposition in temperate peatlands, producing CO_2 and CH_4 deep in the peat (Aravena et al. 1993; Chanton et al. 1995;

Chanton et al. 2008). Recently, fluvial export of dissolved organic carbon (DOC) has been recognized as a significant component of the carbon budget of both temperate and tropical peatlands (Billett et al., 2010, Moore et al., 2013). DOM exported to streams may decompose there, becoming a source of CO_2 to the atmosphere (Cole et al. 2007). Tropical peatlands export dissolved organic carbon at a higher rate (above 80 $g.m^{-2}.y^{-1}$ (Moore et al., 2011; Gandois et al., 2013)) than do temperate and boreal peatlands (10 to 25 $g\ m^{-2}\ y^{-1}$, (Fraser et al., 2001)) so that, although they constitute only 11% of peatlands by area (Page et al., 2011), tropical peatlands may nonetheless release a significant proportion of all peatland dissolved organic carbon exports.

Despite the recent evidence of its crucial role, the composition and fate of peatland DOM remain uncertain, although it is expected to be very diverse because of the likely diversity in its origin and transformation (vegetation, peat, microbial activity). Elucidating DOM composition and fate is crucial to understanding its role in both peatland carbon dynamics and the global carbon cycle.

Most tropical peatlands (77%) are located in South-East Asia (Page et al., 2011). Before development, these peatlands were mostly forested and hosted significant biodiversity (Posa et al., 2011). Tropical peatlands have been rapidly degraded due to drainage, deforestation and conversion to agriculture since the late 1990's (Miettinen et al., 2011). This abrupt change in land use has induced massive release of carbon from peatlands to the atmosphere because of enhanced decomposition of organic matter (Couwenberg et al., 2009; Hergoualc'h et Verchot, 2011). The modification of organic matter from peatland degradation has also affected DOM composition and export. Evidence of anthropogenically induced changes in the quantity, composition and age of exported

DOM in temperate peatlands has been reported (Kalbitz 2001; Freeman et al. 2001; Pastor et al. 2003; Evans et al., 2007; Billett et al. 2010). Recent studies suggest that similar changes have occurred in tropical areas (Gandois et al., 2013; Moore et al., 2013). Investigation of the composition of DOM is necessary to understand its role in the carbon cycle and its response to anthropogenic pressure in tropical peatlands. In the work presented here, complementary tools (isotopic, molecular, optical) were applied to different ecosystem compartments (DOM, solid organic matter, vegetation) to investigate tropical peatland organic matter dynamics. Isotopic shifts ($\delta^{13}C$ and $\delta^{15}N$) between the different pools of an ecosystem indicate organic matter transformation (DeNiro et Hastorf 1985; ŠantRůČková et al., 2000).

The fate of lignin is of primary importance for understanding tropical peat accumulation because tropical peat originates from trees (Durig et al. 1988; Calvert et al., 1991). We assessed lignin source and degradation in vegetation, peat and DOM samples by analysis of CuO oxidation products (Thevenot et al., 2010). Upon oxidation (alkaline CuO), the lignin macropolymer is hydrolyzed to small structural units belonging to three classes of methoxylated phenols: vanillyl (V), ubiquitous in all terrestrial plants, syringyl (S), specific of angiosperms and cinnamyl (C), produced in non-woody tissues. The yields and ration of these phenols can be used to identify lignin origin (Hedges et Mann 1979). Each class of lignin oxidation products in turn comprises an acid, an aldehyde and a ketone (for V and S) or only acids (for C). The ratios of compounds reflect lignin transformation in terrestrial environments arising from microbial activity (Goñi et al. 1993; Dittmar et Kattner 2003), photodegradation (Benner and Kaiser, 2011) or sorption to soil phases (Hernes et al., 2007). This is the first time this tool has been used to study

both solid and dissolved organic matter in tropical peatlands. Investigations of optical properties of DOM provide information on DOM composition, mainly aromatic molecules (Weishaar et al. 2003), origin and transformation in ecosystems (McKnight et al. 2001; Yamashita et al. 2010). We have combined these indicators in the context of a pristine and a deforested tropical peat dome of Brunei to investigate: (1) DOM and lignin origin and transformation in tropical peatlands, (2) Influence of deforestation on organic matter and DOM in tropical peatlands.

2. Material and methods

2.1. Study sites

The study sites are located in the Ulu Mendaram Conservation Area, Belait District, Brunei Darussalam, on the Island of Borneo (Figure 1). Two peat domes were investigated. One is a pristine peat dome (Mendaram dome) and the second (Damit dome) is a former timber concession, where selective logging, but no drainage, occurred from 1980 to 2010. At the pristine site, the main vegetation cover includes *Shorea albida* (dipterocarp species listed in the IUCN (International Union for Conservation of Nature and Natural Resources) red list of threatened species) and *Pandanus* sp. (pandan) as described in the early 1980 (Anderson, 1983). In the deforested site, most of the *Shorea albida* has been harvested, with the exception of a few individuals. Recovery species include *Pandanus* sp. as well as *Nephrolepsis biserrata* (ferns) (Kobayashi, 1999).

2.2. Sample collection

-Peat samples:

Samples were collected at 3 locations along transects from the edge (river) to the center of each dome. At each location, 3 replicates were sampled in a 10 m x 10 m square. Surface peat was collected to 15 cm depth after litter removal. Samples were placed in plastic bags, transported to the laboratory, and dried at 60 °C. Roots were removed and the remaining dry material was ground in an agate mortar.

- Cores

Three cores were collected at each site for radiocarbon dating of the bulk peat using a 5 cm diameter Russian peat corer (Edelman auger, Eijkelkamp, Netherlands). The cumulative length of each retrieved core varied from 3 m at the edge of the domes to 6 m at the center. For dating purposes, three subsamples were collected on each core between 65-69 and 126-130 cm depth and one at the bottom of the peat, before the colour and texture transition with the clay, the depth of which varied with the location of the core on the peat dome. Deep samples were taken at 245-248, 507-510,531-535 cm depth in the pristine site and 187-190, 383-386, 424-427, 451-454 cm in the logged site. Samples were dried (60°C) and ground in an agate mortar.

- Water samples

Water was sampled in the middle of the river draining the two sites (Mendaram River) and in the river draining the north side of the Damit dome (Damit River). Samples were taken at a 20 cm depth using cleaned polypropylene bottles. Porewater was sampled along a transect from the edge to the center of the dome. The 30 cm and 180 cm depth samples were extracted using inox pushpoint samplers (MHE products, USA), connected to Tygon tubing (St Gabon, France) and a hand pump. After flushing the system, a sample was collected using a polypropylene syringe. At each location on the domes,

157 water was also collected from pools at the peat surface. Sampling equipment was cleaned
158 with acid (HCl, 1N) and ultrapure water. Glass bottles, filtration apparatus and filters
159 were baked (550°C) for 43 hours to avoid any carbon contaminations. Samples were
160 filtered within 24 h. An aliquot was stored in glass bottles for total organic carbon (TOC)
161 and optical properties analysis. One liter was freeze-dried to collect dissolved material for
162 isotopic and molecular analysis. Deeper pore water samples were collected at one
163 location in the pristine site using the same sampling protocol as the shallow samples. The
164 samples were not freeze dried and direct analysis of $\Delta^{14}C$ was performed on the filtered
165 sample (acidified with ultrapure HCl). Blank showed no carbon contamination.

166 -Vegetation samples:

167 Vegetation was sampled at both sites to investigate the main sources of organic matter in
168 the peat. *Pandanus* leaves (3 replicates at both sites) and *Shorea albida* leaves, bark and
169 wood (2 replicates) were sampled. In the deforested site, *Nephrolepis biserrata* (2
170 replicates), abundant after deforestation, was also sampled.

171 ### *2.3. Sample analysis*

172 - Porewater organic carbon content

173 Non-purgeable organic carbon (NPOC, referred to hereafter as DOC) was analyzed on
174 filtered samples after acidification to pH 2 with a TOC-V CSH analyzer (Shimadzu,
175 Japan). Certified material (soft river water, Miramichi-02, Environment Canada) was
176 included in the analytical loop and recovery was >95% of the certified value.

177 - Optical properties of DOM

178 The UV absorption spectra from 240 to 700 nm of porewater were measured with a
179 spectrophotometer (UV-1601 PC, Shimadzu, Japan) in a 1 cm quartz cell. The baseline
180 was determined with ultra pure water. The Specific UV Absorbance at 280 nm ($SUVA_{280}$,
181 $l.mg^{-1}\ m^{-1}$) was calculated as follows: $SUVA = \frac{A_{280}}{b.[DOC]}$ ($l.mgC^{-1}.m^{-1}$), where A_{280} is the
182 sample absorbance at 280 nm (non-dimensional), b is the optical path length (m) and
183 DOC is in $mg.l^{-1}$. The absorbance at 280 nm was chosen instead of the usual 254 nm
184 (Weishaar et al., 2003) since the high DOC concentration induced saturation of the
185 spectrophotometer at 254 nm.
186 Fluorescence measurements were performed on porewater samples with a LS 45 Perkin
187 Elmer (Norwalk, CT, USA) fluorescence spectrometer. Emission slits were set at 5 nm
188 with a scan speed of 500 nm min^{-1}. Emissions spectra were recorded from 350 to 700 nm
189 for 370 nm excitation. The intensity of the fluorescence spectra was corrected for inner
190 filtering effect using the absorbance spectra following the procedure described in
191 McKnight et al. (2001). Fluorescence Index was calculated as defined in Maie et al.
192 (2006), by the ratio of the fluorescence intensity at 470nm to intensity at 520 nm for a
193 370 excitation.
194 -Isotopic analysis
195 Total C and N content, as well as stable isotope analyses ($\delta^{15}N$ and $\delta^{13}C$) of DOM and
196 peat samples were performed using a mass spectrometer (Isoprime 100) coupled with a
197 Vario El Micro elemental analyzer. $\delta^{15}N$ and $\delta^{13}C$ were calculated using ($R_{sample}/R_{standard}$-
198 1) x 1000, where R is the ratio of $^{13}C/^{12}C$, or $^{15}N/^{14}N$. Standard was Pee Dee Belemnite

for carbon and atmospheric N_2 for nitrogen. For each analytical sequence, standard and replicates were included.

Radiocarbon analysis of DOM and bulk peat was performed at NOSAMS (Woods Hole, USA) AMS facility following standard methods.

-Molecular biomarkers analysis

Molecular biomarker analysis of DOM and peat samples was performed according to the copper oxidation (CuO) method initially developed by Hedges and Ertel (1982) and modified by Goñi and Montgomery (2000). 3-5 mg of sample (vegetation, peat or freeze-dried DOM) were oxidized with CuO in a 2 mol L^{-1} NaOH solution under exclusion of O_2 in an oven at 150°C for 180 min in 3.2 mL stainless steel mini-bombs (Prime Focus® Inc, Seattle). Once vials were opened, ethyl vanillin and cinnamic acid were added to the solutions as an internal standard. The aqueous solutions were acidified to pH 1 with concentrated HCl and extracted with ethyl acetate. After evaporation in a centrivap cold trap, reaction products were dissolved in pyridine and derivatized with bis(trimethylsilyl) - trifluoroacetamide-trimethylchlorosilane (BSTFA-TMCS) to form trimethylsilyl derivatives. Extraction products were then analyzed on a Gas Chromatograph-Mass Spectrometer system (Model 3800-Saturn 2000, Varian) fitted with a fused capillary column (Varian FactorFour VF-1ms 60 m, 0.32 mm). Each compound was identified according to its retention time and by comparing it to commercially available standards. Standards were analyzed every 4 samples, and the standard deviation of replicate analysis was below 15%. We analyzed 12 CuO derivatives used in recent literature, three lignin derived phenols families: Vanillyl phenols (V: Vl, vanillin; Vn, acetovanillone; Vd, vanillic acid), cinnamyl phenols (C: p-Cd, p-coumaric acid; Fd, feluric acid) and syringyl

phenols (S: Sl, syringaldehyde; Sn, acetosyringone; Sd, syringic acid). These three families are used to determine the source of organic matter along with relative abundance (λ8: sum of ΣV, ΣC and ΣS). P-hydroxyphenols (Pl, p-hydroxybenzaldehyde; Pn, p-hydroxyacetophenone; Pd, p-hydroxybenzoic acid) and a benzene carboxylic acid (3,5-dihydroxybenzoic acid) were also combined with V and S to describe the TOM state of degradation and humification (Houel et al 2006, Dickens et al 2007).

3. Results

Results are summarized in Table 1 for bulk analysis of organic matter and in Table 2 for organic matter biomarkers. Henceforth DOM and peat samples from pristine and deforested domes have been pooled. DOM elemental, isotopic and molecular compositions did not show significant differences (Kruskal Wallis, $p<0.001$) between sampling sites within the same dome and within vertical profiles (flat profiles of DOM characteristics between surface, 30 cm and 180 cm samples).

3.1. Bulk elemental, stable and radiocarbon isotopic composition of peat, DOM and vegetation

- Elemental content

DOC concentrations were high in the peat porewater: 66.1±8.9 $mg.l^{-1}$ in the pristine site and 74.9±9.1 $mg.l^{-1}$ in the deforested site (Table 1). Lower DOC concentrations were measured in the river water: 37.4±0.1 $mg.l^{-1}$ in the pristine river separating the two sites, which receives input primarily from peatlands, and 26.7 in the deforested river draining the north side of the deforested site which has headwaters beyond the peat lands. The carbon concentration in samples was lower in DOM samples (C = 40 to 47 %) than in

vegetation (C= 46 to 52%) and peat samples (C = 48 to 56 %) (Table 1). Nitrogen content ranged from 0.6 to 1.1% in DOM samples, from 0.8 to 1.4% in vegetation (except in ferns (N= 2-3%)) and from 1.8 to 3% in peat samples. Nitrogen was enriched in peat samples (C/N = 30.6±5.7 compared to DOM (C/N=53.2±10) and vegetation samples, which exhibited low N content and high C/N (C/N=55.0±12), except for ferns (Table 1).

- Stable isotopes

The most abundant plant species at the pristine site (*Shorea albida* and *Pandanus* sp.) showed similar carbon isotopic ratios ($\delta^{13}C$ = -29.6±0.04‰, Figure 2a), typical of C_3 vegetation. The ferns (*Nephrolepis biserrata*) that recolonize the deforested site were relatively ^{13}C depleted ($\delta^{13}C$ =-30.8±0.2‰). The isotope ratio of peat samples from the pristine site was on average slightly ^{13}C depleted ($\delta^{13}C$ = -30.5±0.8‰) compared to the deforested site ($\delta^{13}C$ = -29.5±0.6‰). In porewater, $\delta^{13}C$-DOM values were homogeneous with values observed in the peat and vegetation samples with an average of $\delta^{13}C$ = -29.9±0.24‰ in the pristine site and $\delta^{13}C$ = -30.2±0.2‰ in the deforested site. The $\delta^{13}C$-DOM values of river water was similar in the Mendaram river ($\delta^{13}C$ = -29.6±0.05 ‰) and in the Damit river ($\delta^{13}C$ = -29.9‰).

A wide range of $\delta^{15}N$ values was measured in the vegetation (from $\delta^{15}N$ = -3‰ to -8‰) and DOM ($\delta^{15}N$ = -0.8 ‰ to $\delta^{15}N$ = -8.2‰). The $\delta^{15}N$-DOM ($\delta^{15}N$ = -4.18±2.5‰ in the pristine site, $\delta^{15}N$ = -4.13±2.3‰ in the deforested site) was lower than in the peat ($\delta^{15}N$ = -0.9±0.4‰ in the pristine site, $\delta^{15}N$ = -1.2±1.4‰ in the deforested site). A significant ($p<0.05$) increase in $\delta^{15}N$ was observed with C/N decrease when pooling the peat and DOM samples (Figure 2b).

- Radiocarbon

Radiocarbon (Δ^{14}C-DOM) values in porewater and river were all modern (Table 1). All the values were greater than the atmospheric value at the time of sampling (Δ^{14}C = 50‰ in 2008, (Graven et al., 2012)). Averages of Δ^{14}C-DOM = 74.58±8.53‰ and Δ^{14}C-DOM = 87.84±4.5‰ were measured in the pristine (first 3 meters) and in the deforested site. In the pristine site, where additional samples were taken, a slight increase of Δ^{14}C-DOM is noticed after 3 meters, but DOM remains modern down to 4.5 meters. In the river draining the pristine site, values of Δ^{14}C-DOM = 62.7 and 73.84‰ were measured.

Radiocarbon content of bulk peat organic carbon showed a sharp decrease with depth for all cores. Average ages of 254 and 620 yr were measured at 65 and 128 cm depth, respectively for both sites. The deepest peat showed the greatest variability in age: at the bottom of the cores, the measured age of the bulk material ranged from 2230 to 2920 yr. Higher variability was also observed for the shorter (2 to 3 m) cores sampled on the river edges (Figure 3).

3.2. Optical properties of DOM

Optical properties of DOM in porewater and river water of the two sites are described in Gandois et al. (2013). Measured $SUVA_{280}$ values range from 3.4 to 6, with significantly (KW, $p<0.05$) greater values in the deforested site (5.2 ±0.6 $L.mgC^{-1}\ m^{-1}$) compared to the pristine site (4.3±0.6 L $mgC^{-1}\ m^{-1}$), indicating that DOM is more aromatic in the deforested site. Fluorescence index ranged from 1.33 to 1.62, reflecting the predominance of terrestrially-derived DOM (McKnight et al., 2001). Fluorescence index was significantly (KW, $p<0.05$) higher in the pristine site (FI= 1.41±0.05) than in the deforested site (1.36±0.04).

3.3. Lignin phenols content

- Total yield

All the lignin phenols measured in the samples are presented in Table 2. The total yield (λ8) is the sum of ΣC+ΣS+ΣV (detail ΣC+ΣS+ΣV). Higher yields were measured in vegetation and peat samples than in DOM. A significant (Kruskall Wallis test, $\alpha < 0.05$) increase in total lignin yield was observed in peat in the deforested site (λ8 =9.55±4.7 mg.100mg OC^{-1}) compared to the pristine site (λ8 =5.40±2.11 mg.100mg OC^{-1}). This increase was also observed in the dissolved phase (λ8 =1.16±0.35 mg.100mg OC^{-1}) in the pristine site and λ8 =1.51±0.51 mg.10mg dw^{-1} in the deforested site).

- S:V vs C:V

The cinnamyl:vanillyl (C:V) and syringyl:vanillyl phenol (S:V) ratios showed very distinct values for different vegetation types (Figure 4). *Pandanus* leaves showed high S:V ratio (>1) but low C:V ratio (<0.03). On the contrary, fern samples showed very low S:V ratio (<0.2) but higher C:V ratio in leaves (>0.2). The *Shorea* samples showed intermediate S:V ratio (0.6 to 1.4) and higher C:V ratios in leaves than in wood samples (0.34 vs. 0.004). The S:V (from 0.3 to 1.2) and C:V (from 0.3 to 1.2) ratio measured in the peat and DOM at both sites were close to measurements in *Shorea albida* wood. The S:V and C:V ratios were significantly correlated in DOM samples (S:V=-0.065C.V-0.024, n=13, r^2=0.67, p<0.001). No relationship was observed in the peat samples.

- (Ad/Al)V vs (Ad/Al)S

Vanillic acid to vanillin ((Ad/Al)V) and syringic acid to syringaldehyde ((Ad/Al)S) values increased from vegetation to peat and DOM (Figure 6). Measured ratio in *Shorea* and *Pandanus* samples showed similar values ((Ad/Al)S= 0.40±0.01 and

312 (Ad/Al)V=0.40±0.10). Ratios in peat samples ranged from 0.4 to 1 for (Ad/Al)V and 0.4
313 to 0.8 for (Ad/Al)S . The values were linearly correlated in peat samples
314 ((Ad/Al)V=1.3*(Ad/Al)S – 0.03, n=18, r^2=0.66, p<0.001)). The ratios (Ad/Al)S and
315 (Ad/Al)V were not correlated in DOM as they were in peat samples and their values were
316 significantly higher than in peat samples. In DOM samples, syringic acid to
317 syringaldehyde ratios ((Ad/Al)S) were similar in the pristine (1.16±0.08) and the
318 deforested site (1.18±0.05). In contrast, vanillic acid to vanillin ((Ad/Al)V) ratio was
319 significantly (α<0.001) higher in the pristine (1.42±0.12) compared to the deforested site
320 (1.05±0.15). In the river, ratios were close to those measured in porewater of both sites

321 - P:(V+S)

322 The ratio P:(V+S) was low in vegetation samples, except for the fern leaf samples
323 (P:(V+S)= 1.4), related to the very low V content measured in this sample (Figure 5).
324 This ratio greatly increased from peat samples (0.29±0.05 in the pristine site, 0.25±0.12
325 in the deforested site) to DOM samples (1.09±0.22 in the pristine site, 0.86±0.10 in the
326 deforested site, 0.8±0.02 in the river).

327 - 3,5Bd:V

328 The 3,5-dihydroxybenzoic (3.5Bd) was normalized to V content and plotted in relation to
329 P:(V+S) ratio. The 3,5Bd:V ratio value was very low in the vegetation samples (<0.15),
330 except in the *Pandanus* leaves (average value of 0.6), (Figure 5). Values in the peat were
331 also very low (0.12±0.03 in the pristine site, 0.08±0.04 in the deforested site) and
332 dramatically higher in DOM, similar to the pattern for P:(V+S). In DOM, a significantly
333 higher (Kruskall-Wallis, p<0.005) value was observed in the pristine site (3,5Bd:V =

334 1.58±0.25) than in the deforested site (3,5Bd:V = 0.92±0.18). In the river, an intermediate
335 value of 1.31±0.12 was measured.

336 4. Discussion

337 *4.1. Dissolved organic matter origin in tropical peatlands*

338 The radiocarbon ($\Delta^{14}C$) measured in porewater DOM is uniformly modern. Thus, the
339 DOM must contain a fraction of carbon incorporated during the period of enhanced
340 atmospheric ^{14}C from nuclear bomb testing and can contain only a minor component of
341 older carbon. That we find little influx of old organic carbon from upwelling groundwater
342 is not surprising because the entire peat dome experiences net recharge, with downward
343 flow from the surface. However, it is striking that DOM from our deepest 4.5m pore
344 water samples is modern because the peat at this depth is hundreds of years old (Figure
345 3). Thus, radiocarbon-young dissolved organic carbon is found in a matrix of older
346 organic peat, showing that DOM at our sites originates from above, from vegetation, litter
347 or peat leaching; not from the peat at the same depth. Export of modern DOC from
348 peatlands has been reported in boreal (Raymond et al., 2007), temperate (Evans et al.,
349 2007, Billett et al., 2012, Garnett et al., 2012) and tropical areas (Moore et al., 2013).
350 Other studies have also shown that most DOM exported from undisturbed peatlands
351 originates from the young, upper layers of peat, but disturbance by intense drainage can
352 induce the release of very old carbon, as observed in temperate (Kalbitz, 2001) and
353 tropical (Moore et al., 2013) peatlands. This has important implications for the deep
354 carbon dynamics of tropical peat. In temperate peatlands, transport of young DOM to
355 deep layers has been shown to induce microbial activity (Chasar et al., 2000) and

methanogenesis (Chanton et al. 1995; Aravena et al. 1993; Chanton et al. 2008) at depth. The consequences for tropical peatlands have yet to be evaluated. So far, measured methane emissions are low compared to the temperate and boreal peatlands, but major uncertainties remain as to the reasons (Couwenberg et al., 2009).

Stable carbon isotopic ratios measured in the vegetation (*Shorea*, *Pandanus*) samples were typical of contemporary C_3 vegetation. Stable nitrogen isotopic ratios varied much more in vegetation samples. This variability could be related to differing nitrogen fixation strategies (including atmospheric fixation, or use of organic nitrogen) developed by plants in peatlands, which are nitrogen-poor environments (Asada et al., 2005). In contrast to the deforested site, slightly lower $\delta^{13}C$ values were observed at the pristine site in peat samples compared to vegetation. In soils and peatlands, microbial decomposition of organic matter usually induces $\delta^{13}C$ enrichment (Natelhoffer and Fry, 1988; Powers and Schlesinger 2002; Boström et al., 2007). Lower observed $\delta^{13}C$ values in solid peat of the pristine site could also arise from selective enrichment of lignin in the peat because lignin is ^{13}C-depleted relative to bulk organic matter (Benner et al. 1987; Gleixner et al. 1993);.

The higher $\delta^{15}N$ value in solid peat samples at both sites compared to vegetation samples could relate to isotopic enrichment of organic matter following microbial processing of litter as suggested by numerous observations in the organic layer of soils (Natelhoffer and Fry, 1988; Kramer et al., 2003) and sphagnum peatlands (Martínez Cortizas et al., 2007).

At both sites, the $\delta^{15}N$ value for DOM was lower than for peat, and similar to vegetation (Figure 2a and 2b). The relationship between $\delta^{15}N$ and C/N values in different pools showed that increase of $\delta^{15}N$ in peat and DOM was related to the decrease of the C/N ratio, meaning that loss of carbon due to microbial transformation was related to a

379 preferential loss of ^{14}N (Malmer et Holm 1984; Kokfelt et al., 2009). The contribution of
380 throughfall and litter on DOM composition in pore water has already been highlighted in
381 mineral forests (Fillion et al., 1998; Hou et al., 2005) but not yet in peatland forests,
382 where the most obvious source of DOM is peat itself.

383 *4.2. Lignin transformation in tropical peatlands*

384 Tropical peats, mainly derived from wood (Anderson 1983) are mostly composed of
385 lignin and its biodegradation products (Durig et al., 1988; Calvert et al., 1991;Williams et
386 al. 1998). Our analysis of lignin oxidation products in vegetation, solid peat OC, as well
387 as porewater and river DOM, in a tropical peatland provides the first assessment of lignin
388 transformation in these ecosystems. The lignin yields λ8 and λ11 (λ8+∑P) quantify the
389 phenols analyzed following CuO oxidation but underestimate total lignin content
390 (Williams et al. 1998). The yields measured are in the highest range of values measured
391 in soils (reviewed by Thevenot et al., 2010), highlighting the high concentration of lignin
392 in tropical peatlands.
393 Cinnamyl:vanillyl (C:V) and syringyl:vanillyl phenol (S:V) ratios are often used as
394 indicators of vegetative origin of the lignin fraction, because ratios are distinct for several
395 large groups of plants (Hedges and Mann 1979). C:V and S:V ratios measured in the peat
396 samples were similar to those measured by Tarek et al., (2004) in a core collected from a
397 peat swamp in Java (low values of C:V < 0.2 and S:V <1.5). The variability of each of
398 these ratios in our surface samples was similar to that in the whole core. Comparison of
399 lignin phenol composition between peat and *Shorea albida* wood and leaves suggest that
400 peat is mostly composed of wood, but can contain some pandan. In sphagnum-dominated

401 temperate peatlands, (Williams et al. 1998) and (Williams and Yavitt, 2003) report
402 similar S:V values but higher C:V values (up to 0.38±0.4), in accordance with the higher
403 content in non-woody lignin.
404 Numerous lignin phenol ratios can be used to assess the extent of lignin transformation.
405 Microbial lignin transformation mainly consists of demethylation of the aromatic phenol.
406 Demethylation therefore reduces the yield of methoxylated phenols (vanillyl and syringyl
407 phenols) but does not affect the yields of phenols without methoxyl groups (*p*-hydroxyl
408 phenols). Therefore, the ratio P:(V+S) can be an indicator of lignin transformation by
409 microorganisms (Dittmar et Kattner, 2003). Photodegradation of DOM can also lead to
410 an increase of the P:(V+S) ratio because higher decay rates have been observed for V and
411 S phenols compared to P phenols (Benner and Kaiser, 2011). The origins of benzene
412 carboxylic acids like 3,5-dihydroxybenzoic acid (3,5Bd) are diverse in terrestrial
413 environments. The main source in soils is lignin phenol transformation, although they
414 may also originate from tannins and flavonoids (Dickens et al., 2007). The ratio 3,5Bd/V
415 is used as an indicator of lignin transformation in various environments (Houel et al.,
416 2006, Amon et al., 2012). The acid to aldehyde ratios of vanillin and syringyl phenols are
417 also transformation indicators because they increase as a result of propyl side chain
418 oxidation (Ertel et Hedges, 1984), although these ratio can increase from litter to DOM
419 during solubilization. The values of the indicators of lignin transformation ((P:(V+S),
420 3,5Bd:V) did not vary greatly between vegetation and solid peat samples. The (Ad/Al)V
421 and (Ad/Al)S ratios were only slightly higher in peat than in vegetation. This indicated
422 only a limited transformation of lignin from litter to peat or leaching from litter. Similar
423 conservation of lignin structure has been observed for the whole peat column by Tarek et

al. (2004). In DOM, a substantial decrease in lignin yield (λ8) was observed, as well as a consistent increase in all indicators of lignin transformation (P:(V+S), 3,5Bd:V, (Ad/Al)V, (Ad/Al)S)), (Figure 5 and 6), compared to the solid peat and vegetation at the both sites. They all indicate fungal (mostly white rot fungi) and bacterial degradation (Hedges et al 1988, Goñi et al. 1993, Opsahl et Benner 1995) as well as photodegradation (Benner and Kaiser, 2011) of lignin of DOM in the surface layers. Together, these indicators of more advanced decomposition of DOM demonstrate that transformation of lignin can occur much faster in porewater than in solid peat. Whereas in the solid peat lignin is preserved for centuries and millennia (Tareq et al., 2004), it is transformed in the dissolved phase within years. The transformation might happen mostly at the very surface of the peat (both photo-oxidation and microbial degradation), because the O_2 content decreases sharply in the porewater below 10 cm (Gandois et al., 2013). Lignin, usually considered as one of the most refractory compounds of organic matter can be decomposed quickly in the vadose zone. The transformed lignin is then likely advected downwards in the porewater. The conditions for accumulation of tropical peatland are not only the high content of lignin (Yule et Gomez 2009), but the environmental factors, including anoxia, and to a lesser extent darkness and low pH.

4.3. Link between optical, bulk isotopic and molecular properties of DOM

Optical properties of DOM are useful for assessing its composition. Easy to perform and non-destructive, these analyses have been performed at ecosystem (Yamashita et al., 2010) and country (Butman et al. 2012) scales. Here we have combined the optical approach with more expensive and labor-intensive isotopic and molecular analyses to

446 assess their potential for providing detailed information on DOM (Tfaily et al. 2013).
447 Here, in this homogenous ecosystem, we observed that optical properties of DOM were
448 related to molecular properties, which greatly expands the potential usefulness of
449 fluorescence measurement of DOM. Although lignin analysis and optical properties refer
450 to different fractions of DOM, lignin composition can be reconstructed based on
451 fluorescence spectra (Hernes et al. 2009). We observed a significant correlation between
452 the C:V and S:V ratio and the fluorescence index (Figure 7a). The correlation indicated
453 that lower C:V and S:V ratios in the lignin fraction of DOM were related to DOM
454 containing more carbon of terrestrial origin, as indicated by lower FI (McKnight et al.,
455 2001; Yamashita et al., 2010). The radiocarbon content of DOM in pore and river water
456 was also related to its optical properties in our samples: Δ^{14}C-DOM showed a significant
457 negative relationship with FI (Figure 7b) and a significant (r^2=0.37, $p<0.01$, n=11)
458 positive relationship with $SUVA_{280}$. The higher values of Δ^{14}C, indicating lower
459 residence time of DOM were related to lower fluorescence index and higher $SUVA_{280}$
460 values, indicating less microbial processing of DOM and higher aromaticity. Correlation
461 between DOM radiocarbon content and water optical properties was also reported by
462 Sanderman et al., (2009) in a coastal watershed of California and by Butman et al., (2012)
463 in American rivers not draining peatlands.

464 *4.4. Impact of logging activity on OM fate*

465 Logging activity can be expected to modify organic matter transformations in peatlands.
466 The induced change in hydrology, change in litter quality and addition of extra litter
467 (forestry residues) can influence organic matter cycling. In the present case of

deforestation without engineered drainage, an initial study suggested an increase in peat decomposition in some areas of the deforested site based on the observed increase of the elemental N, S content and change in the OC properties of peat (Gandois et al., 2013). A wider range of $\delta^{15}N$ values was found in the peat samples at the deforested site (Table 1). The increase of $\delta^{15}N$ in relation to the increase of N content confirmed the hypothesis that the increase of N content was related to an increase microbial decomposition of the peat at the deforested site.

Higher lignin yields (λ8) were measured in both peat (+75%) and DOM (+40%) samples in the deforested site compared to the pristine site (Table 2). These higher lignin yields suggested an additional source of lignin at the deforested site: this could reflect the addition of the logging residues to the peat surface (the highest lignin yield has been measured in the *Shorea* wood samples). In the solid peat samples, no significant difference appeared for the lignin diagenesis indicators between the two sites. If a significant amount of lignin has been added at the deforested site, it has not been transformed to a greater extent than at the pristine site. In contrast, significant differences were observed for both bulk ($\Delta^{14}C$, fluorescence index) and lignin fractions (3,5Bd:V, (Ad/Al)V) of DOM between pristine and deforested sites. A significantly higher DOC concentration at the deforested site was observed (Gandois et al., 2013). The higher $\Delta^{14}C$ content of DOM at the deforested site clearly indicated that logging activity has introduced a new DOM source in the peatland porewater. The lower FI indicated less microbial transformation of DOM (McKnight et al. 2001), in agreement with the increased lignin yield. The lignin decomposition indicators were all consistent with a less

transformed lignin fraction of DOM at the deforested site, suggesting an input of extra litter that has not reached the characteristic decomposition status of the pristine site.

5. Conclusions

Based on a combination of analytical tools (stable and radiogenic isotopes, lignin biomarkers, optical properties) on both solid and dissolved organic matter in tropical peatlands, this study demonstrates that composition of DOM differs from that of solid organic matter, as indicated by $\delta^{15}N$, $\Delta^{14}C$ and lignin biomarkers. DOM originates to a great extent from living vegetation or litter. Dissolved organic matter is quickly transformed near the peat surface in the upper layer of peat and then advected to deep layers, becoming a source of young carbon deep in the peat. Our study has focused on lignin composition and has demonstrated that lignin is rapidly transformed in the upper layer porewater. Logging activity induced an extra input of lignin in both solid and dissolved phase in the deforested site. DOM composition reflects the change of litter input and organic matter evolution in the deforested site. The analysis of DOM composition is a sensitive tool to assess the impact of change of land use on organic matter cycle, since dissolved organic matter in tropical peatlands is more quickly modified in quantity and composition by changes of land use than is solid organic matter

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692 8. Captions

693 Table 1. Bulk analysis of solid and dissolved organic matter. Mean (min/max) values
694 Table 2. CuO oxidation products. V, organic carbon normalized yields of the vanillyl
695 phenols (Vl, vanillin; Vn, acetovanillone; Vd, vanillic acid); S, organic carbon
696 normalized yields of the syringyl phenols (Sl, syringealdehyde; Sn, acetosyringone; Sd,
697 syringic acid); C, organic carbon normalized yields of the cinnamyl phenols (p-Cd, p-
698 coumaric acid; Fd: ferulic acid); P, carbon normalized yields of p-hydroxyphenols (Pl, p-
699 hydroxybenzaldehyde; Pn, p-hydroxyacetophenone; Pd, p-hydroxybenzoic acid); 3,5Bd,
700 3,5-dihydroxybenzoic acid. All the content are expressed in mg 100 mg OC^{-1}. Mean
701 (min/max) values are indicated.
702

703 Figure 1: Map of Borneo Island, Brunei Darussalam and the study area (Ulu Mendaram
704 Conservation Area). Study sites are two domes, located on both sides of the Mendaram
705 river.

706 Figure 2: (a) $\delta^{13}C$ (‰) content of vegetation, peat and DOM samples of porewater and
707 river water. (b): $\delta^{15}N$ (‰) in relation to C/N ratio of solid and dissolved organic matter.

708 Figure 3: $\delta^{14}C$ (‰) content versus depth for peat cores and DOM samples.

709 Figure 4: S:V vs C:V content of vegetation, peat and DOM samples of porewater and
710 river water.

711 Figure 5: P:(V+S) vs 3,5Bd:V content of vegetation, peat and DOM samples of porewater
712 and river water.

713 Figure 6: (Ad/Al)V vs (Ad/Al)S content of vegetation, peat and DOM samples of
714 porewater and river water.

715 Figure 7: C:V (a) and $\Delta^{14}C$ (b) relationship with fluorescence index.

716 Table 1. Bulk analysis of solid and dissolved organic matter. Mean (min/max) values.

717

Nom	n	C (%)	N (%)	$\delta^{13}C$ (‰)	$\delta^{15}N$ (‰)	$\Delta^{14}C$ (‰)	DOC (mg L^{-1})	$SUVA_{280}$ (L m^{-1}·mg C^{-1})	SUVA350	FI -
DOM_River_Pristine	2	42.4(41.7/43.1)	1.08(1.06/1.11)	-29.66(-29.7/-29.62)	-2.37(-3.35/-1.39)	68.28 (62.73-73.84)	37.4 (37.3-37.4)	4.48(4.42/4.53)		1.50(1.50/1.49)
DOM_River_Deforested	1	31.3	0.84	-29.69	-7.5		26.7	4.00		1.62
DOM _ Pristine	5	41.8(40.7/43.14)	0.90(0.67/1.04)	-29.9(-30.08/-29.47)	-4.18(-7.4/-0.79)	74.58 (70.87-77.22)	66.1 (59.7 -81.4)	4.28(3.43/4.63)		1.41(1.39/1.46)
DOM_deforested	7	44.5(40.2/47.27)	0,10(0.6/1.19)	30.18(-30.50/-29.84)	-4.13(-8.3/-1.3)	87.84 (83.77-94.4)	74.9 (73.5-79.4)	5,16(4.38/5.99)		1.36(1.33/1.43)
Shorea	3	50.6(49.5/52.7)	0.98(0.4/1.38)	-29.69(-29.82/-29.59)	-6(-7.88/-3.1)					
Pandan	2	47.35(47.3/47.52)	1.12(0.7/1.2)	-29.67(-29.69/-29.66)	-1.82(-7.46/-1.46)					
Fern	2	43.34(43.1/43.53)	2.67(2.6/3.18)	-30.87(-31/-30.75)	-5.31(-5.31/-4.91)					
Peat_pristine	9	52.4(49.6/55.5)	1.95(1.68/2.18)	30.49(-32.32/-29.79)	0.92(-1.72/-0.22)					
Peat_deforested	9	50.95(48.1/55.5)	2.09(1.33/2.72)	29.48(-30.65/-28.32)	1.22(-2.74/0.91)					

718 Table 2 . CuO oxidation products. Mean (min/max) values. ΣS = syringealdehyde (Sl)+ acetosyrigon (Sn) + syringic acid (Sd); ΣV=
719 vanillin (Vl) + acetovanillon (Vn) + vanillic acid (Vd); ΣC= coumaric acid, (p-Cd) + ferulic acid (Fd); ΣP= p-hydroxybenzaldehyde
720 (Pl)+ p-hydroxyacetophenon (Pn)+p-hydroxybenzoic acid (Pd). 3,5Bd= 3,5-dihydroxybenzoic acid (3,5Bd). (Ad/Al)S = syringic acid/
721 syringealdehyde, (Ad/Al)V= vanillic acid/ vanillin.

Nom	n	λ8	ΣS	ΣV	ΣC	ΣP	3-5Bd:V	(Ad/Al)S	(Ad/Al)V
		mg 100mgOC^{-1}	mg.100mgOC^{-1}	mg.100mgOC^{-1}	mg.100mgOC^{-1}	mg.100mgOC^{-1}			
DOM_River_Pristine	2	1.25(0.96/1.53)	0.6(0.4/0.8)	0.5(0.4/0.6)	0.031(0.02/0.04)	0.9(0.69/1.13)	1.343(1.24/1.44)	0.91(0.70/1.12)	1.6(1.57/1.64)
DOM_River_Deforested	1	1.63	0.9	0.6	0.04	1.28	1.26	1.48	0.95
DOM _ Pristine	5	1.16(0.80/1.50)	0.6(0.3/0.8)	0.5(0.3/0.6)	0.019(0.01/0.05)	1.14(1.05/1.3)	1.58(1.31/1.98)	1.16(0.82/1.5)	1.42(1.13/1.65)
DOM_Deforested	7	1.51(0.65/1.99)	0.7(0.2/0.8)	0.8(0.3/1.2)	0.03(0.01/0.03)	1.22(0.74/1.80)	0,92(0.75/1.17)	1.18(1.07/1.27)	1.05(0.86/1.17)
Shorea	3	10.70(8.18/12.48)	4.6(4.1/5)	5.6(3/7.7)	0.44(0.03/1.0)	0.96(0.14/1.85)	0.049(0.01/0.11)	0.39(0.38/0.41)	0.45(0.36/0.62)
Pandanus	2	9.15(8.11/10.18)	5.1(4.6/5.1)	3.9(3.9/5)	0.067(0.05/0.08)	0.29(0.27/0.31)	0.66(0.58/0.74)	0.41(0.41/0.42)	0.39(0.36/0.42)
Fern	2	3.55(0.96/6.14)	0.1(0.1/0.1)	3.3(0.6/6)	0.102(0.1/0.1)	0.80(0.8/1.1)	0.09(0.03/0.15)	1.1(1.05/1.15)	0.42(0.42/0.45)
Peat_pristine	9	5.40(4.04/10.49)	2.2(1.1/5.7)	3(2.1/4.5)	0.17(0.01/0.31)	1.55(0.84/3.56)	0.12(0.07/0.19)	0.57(0.43/0.69)	0.74(0.54/1)
Peat_deforested	9	9.55(4.60/18.97)	4.2(1.4/9.6)	5.1(2.5/9)	0.23(0.15/0.54)	2.18(0.77/4.05)	0.08(0.03/0.16)	0.55(0.43/0.72)	0.66(0.52/0.85)

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723

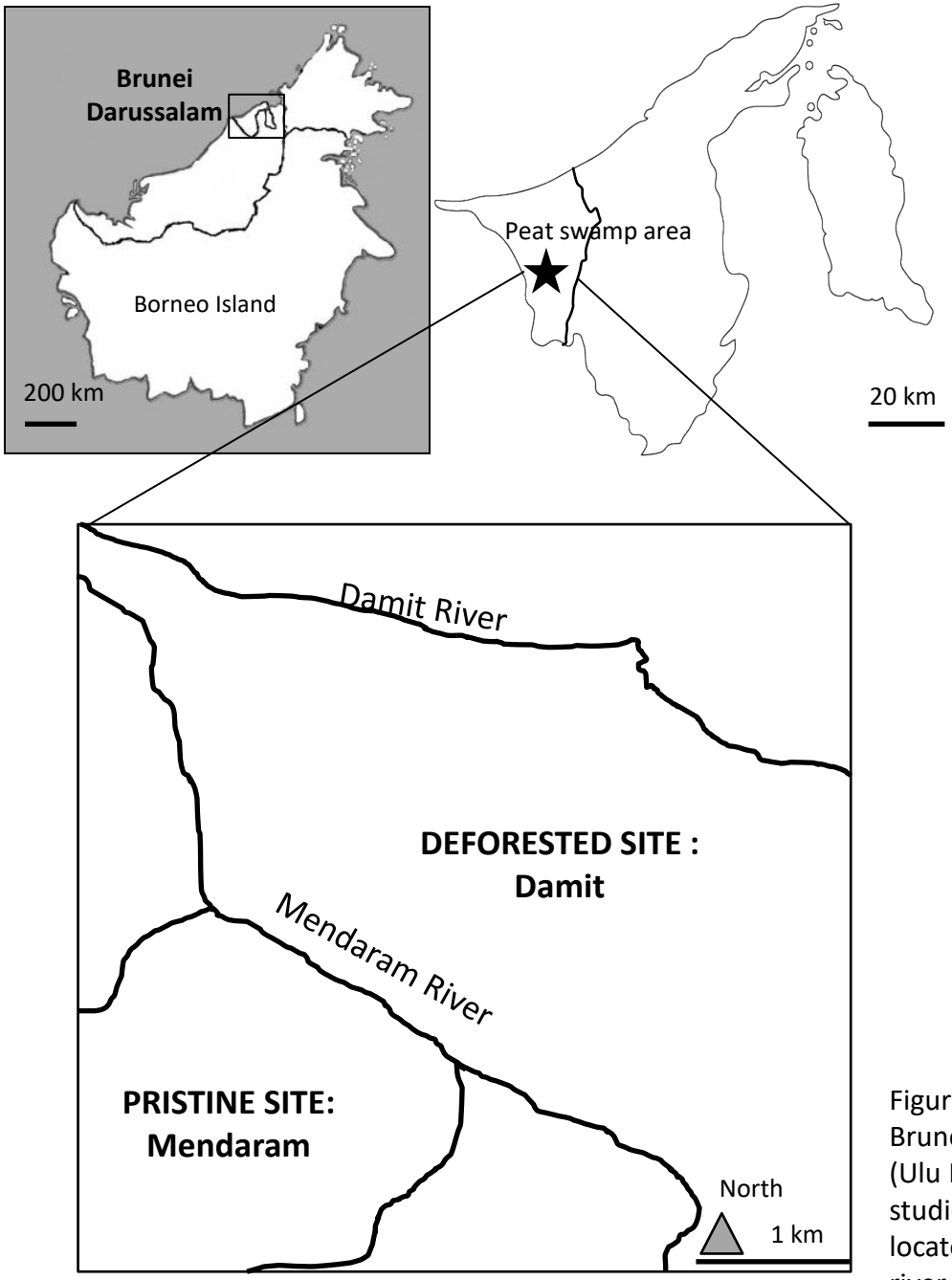


Figure 1: Map of the Borneo Island, Brunei Darussalam and the studied area (Ulu Mendaram conservation area). The studied sites are two peat domes, located on both sides of the Mendaram river.

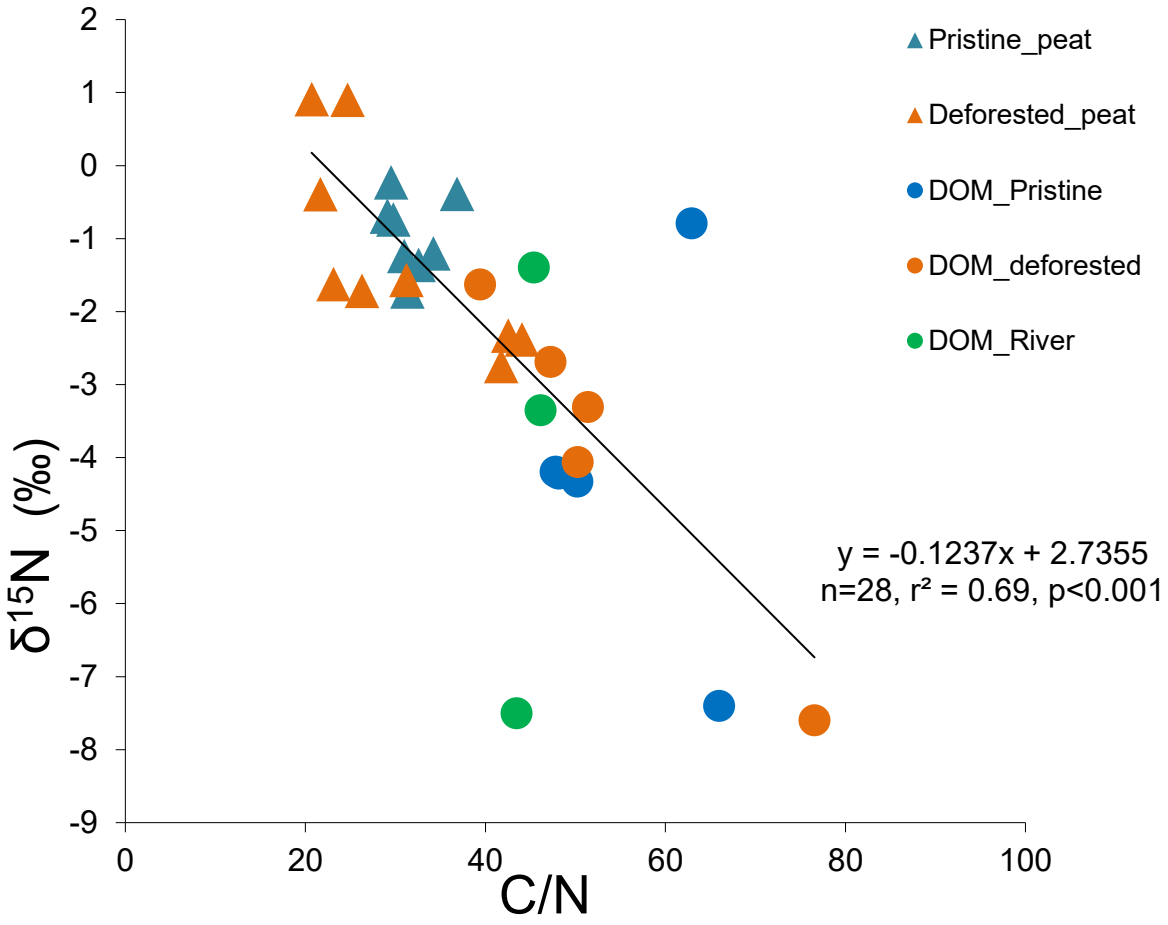


Figure 2: $\delta^{15}N$ (‰) in relation to C/N ratio of solid (peat) and dissolved organic matter (DOM).

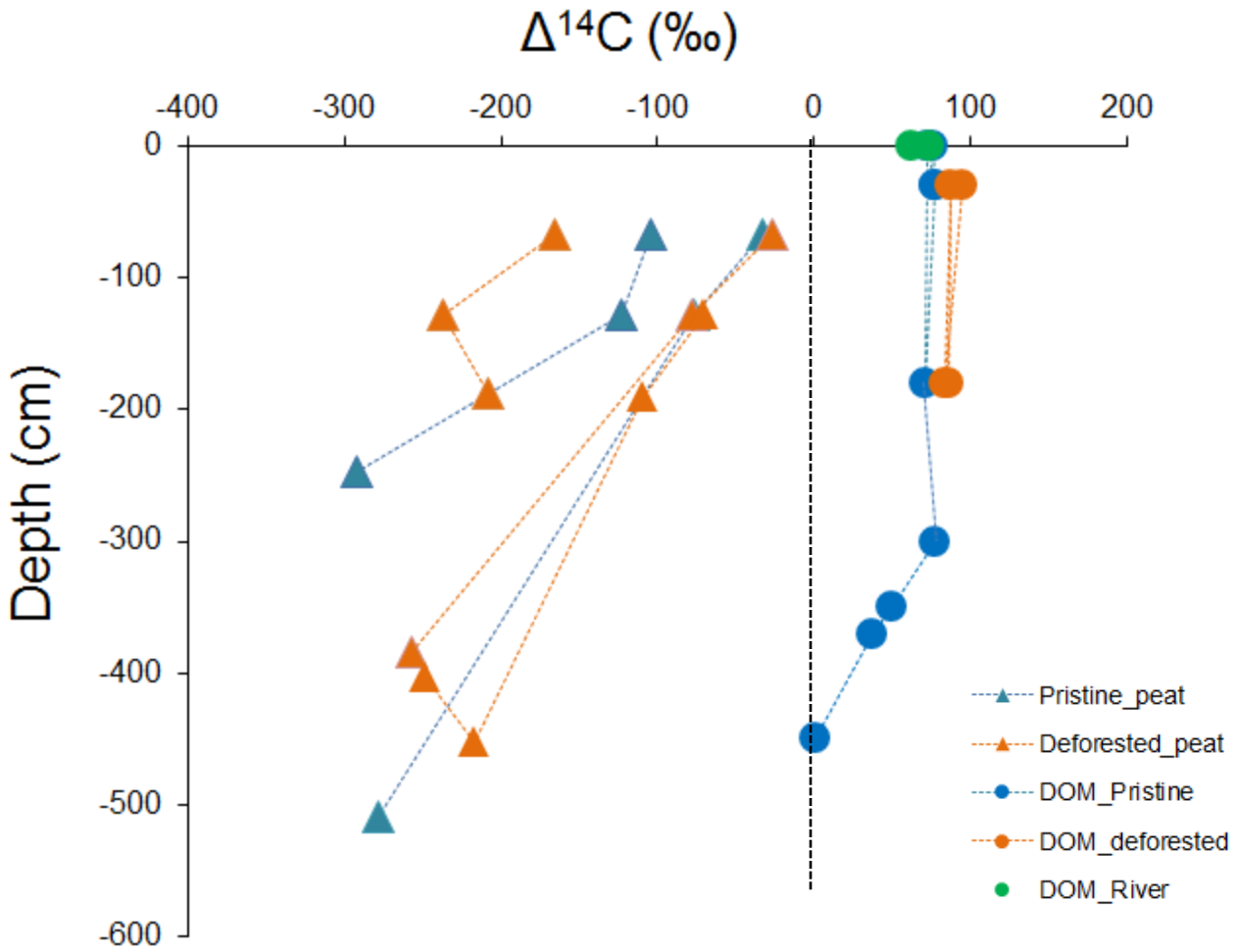


Figure 3: $\Delta^{14}C$ (‰) content versus depth for peat cores and DOM samples. Positive values indicate Modern DOM.

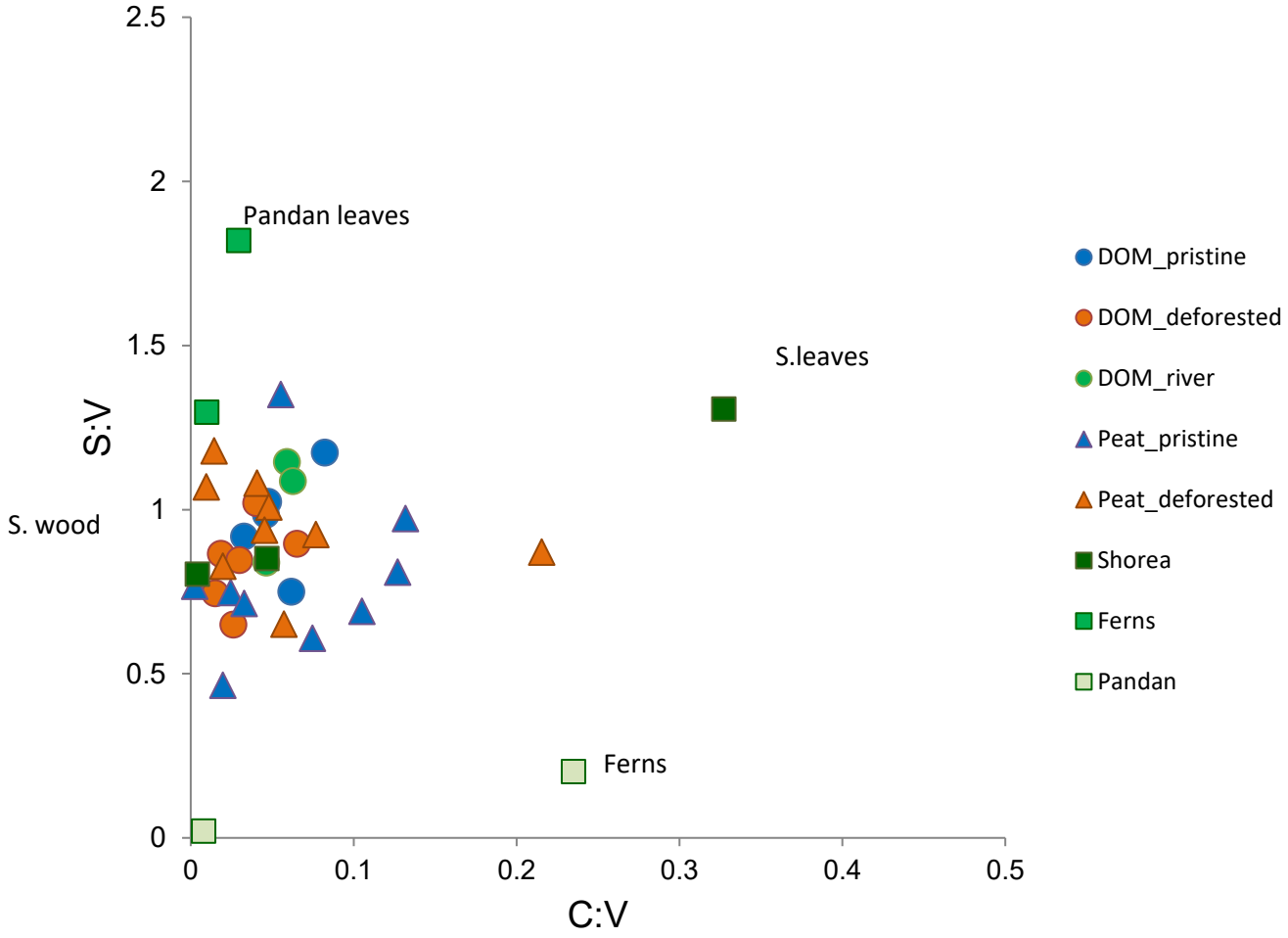
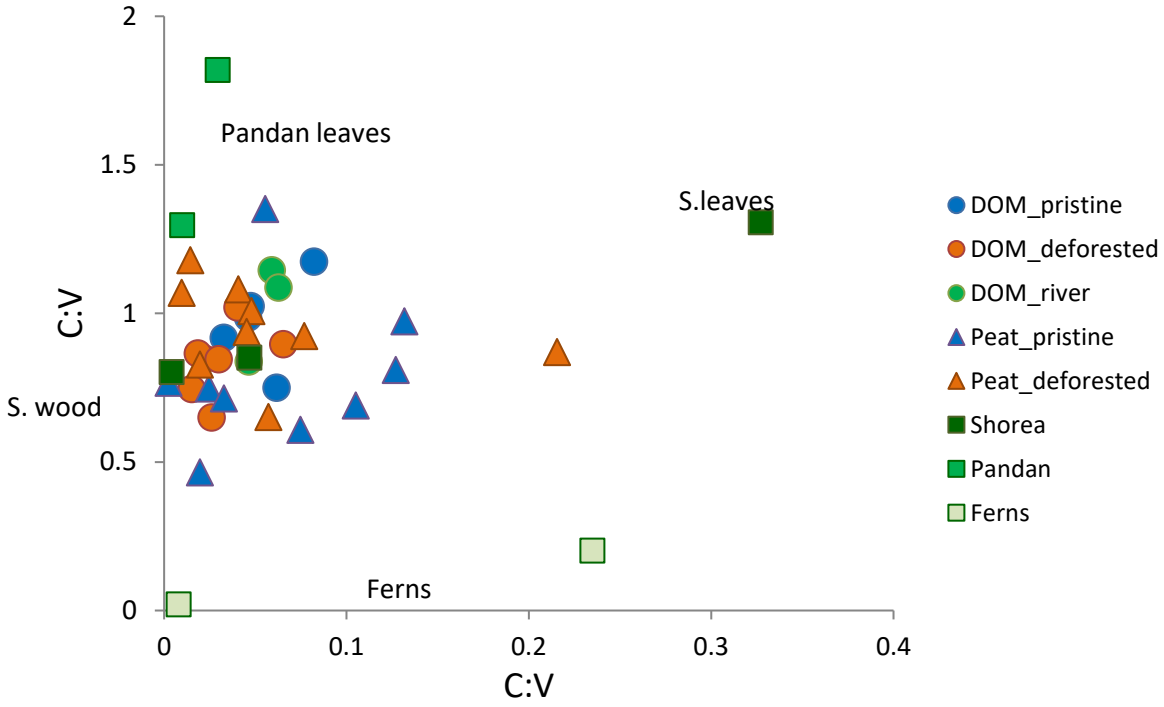


Figure 4a: S/V vs C/V content of vegetation, peat and DOM samples of pore water and river water.



OR : Figure 4a: S/V vs C/V content of vegetation, peat and DOM samples of pore water and river water.

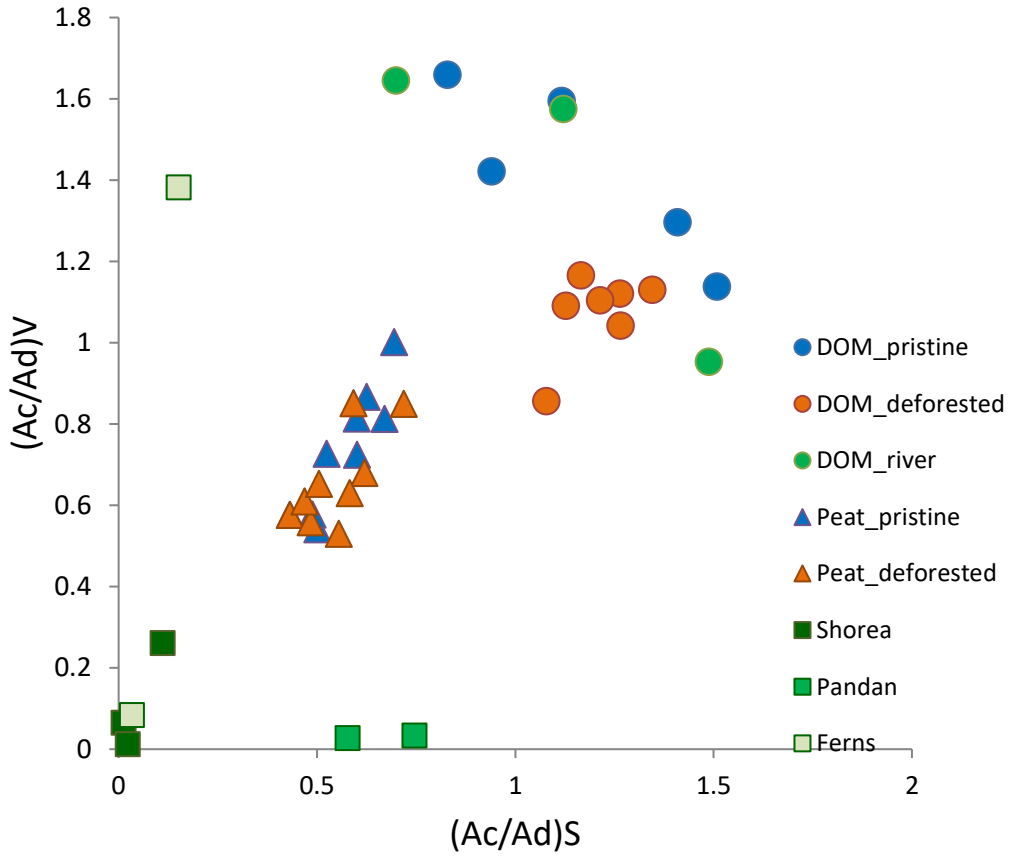


Figure 4c: (Ac/Ad)V vs (Ac/Ad)S content of vegetation, peat and DOM samples of pore water and river water.

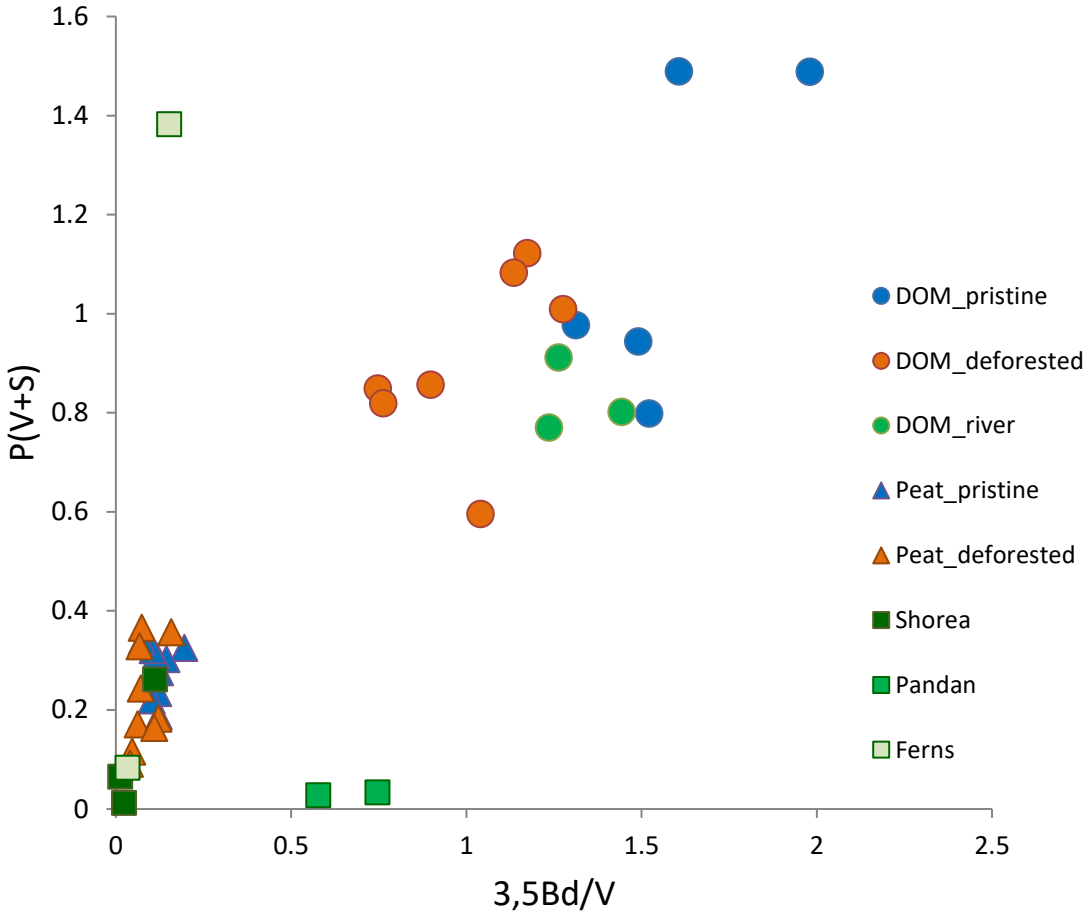
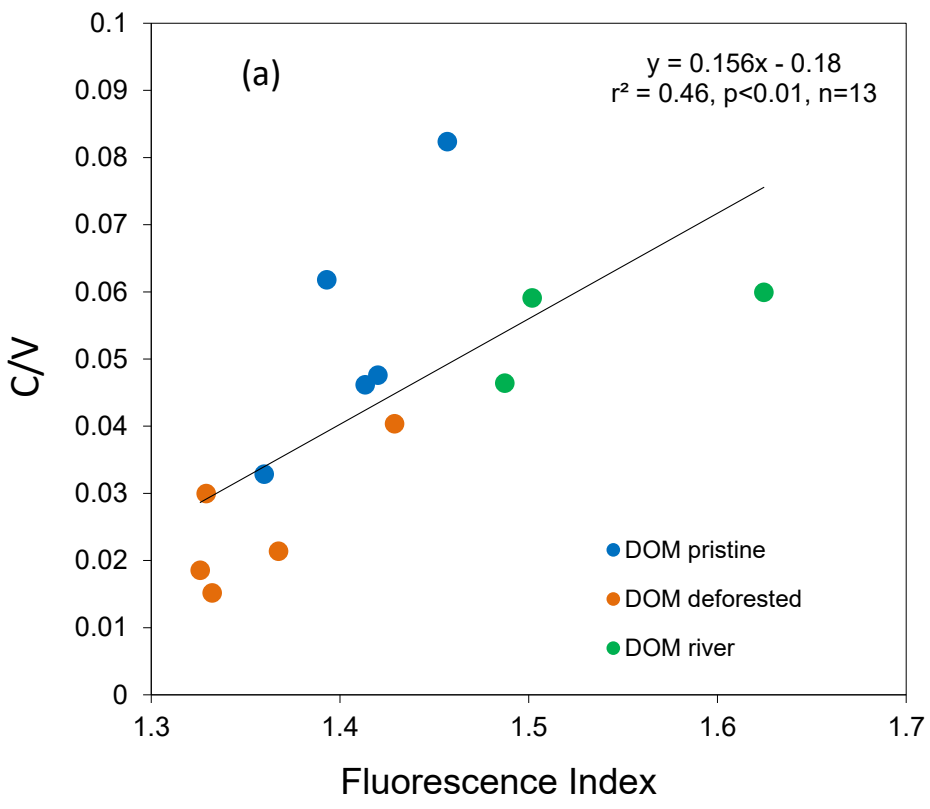


Figure 4b: P/(V+S) vs 3,5Bd/V content of vegetation, peat and DOM samples of pore water and river water.



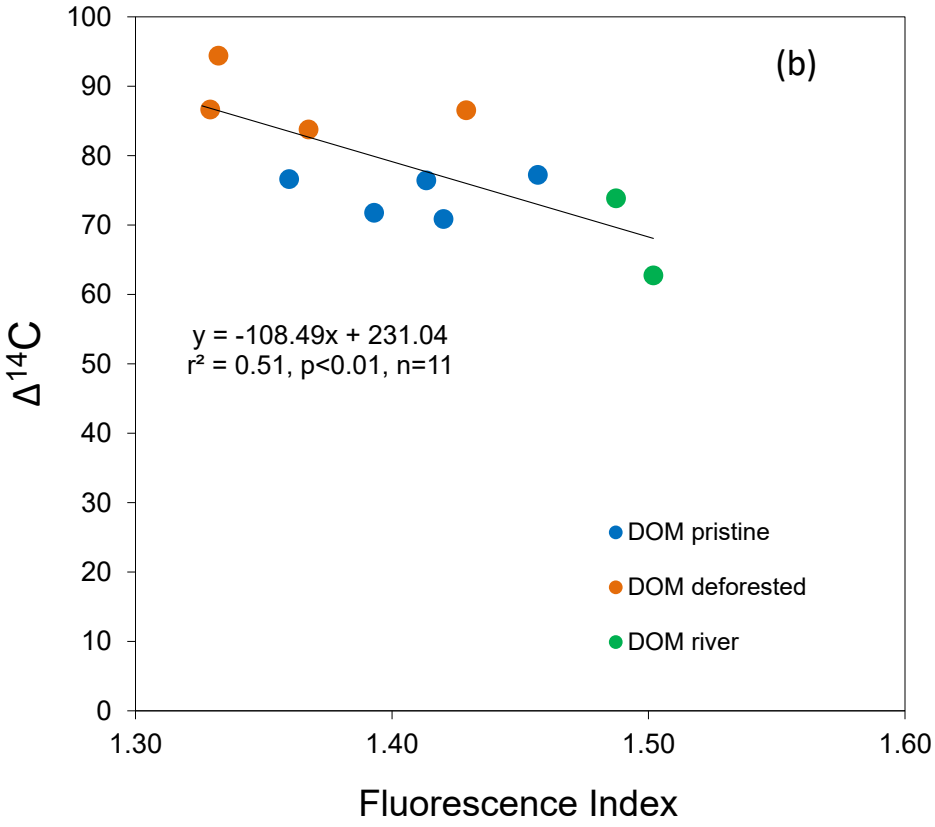


Figure 5: C/V (a) and $\Delta^{14}C$ (b) relationship with fluorescence index.