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► **To cite this version:**

Laure Gandois, Alison May Hoyt, Stéphane Mounier, Gaël Le Roux, Charles Franklin Harvey, et al.. From Canals to the Coast: Dissolved Organic Matter and Trace Metal Composition in Rivers Draining Degraded Tropical Peatlands in Indonesia. *Biogeosciences*, 2020, 17 (7), pp.1897-1909. 10.5194/bg-17-1897-2020 . hal-02536749

HAL Id: hal-02536749

<https://hal.science/hal-02536749>

Submitted on 8 Apr 2020

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1 From Canals to the Coast: Dissolved Organic Matter and Trace 2 Metal Composition in Rivers Draining Degraded Tropical 3 Peatlands in Indonesia

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16 **Abstract.** Worldwide, peatlands are important sources of dissolved organic matter (DOM) and trace metals (TM) to
17 surface waters and these fluxes may increase with peatland degradation. In Southeast Asia, tropical peatlands are being
18 rapidly deforested and drained. The black rivers draining these peatland areas have high concentrations of DOM, and
19 the potential to be hotspots for CO₂ release. However, the fate of this fluvial carbon export is uncertain, and its role as
20 a trace metal carrier has never been investigated. This work aims to address these gaps in our understanding of tropical
21 peatland DOM and associated elements in the context of degraded tropical peatlands of Indonesian Borneo. We
22 quantified dissolved organic carbon and trace metals concentrations in the dissolved and fine colloidal (<0.22µm) and
23 coarse colloidal (0.22 – 2.7 µm) fractions and characterized the characteristics (δ¹³C, Absorbance, Fluorescence
24 :excitation-emission matrix and PARAFAC analysis) of the peatland-derived DOM as it drains from peatland canals,
25 flows along the blackwater Ambawang River, and eventually mixes with Kapuas Kecil River before meeting the ocean
26 near the city of Pontianak in West Kalimantan, Indonesia. We observe downstream shifts in indicators of in-stream
27 processing. The increase in the δ¹³C of DOC, along with an increase in the C1/C2 ratio of PARAFAC fluorophores,
28 and decrease in SUVA (Specific UV Absorbance) along the continuum suggest the predominance pf photo-oxidation.
29 However, we also observe very low dissolved oxygen concentrations, suggesting that oxygen is quickly consumed by
30 microbial degradation of DOM in the shallow layers of water. Black rivers draining degraded peatlands show
31 significantly higher concentrations of Al, Fe, Pb, As, Ni, and Cd. A strong association is observed between DOM, Fe,
32 As, Cd and Zn in the dissolved and fine colloid fraction, while Al is associated to Pb and Ni and present in a higher
33 proportion in the coarse colloidal fraction. We additionally measure the isotopic composition of lead released from

34 degraded tropical peatlands for the first time and show that Pb originates from anthropogenic atmospheric deposition.
35 Degraded tropical peatlands are important sources of DOM and trace metals to rivers and a secondary source of
36 atmospherically deposited contaminants.

37 **Keywords:** Tropical peatlands, Dissolved Organic Matter, Absorbance, Fluorescence, PARAFAC, Stable isotopes,
38 Trace metal, Lead isotopes

39 **1. Introduction**

40 Most Southeast Asian tropical peatlands developed as domes beneath ombrotrophic peat swamp forests (Page et al.,
41 2006; Cobb et al. 2017). They store at least 68.5 Pg C, or 15-19% of the global peat carbon stocks (Page et al., 2011;
42 Dargie et al., 2017; Lahteenoja et al., 2012). They have experienced widespread degradation as a result of deforestation,
43 conversion to agriculture and drainage, which all accelerated in the late 1970s (Miettinen et al., 2011). This abrupt
44 change in land use, and corresponding lowering of the water table, has led to subsidence and a massive release of
45 carbon from peatlands to the atmosphere due to enhanced aerobic decomposition of organic matter from the drained
46 peat. Extensive work has focused on quantifying the resulting CO₂ fluxes (Couwenberg et al., 2010; Jauhiainen et al.,
47 2012; Miettinen et al., 2017) and land surface subsidence (e.g. (Hooijer et al., 2012; Carlson et al., 2015).

48 Drainage canals are dug in forested peatlands for multiple reasons: first, as a mechanism to transport timber out of the
49 peatland during deforestation, and later to lower the water table, making the land suitable for agriculture. These
50 peatland drainage canals channel water from the peatlands to surrounding surface waters. The resulting fluvial export
51 of dissolved organic matter (DOM) has been recognized as a significant component of the carbon budget of tropical
52 peatlands, that could increase with deforestation and peatland exploitation (Moore et al. 2011; Gandois et al. 2013).
53 Indonesia alone contributes over 10% of the global riverine dissolved organic carbon (DOC) input into the ocean
54 (Baum et al., 2007), as a result of both high peatland coverage and high precipitation rates. This proportion is likely to
55 increase with rapid peatland conversion to agriculture, which destabilizes long-term peat C stocks (Moore et al., 2013).

56 Another implication of DOM transfers from peatlands to surface water is the transport of associated elements,
57 especially trace metals (TM). Tropical peatlands in Southeast Asia are mainly ombrotrophic systems, which receive
58 critical nutrients through atmospheric deposition, and serve as a sink for atmospheric pollutants (Weiss et al., 2002).
59 Northern peatlands have been shown to constitute a source of major and trace elements to surface waters (J. J. Rothwell
60 et al. 2007; Tanja Broder and Biester 2017; Jeremiason et al. 2018). This has important implication : as a result of
61 colloidal association between peatland-derived organic molecules and Fe, northern peatlands are responsible for a
62 significant transfer of Fe to the Atlantic Ocean (Krachler et al. 2010, 2012). In the UK, peat degradation and erosion
63 has led to the dispersion of lead into watersheds, which previously accumulated through atmospheric deposition over
64 decades (Rothwell et al., 2008). Although drainage of tropical peatlands is occurring at a rapid rate across Southeast
65 Asia, to our knowledge no data are available on trace metal release in black rivers draining tropical peatlands.

66 Black rivers draining peatlands (as defined in Alkhatib et al (2007)) also have the potential to be hotspots of fluvial
67 carbon degassing (Müller et al., 2015; Wit et al., 2015). By measuring pCO₂ in Indonesian and Malaysian black rivers,
68 Wit et al. (2015) estimated that 53% of DOC entering surface waters was converted to CO₂, which is similar to global
69 averages for inland waters. In contrast, blackwater river measurements and incubations by Martin et al., (2018) found
70 a smaller proportion of DOC was processed in rivers. Rixen et al., (2008) also found a large proportion of the DOM
71 was resistant to decomposition in a laboratory incubation study. These studies have focused on CO₂ measurements and
72 incubations to assess the potential for DOM processing.

73 Monitoring changes in DOM composition in canals and rivers can provide complementary information on the extent
74 of in-stream processing of fluvial carbon, and potential reemission of greenhouse gas (GHG) to the atmosphere.
75 Qualitative evaluation of in-stream DOM transformation by UV light and microbial processes can be performed using
76 isotopic and optical characterization of DOM. The stable isotope signature of DOM is an indicator of its origin (Hood
77 et al., 2005; Barber et al., 2017), but also transformation processes. Lalonde et al (2014) assessed photochemical
78 processing of DOM in major large rivers worldwide, and found that it caused an increase in the δ¹³C of DOM of 0.5
79 to 2.3%. However, microbial processing is also expected to lead to an increase in the δ¹³C of DOM. Optical properties
80 of DOM are also sensitive indicators for DOM processing (Spencer et al. 2009; Harun et al. 2015; Hansen et al. 2016),
81 with contrasted effects on optical properties. Microbial processing is generally found to increase the aromaticity of
82 DOM by selective processing of less aromatic molecules, while photo-oxidation tends to decrease aromaticity, because
83 of selective photo-oxidation of aromatic moieties (Spencer et al., 2009; Hansen et al., 2016).

84 In summary, although there has been an increase in efforts to quantify DOC exports from tropical peatlands, our
85 complementary understanding of the transfer of associated elements and in-stream processing of DOM remains limited.
86 This work aims to address these gaps in our understanding of the composition and evolution of tropical peatland DOM
87 and how it could act as a carrier of trace metals to surface waters, in the context of highly degraded tropical peatlands
88 of Indonesia. We characterize the quality of the peatland-derived DOM and trace metals as they drain from peatland
89 canals, flow along blackwater rivers, and eventually mix with a whitewater river before meeting the ocean. We assess
90 spatial and seasonal changes in the organic matter quality, and document changes in DOM composition due to
91 transport, mixing, and processing. We also assess black river trace metal release to surface waters, analyzing trace
92 metal concentrations and the isotopic composition of lead released from degraded tropical peatlands for the first time.

93 **2. Material and methods**

94 **2.1 Study area**

95 The study area is located in West Kalimantan, Indonesia, near the city of Pontianak (0.09°N, 109.24°E) on the island
96 of Borneo. The climate is humid equatorial with 3041±532mm of rainfall and a mean annual temperature of 27°C
97 (1985-2017 data). The study focused on the Ambawang River, which flows into the Landak and Kapuas Kecil rivers.
98 It is a black river draining a watershed (approximately 706 km²) entirely covered with peatlands. This river was

99 selected to represent water of exclusively peatland origin. All peatlands in the sampling area have been drained and
100 converted to agriculture.

101 **2.2 Sample collection and treatment**

102 Two sampling campaigns were conducted during the dry season in June 2013 and during the wet season in January
103 2014. Using a boat, samples were collected in the center of the river, from the origin of the Ambawang river (BR,
104 black river sites) to its downstream confluence with the Landak and Kapuas Kecil Kecil (WR, white river sites). White
105 river samples collected upstream of the confluence with the white river (WRu). Drainage canals (DC) flowing into the
106 black river were also sampled during the second sampling campaign. During the wet season campaign, a rain collector
107 was installed on the roof of the Pontianak's meteorological station to collect rain samples for lead isotopic analysis. In
108 situ parameters (pH, conductivity and dissolved oxygen) were measured using a multiparameter probe (WTW,
109 Germany). Depth profiles of dissolved oxygen in the black river were also measured with an oxygen microelectrode
110 (MI-730 dip-type micro-oxygen electrode and O2-ADPT adapter; Microelectrodes, Inc., Bedford, NH, USA). Frequent
111 calibration was performed with a zero oxygen solution and distilled water equilibrated to ambient oxygen
112 concentrations, where temperature was carefully monitored. To create the zero oxygen solution, 1 g of sodium sulfite
113 (Na_2SO_3) and a few crystals (~1 mg) of cobalt chloride (CoCl_2) was dissolved in 1 L of distilled water. For
114 measurements of additional parameters, a larger volume of water was collected for further analysis. Samples were
115 filtered immediately following collection on the boat using a portable peristaltic pump (Geotech, USA) and prebaked
116 and pre-weighed GF/F filters (0.7 μm) and stored in glass bottles for DOC, $\delta^{13}\text{C}$ -DOC and optical properties of DOM
117 analysis. Samples were filtered with cellulose acetate filters (0.22 μm) and stored in polypropylene vials for analysis
118 of major nutrients and trace element. DOC analysis was repeated on the cellulose acetate samples and DOC
119 concentrations did not differ significantly based on filtration at 0.2 or 0.7 μm . During the wet season, at selected sites
120 (8), samples were first filtered with GF/D filters (2.7 μm) to assess to the coarse colloidal fraction of trace metals and
121 DOC.

122 **3. Sample analysis**

123 Non-purgeable organic carbon (NPOC, referred to hereafter as DOC) was analyzed on filtered (GF/F Whatman)
124 samples after acidification to pH 2 (HCl) with a TOC-V CSH analyzer (Shimadzu, Japan), with a quantification limit
125 of 1 mg L^{-1} . Major cations and anions were analysed using an HPLC (Dionex, USA). The quantification limit was 0.5
126 mg L^{-1} for chloride, nitrate and sulphates and 0.025 mg L^{-1} for ammonium, potassium, magnesium and calcium.
127 Certified material (ion 915 and ion 96.4 Environment and Climate Change Canada, Canada) was included in the
128 analytical loop and recovery was >95% of the certified value. For trace element analysis, samples were acidified with
129 ultrapure HNO_3 prior to ICP-MS (7500 ce, Agilent Technologies) analysis. ^{115}In was used as an internal standard, and
130 SLRS-4 (River water certified for trace elements) was used as a reference material on every run and accuracy
131 (recovery>95%) was checked. Determination limits were < 0.5 $\mu\text{g g}^{-1}$ for Fe and Al, <0.05 $\mu\text{g g}^{-1}$ for Ni, Cu and Zn
132 and < 0.005 $\mu\text{g g}^{-1}$ for Cd and Pb. Pb isotope ratios ($^{206}\text{Pb}/^{207}\text{Pb}$; $^{208}\text{Pb}/^{206}\text{Pb}$) in water samples were analyzed using a

133 High Resolution ICP-MS (Thermo Element II XR; OMP service ICP-MS, Toulouse, France). Measurements were
134 corrected for mass bias using individual sample bracketing with certified and adequately diluted NIST NBS-981 (100
135 ng L⁻¹ to 500 ng L⁻¹) according to Krachler et al. (2004).

136 The UV absorption spectra of pore water were measured with a spectrophotometer (Secoman UVi-lightXT5) from 190
137 to 700 nm in a 1 cm quartz cell. The Specific UV Absorbance at 254 nm (SUVA, L mg⁻¹ m⁻¹) was calculated as follows:
138 $SUVA = A_{254} / (b * DOC)$ (Weishaar et al., 2003), where A_{254} is the sample absorbance at 254 nm (non-dimensional), b
139 is the optical path length (m) and DOC is in mg L⁻¹. The baseline was determined with ultra-pure water.

140 Emission Excitation Matrices (EEM) were acquired using a Hitachi F4500 fluorescence spectrometer. Emission
141 spectra were acquired from 250 to 550 nm for excitation ranging from 250 to 550 nm. The slits were set to 5 nm for
142 both the excitation and emission monochromators. The scan speed was 2400 nm min⁻¹ and the integration response
143 was 0.1 s. Fluorescence intensity was corrected from the excitation beam to ensure stability. The inner filter effect
144 water was taken into account using a dilution approach as developed by Luciani et al. (2009). The fluorescence index
145 was calculated as defined by McKnight et al. (2001) and Jaffé et al. (2008), by the ratio of the fluorescence intensity
146 at 470 nm to the intensity at 520 nm for a 370 nm excitation. The PARAFAC analysis (PARAllel FACtor analysis
147 (Bro, 1997)) was performed on all samples using the PROGMEEF program in Matlab (Luciani et al. 2008).

148 The isotopic composition ($\delta^{13}C$) of DOC was determined at the UC Davis Stable Isotope Facility, following the
149 described procedure (<http://stableisotopefacility.ucdavis.edu/doc.html>). Briefly, a TOC Analyzer (OI Analytical,
150 College Station, TX) is interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK)
151 utilizing a GD-100 Gas Trap Interface (Graden Instruments).

152 **4. Statistical analysis**

153 Statistical analysis was performed using the Rstudio software (Version 1.2.1335), using ggplot, dplyr, ade4 and
154 dunn.test packages. Significant differences ($p < 0.05$) between groups were evaluated using Kruskal Wallis and Dunn's
155 post hoc multiple test.

156 **5. Results**

157 **5.1. Trends in water chemistry from the source of the black river to the ocean**

158 The observed water chemistry of the Ambawang river and drainage canals is typical of black rivers draining peatlands
159 (Table 1, Figure 2), and does not show significant differences between the wet and dry seasons. It is acidic with a pH
160 of 3.2 ± 0.6 and 3.5 ± 0.3 in the drainage canals (DC) and black river (BR) respectively, has a low conductivity (DC:
161 $89.8 \pm 21.4 \mu S cm^{-1}$, BR: $85.2 \pm 21.6 \mu S cm^{-1}$), is anoxic (DC: 2.3 ± 0.3 , BR: $1.9 \pm 0.7 mg L^{-1}$), and has extremely high
162 DOC concentrations (DC: 35.2 ± 5.5 , BR: $35.8 \pm 3.4 mg L^{-1}$). The Cl concentrations are low and homogeneous (DC:
163 2.6 ± 0.7 , BR: $2.4 \pm 0.6 mg L^{-1}$). After the confluence with the White River, the chemistry of the river radically changes.

164 An abrupt increase in pH is observed (WR: 5.3 ± 0.7). The dissolved oxygen concentration increases up to 3.7 ± 1.0 mg
165 L⁻¹ and DOC concentrations drop sharply to 9.2 ± 3.2 mg L⁻¹. Across all samples, the DOC concentrations show a
166 significant negative correlation with DO concentrations ($r^2=0.63$, $n=40$, $p<4.10^9$). In contrast, no increase in Cl is
167 observed until close to the ocean (3 samples corresponding to ocean water intrusion were excluded from Figure 2).
168 After the confluence with the black river, The DOC/Cl ratio also drops sharply from 15 in the black river and drainage
169 canals to 5 in the white river (Figure SI.1).

170 **5.2. DOM optical characteristics and stable isotopic signature**

171 No systematic differences were observed for the DOM characteristics between the dry and the wet season sampling
172 campaigns. The $\delta^{13}\text{C}$ signature of DOC (Figure 3a) is very negative, reaching $-30.3 \pm 0.4\%$ in the drainage canals. It
173 increases along the continuum from upstream in the black river to the ocean. Significant differences are observed
174 between the drainage canals and black river compared to the white river. The $\delta^{13}\text{C}$ signature of DOC is significantly
175 negatively correlated with DOC concentration ($r^2=0.68$, $p<10^{-4}$, $n=40$), with the highest DOC values being associated
176 with the lowest $\delta^{13}\text{C}$ -DOC values.

177 The SUVA index (Figure 3b) shows high values in the black river (5.3 ± 1.2), the highest values measured upstream. A
178 wide range of values is measured in the drainage canals (4.3 ± 1.4). The SUVA values of the Black River are
179 significantly higher than those measured in the Kapuas Kecil (4.5 ± 0.3) and its tributaries (4.2 ± 0.2). The fluorescence
180 index varies widely in the drainage canals (1.60 ± 0.17) and black river (1.55 ± 0.06), but is more uniform in the white
181 river, both upstream (1.55 ± 0.03) and downstream (1.55 ± 0.05) of the confluence with the Black river. These two optical
182 indices show coherent spatial patterns within the black river and drainage canals (Figure 3b&d), with lower SUVA
183 values being associated with higher FI values, in 3 drainage canals and in the black river close to their connection,
184 sampled during the wet season. Across all samples, a significant correlation is observed between FI and SUVA values
185 ($r^2=0.37$, $p<10^{-4}$, $n=41$).

186 The EEMS of all water samples have two main peaks (Figure SI.2). The main one ($\lambda_{\text{ex}}=250$ nm, $\lambda_{\text{em}}=460$ nm), is
187 coupled with a less intense peak ($\lambda_{\text{ex}}=350$ nm, $\lambda_{\text{em}}=460$ nm). The peaks are typical of high molecular and aromatic
188 molecules, which have been observed in wetlands (Fellman et al., 2010). The PARAFAC analysis reveals two
189 fluorophores: C1 ($\lambda_{\text{ex}}=255$ nm, $\lambda_{\text{em}}=450$ nm) and C2 ($\lambda_{\text{ex}}=285$ nm, $\lambda_{\text{em}}=485$ nm, Figure SI. 2) The first component
190 constitutes from 60 to 73 % of the total fluorescence of samples. The relative contribution of these two fluorophores
191 evolves along the sampled continuum, with the lowest values measured upstream in the black river (Figure 3c). The
192 spatial evolution of C1/C2 ratio and $\delta^{13}\text{C}$ -DOC are consistent. A significant ($r^2=0.43$, $p<0.001$, $n=41$) relationship is
193 observed across all the samples. A stronger relationship ($r^2=0.85$, $p<0.001$, $n=5$) is observed when the drainage canals
194 samples alone are considered.

195 **5.3. Trace element concentrations and physical fractionation**

196 Black rivers originating from drained peatlands have a unique composition of inorganic elements. The concentrations
197 of trace metals (Pb, Ni, Zn, Cd) as well as Al and Fe and are significantly higher in the black river and drainage canals
198 than the concentrations in the white river (Table 1, Figure 4). For Al, Fe and As, high concentrations were measured
199 in the Black River during the dry season. In contrast to other TM, higher Cu concentrations are measured in the white
200 river. A PCA analysis (Figure 5) of TM concentration and DOM properties reveals specific association between DOC,
201 Fe and As and to a lesser extent Zn and Cd, while another group is formed by Al, Pb and Ni (Figure 5). Cu shows no
202 association with DOM but does show increased concentrations with higher FI. The first axis of PCA (load of DOC,
203 Fe, As) strongly discriminates the black river and drainage canals samples from the white river.

204 The distribution of DOC and TM is presented in Table 2. Dissolved organic matter is mostly (>98%) in the dissolved
205 and fine colloids form (<0,22 μm) all along the studied continuum. Iron and As are mostly present in the form of
206 dissolved and fine colloids in the black river and drainage canals (>96%). However, after transfer to the white river,
207 half of Fe and a third of As is in the coarse colloidal form. Zinc and Cd do not show similar patterns. Aluminium is
208 mostly present in the coarse colloidal phase (>60%) in the black river and drainage canal and this proportion further
209 increases in the white river (>80%). Lead is mostly present in the dissolved and fine colloid phase (>75%) in the
210 drainage canals and black river and shifts to coarse colloidal (>60%) forms after the confluence with the white river.
211 Nickel and Cu is mostly present in the dissolved and fine colloidal phase in the DC and BR but almost entirely in the
212 coarse colloidal fraction in the white river.

213 **5.4. Pb isotopic composition**

214 We observe distinct differences between the lead isotope ratios in the white river and those in the black river and
215 drainage canals. A decrease in the $^{206}\text{Pb}/^{207}\text{Pb}$ isotopic ratio is observed with increasing Pb concentrations in the black
216 river but not the white river (Figure 6a). Furthermore, the biplot of the $^{206}\text{Pb}/^{207}\text{Pb}$ and the $^{208}\text{Pb}/^{206}\text{Pb}$ signatures
217 illustrates significant differences between the white water and black river/drainage canal groups (Figure 6b).

218 **6. Discussion**

219 **6.1. In-stream processing of DOM in black rivers**

220 We observe in-stream processing of DOM, but the total DOM exported from tropical peatlands exceeds the processing
221 capacity of the rivers which drain them and a large proportion of DOM is transported to the ocean. We find persistently
222 high DOC concentrations in both drainage canals and black rivers draining degraded peatlands consistent with the
223 range of previously reported values in Borneo (Moore et al., 2013; Cook et al., 2018) and in the upper range of black
224 rivers in Sumatra (Rixen et al., 2008; Baum et al., 2007). We also find indicators of in-stream processing of DOM.
225 The transformation of DOM we observe along the continuum is likely due to dominant photo-oxidation and a lower
226 contribution of microbial processing. We observe an increase in the $\delta^{13}\text{C}$ -DOC values along the studied continuum
227 (Figure 3a). This shift toward higher $\delta^{13}\text{C}$ -DOC is correlated with an increase in the C1/C2 ratio of PARAFAC
228 fluorophores (Figure 3c). The two fluorophores are typical of terrestrial input of DOM (Yamashita et al. 2008). An

229 increase in this C1/C2 ratio reflects a shift toward lower wavelengths and therefore toward lower aromaticity and lower
230 molecular weight (Austnes et al. 2010). Moreover, a decreasing trend of SUVA values is observed along the continuum
231 (Figure 3b). These observations indicate that at our site, aromatic features are preferentially processed in-stream,
232 consistent with a dominant effect of photo-oxidation (Spencer et al., 2009; Amon and Benner, 1996; Sharpless et al.,
233 2014). This has also been observed in the Congo River where photo-oxidation led to an increase in $\delta^{13}\text{C}$ -DOC and a
234 decrease in aromatic features (Spencer et al. 2009).

235 However, photo-oxidation is not the only process of DOM processing. The low oxygen levels in the black river and
236 drainage canals and the significant relationship between DOC and DO concentrations suggest that nearly all oxygen
237 entering the well-mixed water is quickly consumed by DOM oxidation (Figure 2a&b). The sharply decreasing oxygen
238 profiles measured in the black river suggest that the transformation of DOM is restricted to the shallow surface layers
239 of these waters (Figure SI.3). However, localized increase in FI index (reflecting a higher proportion of microbial
240 derived DOM, Figure 3d) suggests that microbial processing occurs at a higher extend in drainage canals and the black
241 river. Both photo-oxidation and microbial processing have been quantified in laboratory experiments for DOM
242 originating from tropical peatlands. Martin et al. (2018) found that up to 25 % of riverine DOC from a black river in
243 Sarawak, Malaysia, was lost within 5 days of exposure to natural sunlight. Microbial long-term incubation studies by
244 Rixen et al. (2008), showed that 27% of DOC was degraded after two weeks, and that as a whole, 73 % of DOC was
245 considered refractory to microbial degradation. Another hypotheses is that in-stream microbial processing of DOM is
246 further limited by the low pH, and low nutrient levels (especially inorganic nitrogen), of the Black River (Wickland et
247 al., 2018), rather than intrinsic refractory characteristics. Although the precise extent of in-stream processing cannot
248 be quantified here, our results are consistent with in stream transformation of DOM by important photo-oxidation but
249 also microbial degradation in the shallow surface layers. Additionally, quantitative assessment of outgassing in tropical
250 peatland drainage canals would improve the evaluation of carbon release following peatland drainage. Overall, more
251 work is needed to understand the extent of upstream processing of peatland DOM.

252 **6.2. Role of DOM, Al and Fe in trace metal dynamics in peat draining waters**

253 This study provides the first record of trace metals in black rivers originating from degraded tropical peatlands. We
254 observe strong enrichment of Al and Fe, as well as Pb, As, Ni and Cd in peat-draining waters. The measured
255 concentrations are comparable to those measured by Kurasaki et al. (2000) in Borneo rivers for Pb, Zn, Cu and Cd, but
256 significantly higher (5 to 10 times) for Fe. The concentration levels, however, remain low compared to highly impacted
257 regions of Indonesia (Arifin et al., 2012). The elevated concentrations of Al and Fe in water draining tropical peatlands
258 is consistent with existing observations of elevated Fe concentrations from black rivers in the tropics (Zhang et al.,
259 2019) and northern peatlands. This enrichment is likely due to the weathering of mineral material under the peat during
260 peat accumulation processes (Tipping et al., 2002; Pokrovsky et al., 2005). As a consequence, in water draining
261 peatlands, strong organo-mineral associations between DOM and Fe (Krachler et al. 2010, 2012; Broder and Biester
262 2015), as well as DOM and Al (Helmer et al., 1990) have been observed. These colloidal associations between DOM
263 and Al and Fe in the form of hydroxides strongly control TM transfer and speciation in peat draining waters (Tipping

264 et al., 2002). In the present study, specific associations of trace metals with Al and Fe are observed, including strong
265 links between Al and Pb and Ni. However, the lack of a direct relationship between Pb and DOM contrasts with
266 reported observations in the literature (Graham et al. 2006; Pokrovsky et al., 2016; Jeremiason et al., 2018). Despite
267 this, we do observe strong links between Fe, As, Zn, Cd and DOM, which have been previously reported in water
268 draining peatlands (Broder and Biester, 2015; Neubauer et al., 2013; Pokrovsky et al., 2016). The coupled dynamic
269 of Fe and As might be related to similar mobilization processes within the peat column, with the sorption of As to
270 Fe(III)-(oxyhydr)oxides (ThomasArrigo et al., 2014) in anoxic peat water. Widespread drainage of tropical peatlands
271 and the corresponding release of anoxic water to surface water networks could induce a coupled increase in DOM and
272 Fe concentrations, similar to that which has occurred in Sweden (Kritzberg and Ekström, 2011).

273 **6.3. Peatlands as secondary sources of atmospheric pollutants**

274 The isotopic composition of Pb in peat draining water strongly suggests its anthropogenic origin. The isotopic
275 signatures measured in river samples are a combination of the signature of undisturbed soils of Borneo (Valentine et
276 al., 2008), and a mix of both present and past anthropogenic inputs. Older anthropogenic inputs are reflected by the
277 signature of atmospheric deposition from Java aerosols (Bollhöfer and Rosman, 2000), while the signature of recent
278 regional anthropogenic inputs was characterized by rain samples collected in Pontianak as part of this study (Figure
279 6b). In the black river and drainage canals, the isotopic ratio is close to the aerosols and recently sampled rainwater
280 and dominated by anthropogenic inputs, whereas the isotopic ratio in the white river is closer to the natural signal
281 (Figure 6). This isotopic difference is consistent with the difference between the watersheds drained by these two
282 rivers: tropical peatlands are ombrotrophic systems, and the trace metal content in peat soil is derived from the
283 atmosphere (Weiss et al. 2002), whereas the Kapus Kecil is recharged from a larger watershed and reflects contribution
284 of mineral soils. Tropical peatlands can serve as secondary sources of atmospheric pollutants to the environment. With
285 peatland drainage, black rivers release the accumulated atmospheric deposition over hundreds of years on much shorter
286 timescales. For example, the isotopic signature observed in the black river reflects anthropogenic sources deposited at
287 different times, including older deposition such as the lead measured in the Java aerosols (Bollhöfer and Rosman,
288 2000), and more recent deposition following the widespread introduction of unleaded fuel (characterized by samples
289 collected from rainwater during the wet 2014 sampling period in this study). This release of lead by degraded tropical
290 peatlands has the potential to impact records from environmental archives, for example the orals of the Singapore
291 Strait (Chen et al., 2015). Although this is the first measurement of the aquatic release of trace metals from tropical
292 peatlands, the role of tropical peatlands as a secondary source of contaminants has also been highlighted by the trace
293 metal content analysis of dust emitted to the atmosphere by peat fires (Betha et al., 2013).

294 **6.4. From degraded tropical peatlands to the ocean**

295 Sharp changes in physico-chemical conditions are observed after the mixing of the black and the white river, including
296 sharp increases in DO concentration and pH values. This strongly controls the transport of DOM and TM drained from
297 degraded tropical peatlands. After the confluence with the white river, DOC concentrations decrease abruptly. At the
298 same time, the DOC/Cl ratio decreases sharply from the black river and drainage canals to the white river. This suggests

299 that dilution alone is insufficient to explain the drop in DOC concentrations. Instead, in stream processing of DOM
300 likely plays a role, with the sudden elevation of pH and DO creating favorable conditions for microbial processing of
301 DOC, making the mixing zone a likely hotspot of GHG emissions (Palmer et al., 2016). This would also be consistent
302 with the decrease in the SUVA index observed after the confluence. Despite processing of DOM in the mixing zone,
303 a significant proportion of DOM originating from degraded peatlands actually reaches ocean. We observe high DOC
304 concentrations at all sampling locations, with concentrations remaining high even close to the ocean (Figure 2a).
305 Additionally, the results of our physical fractionation show that even close to the estuary, DOC remains in the dissolved
306 and fine colloid form ($<0.22 \mu\text{m}$), and that flocculation processes might be limited. The decrease in trace metal
307 concentrations after the confluence might be influenced by shifts in physical fractionation and increase proportion of
308 colloidal form. This is especially true for Al and Pb. Some flocculation at the estuary might limit their transfer to the
309 ocean. A higher proportion of Fe and As remains in the form of fine colloids after mixing with the whiter river, and is
310 still associated with DOC. Similar conservative behavior of LMW organic molecules associated with Fe was observed
311 at the outlet of northern peatlands (Krachler et al., 2012), and in Arctic rivers (Pokrovsky et al., 2014). This highlights
312 that dissolved organic molecules derived from tropical peatlands can also act as carriers of trace metals to the ocean.

313 **7. Conclusions**

314 This study characterizes the composition and concentration of DOM and TM in the canals and rivers draining the
315 degraded tropical peatlands of Indonesian Borneo. It highlights in-stream processing of DOM in drainage canals and
316 rivers draining degraded peatlands. Both stable isotopic and optical properties of DOM are consistent with photo-
317 oxidation along the continuum from the black river to the ocean. In the black river and drainage canals, rates of
318 microbial processing are likely limited by the low dissolved oxygen concentrations, and concentrated at shallow depths.
319 In contrast, after mixing with the white river, higher rates of microbial processing of DOM are expected. Along the
320 continuum, DOM is found at relatively high concentrations in the dissolved and fine colloidal phases, suggesting a
321 substantial fraction of DOM derived from degraded peatlands reaches the ocean. Additionally, we provide the first
322 assessment of trace metal concentrations in rivers draining degraded tropical peatlands. Rivers draining these peatlands
323 are enriched in some trace metals (Pb, Ni, Zn, Cd) as well as Al and Fe. Using the isotopic signature of Pb, we show
324 that degraded tropical peatlands are secondary sources of atmospherically deposited contaminants to surface waters.
325 Trace metal dynamics after transfer to the white river show clear trends: while Pb and Ni are associated with Al, As,
326 Zn and Cd are associated with Fe and DOM. Lead and Al are present in coarse colloidal form and may be transferred
327 to sediments after flocculation. In contrast, DOM, Fe and As are found predominantly in fine colloidal form even after
328 the confluence with the white river, and as a result may be transferred to the ocean. The role of degraded tropical
329 peatlands as a source of DOM, as well as Fe and As to the ocean requires further investigation.

330 **Acknowledgements**

331 This project was funded by the PEER project “Assessing Degradation of Tropical Peat Domes and Dissolved Organic
332 Carbon (DOC) Export from the Belait, Mempawah and Lower Kapuas Kecil Rivers in Borneo” lead by G. A. A.M.H.
333 and C.F.H were supported by the National Research Foundation Singapore through the Singapore–MIT Alliance for

334 Research and Technology's Center for Environmental Sensing and Modeling Interdisciplinary Research Program, and
335 by the US National Science Foundation under Grants 1114155 and 1114161 (to C.F.H.). The authors thank F. Julien,
336 V. Payre-Suc and D. Lambrigot for DOC and major elements analysis (PAPC platform, EcoLab laboratory).

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535 **Table 1.** Water chemistry of the white river, black river and drainage canals for the two sampling campaigns. The first line is the mean and the second line is the standard
 536 deviation. DO: Dissolved oxygen, FI: Fluorescence Index, SUVA: Specific UV Absorbance.

		pH	DO	Cond	DOC	$\delta^{13}\text{DOC}$	FI	SUVA	C1.C2	Cl	Al	Fe	Pb	As	Zn	Cu	Ni	Cd
	Unit	/	mg L ⁻¹	$\mu\text{S cm}^{-1}$	mg L ⁻¹	‰	-	L mg ⁻¹ m ⁻¹	-	mg L ⁻¹	$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$
White River	dry	5.20	4.49	37.2	8.43	-29.46	1,51	4,28	2.26	4.83	312.160	444.893	0.262	0,28	18.572	1.140	0.528	0,005
		0.33	0.26	13.2	1.61	0.23	0,03	0,00	0.08	4.03	407.057	383.954	0.236	0,09	9.028	0.158	0.106	0,002
	wet	4.43	3.37	1220.6	11.25	-29.41	1,60	4,57	2.30	409.16	147.242	547.500	0.129	0,32	10.264	0.868	1.186	0,006
		0.86	0.96	981.8	4.29	0.41	0,04	0,33	0.18	342.02	124.616	497.278	0.102	0,09	6.136	0.089	1.169	0,003
White River Upstream	dry	5.45	4.91	24.0	6.89	-29.32	1,55	n.a	2.54	1.31	101.610	242.500	0.139	0,21	15.290	1.059	0.519	0,003
		5.71	0.17	3.8	1.28	0.06	0,08	0,22	0.64	27.490	44.500	408.733	0.027	0,02	3.060	0.007	0.077	0,000
	wet	5.37	4.15	268.7	8.69	-29.56	1,56	4,15	2.30	47.87	148.617	408.733	0.236	0,30	9.702	1.186	0.724	0,003
		0.06	0.39	92.0	0.78	0.13	0,01	0,15	0.14	65.16	71.999	170.153	0.167	0,04	6.233	0.244	0.441	0,000
Black River	dry	3.45	1.69	98.7	36.42	-30.29	1,50	5,97	1.77	2.78	592.804	2143.500	0.467	0,59	119.386	0.582	1.958	0,012
		0.06	0.39	18.2	2.54	0.38	0,06	0,46	0.07	0.50	43.008	187.609	0.054	0,04	86.473	0.194	1.672	0,006
	wet	2.97	1.98	77.3	35.37	-30.04	1,59	4,94	2.12	2.19	443.136	1440.991	0.316	0,40	10.948	0.720	1.294	0,007
		0.13	0.75	18.3	3.70	0.38	0,15	1,32	0.15	0.57	137.488	493.547	0.110	0,10	6.980	1.127	0.527	0,003
Drainage canal	wet	3.08	2.34	89.8	35.17	-30.27	1,60	4,33	2.05	2.57	489.183	1348.017	0.313	0,35	14.518	0.369	1.535	0,008
		0.43	0.30	19.6	5.47	0.40	0,17	1,27	0.18	0.64	194.889	494.078	0.048	0,08	11.620	0.070	0.801	0,006

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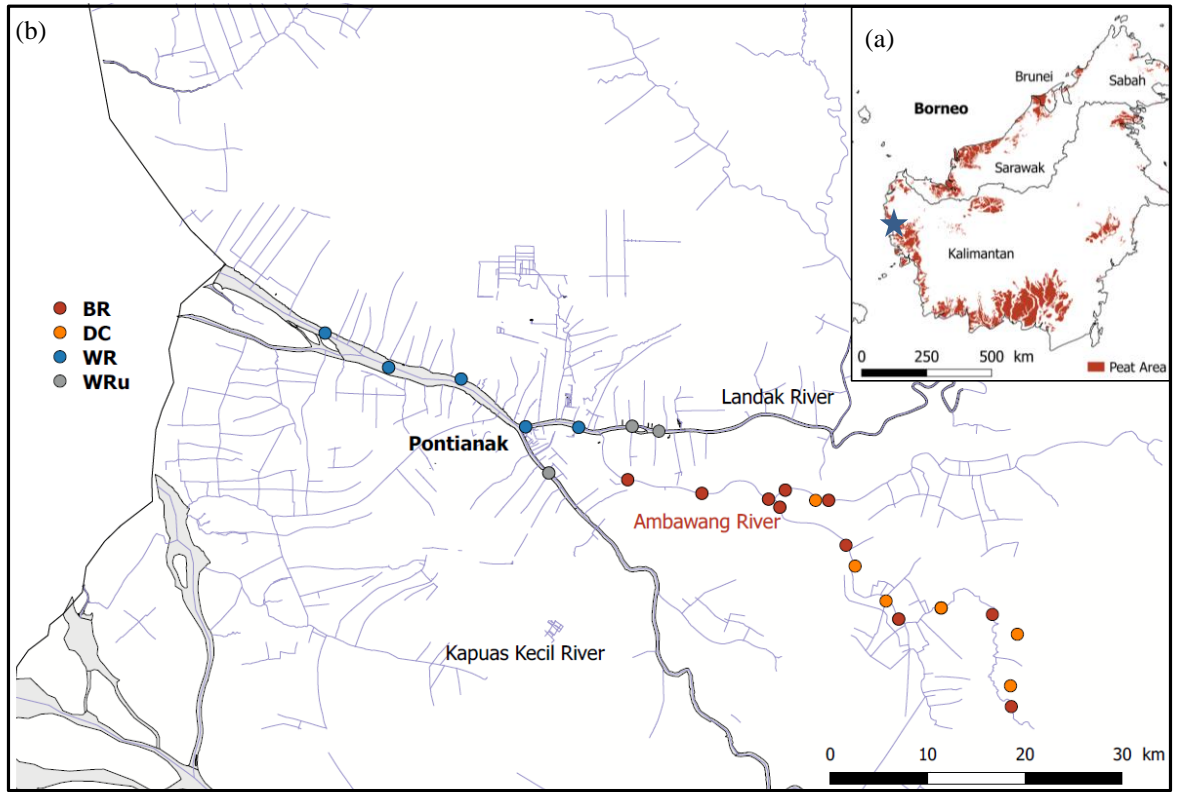
544 **Table 2.** Proportion of DOC and selected trace metals in the form of dissolved and fine colloids (< 0.22 µm) and coarse colloids (0.2-2.7 µm)

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	Drainage Canals		Black River		White River	
	<0.2 µm	0.2-2.7 µm	<0.2 µm	0.2-2.7 µm	<0.2 µm	0.2-2.7 µm
DOC	97	3	98	2	100	0
Al	39	61	36	64	18	82
Fe	100	0	99	1	45	55
Pb	75	25	78	22	34	66
As	98	2	96	4	67	33
Ni	72	28	50	50	1	99
Cu	68	32	48	52	1	99
Zn	13	87	12	88	26	74
Cd	66	34	100	0	83	17

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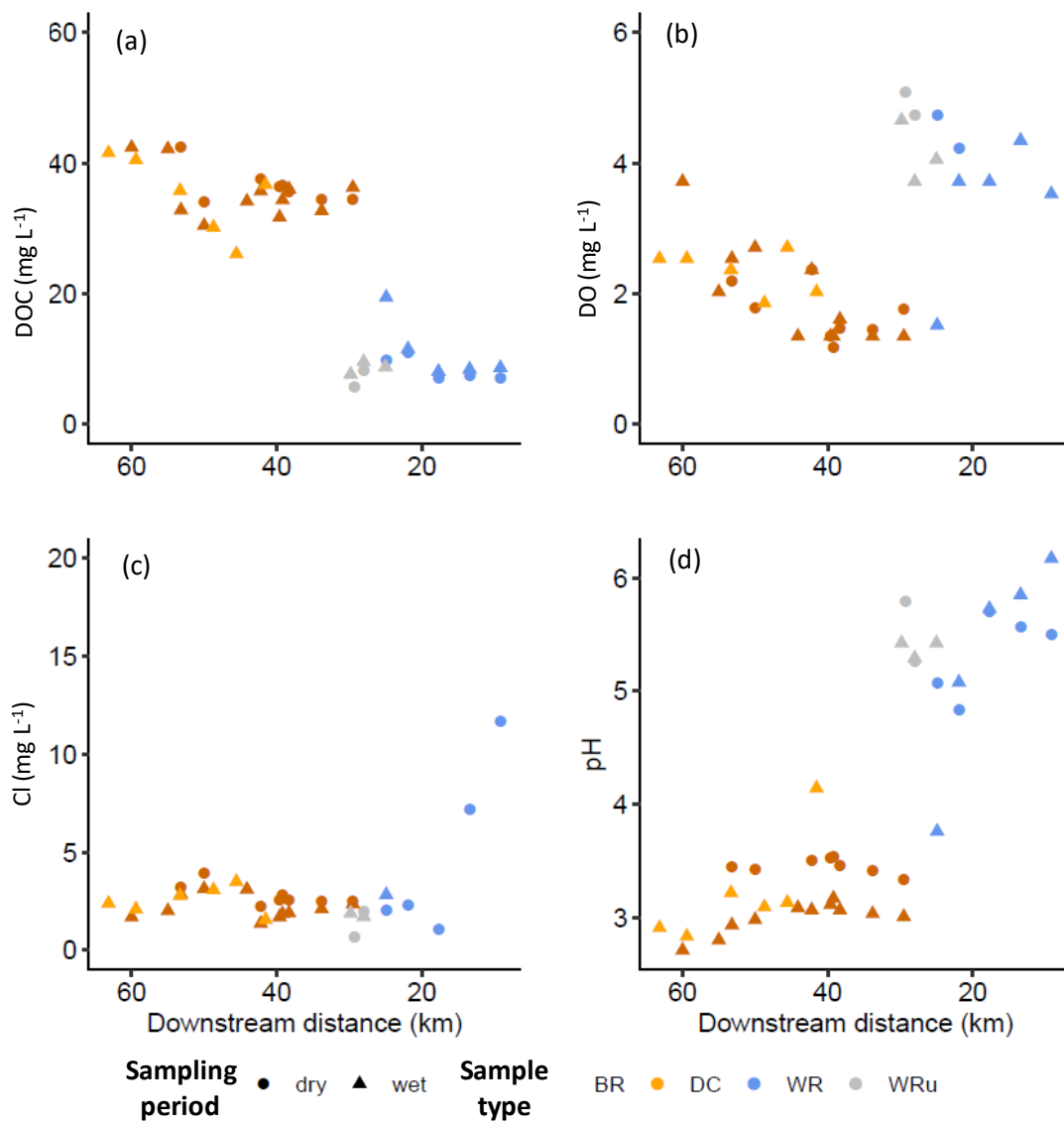
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Figure 1: (a) Location of the study area on Borneo island. (b) Location of sampling sites and types of water: Black River (BR), Drainage Canals (DC), White River (WR), and white River upstream of the confluence with the black river (WRu).

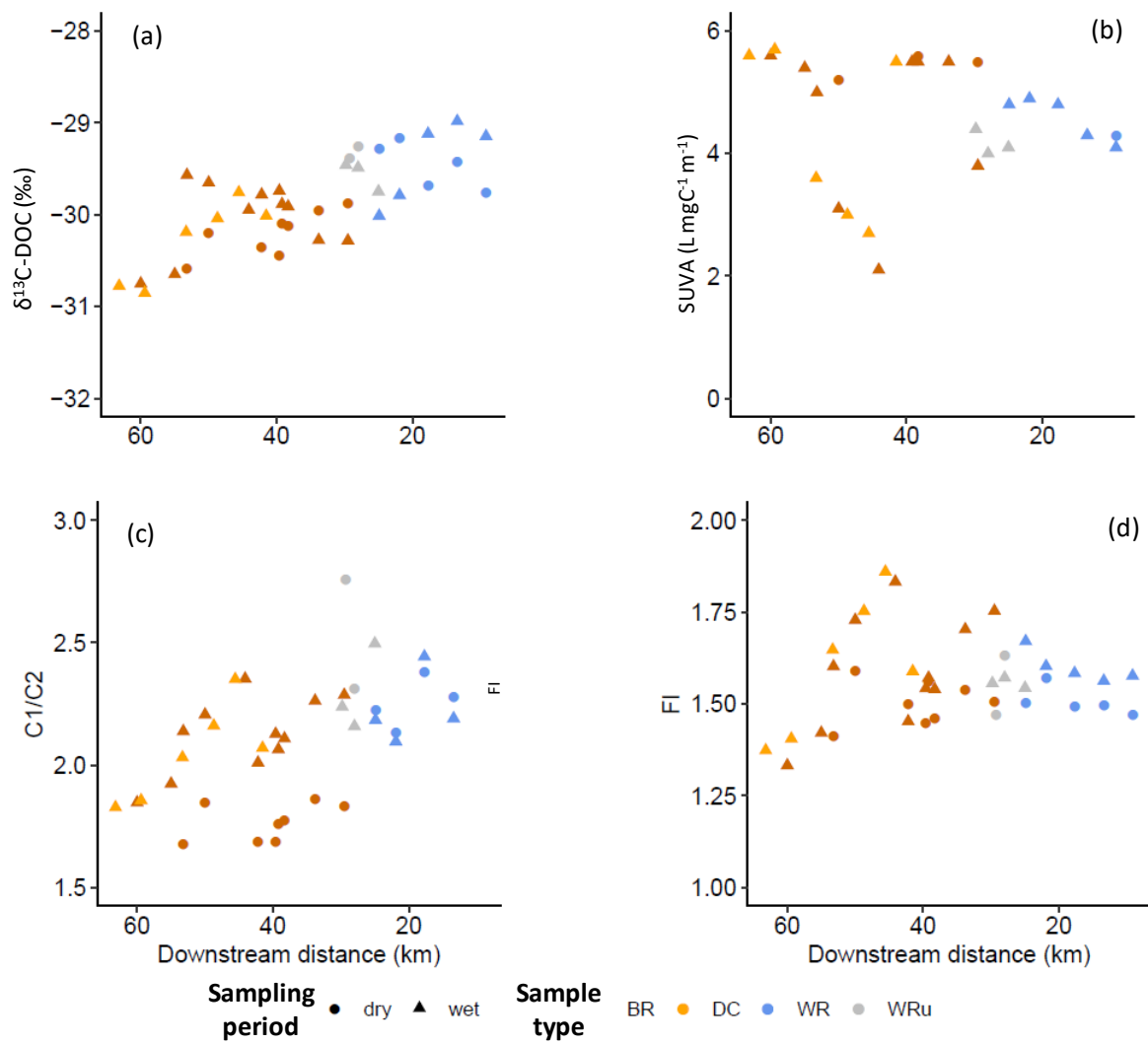
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Figure 2: Evolution of (a) dissolved organic carbon concentration, (b) dissolved oxygen concentration, (c) chloride concentration and (d) pH along the continuum from the black river to the ocean.

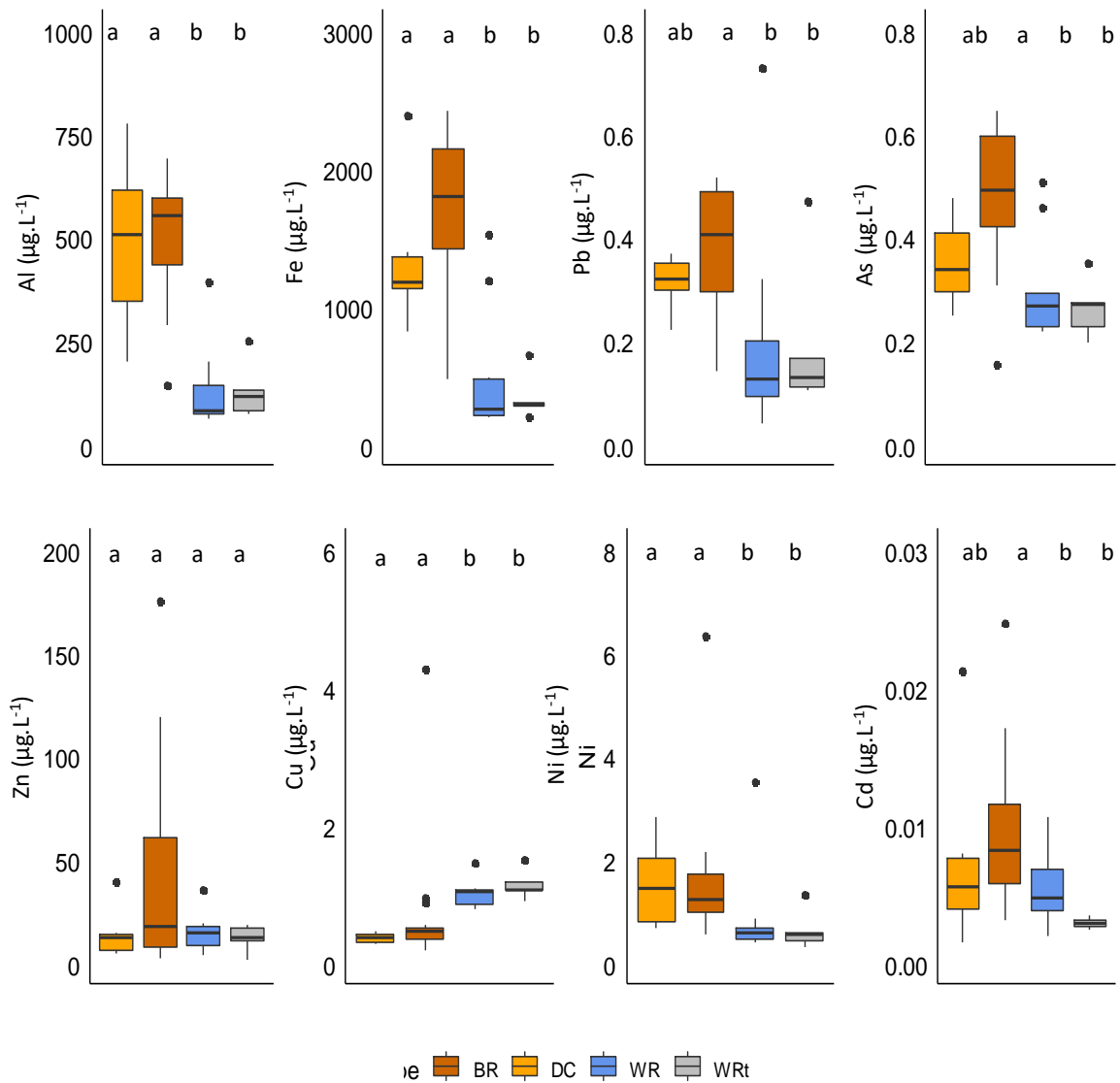
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Figure 3: Evolution of DOM along the black river to the ocean continuum. (a) $\delta^{13}\text{C-DOC}$, (b) SUVA (Specific UV Absorbance) index, (c) C1/C2, (d) FI (Fluorescence Index).

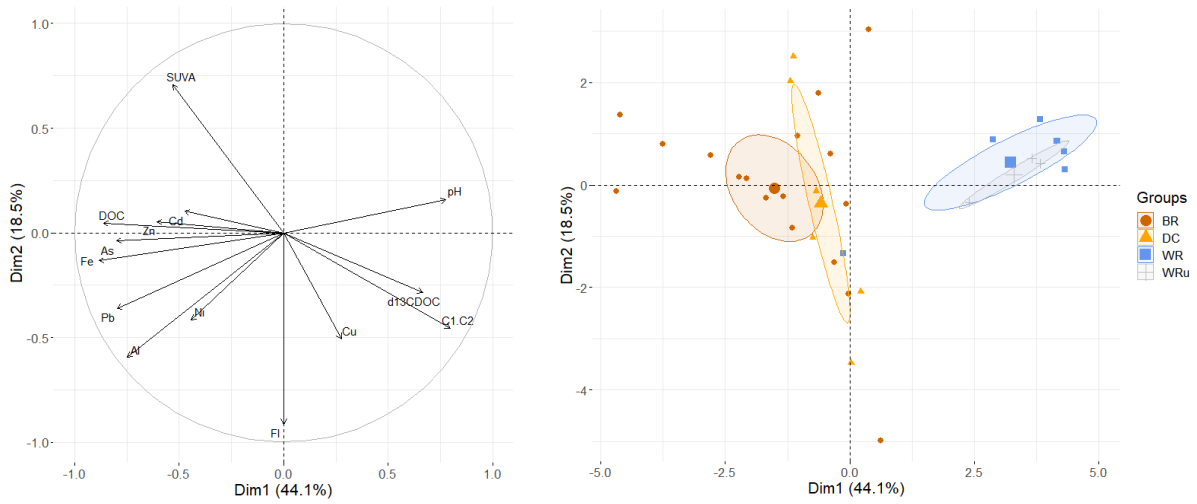
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Figure 4: Ranges of selected TM concentration for different sampled water types. Letters represent significantly different groups (Kruskal Wallis and Dunn's post hoc multiple test ($p < 0.05$))

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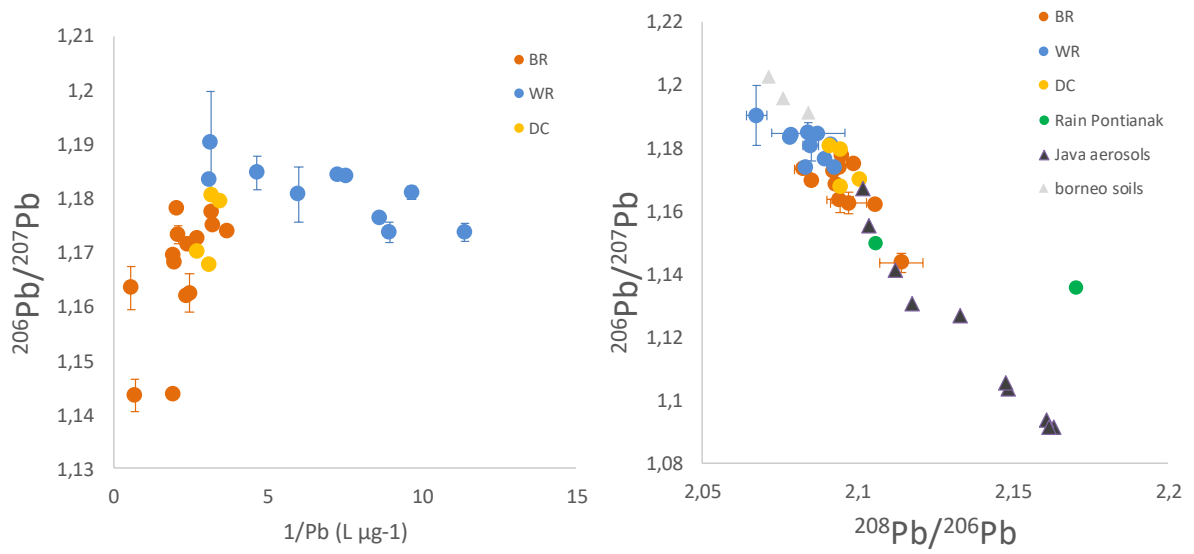


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601 **Figure 5:** The first two factors of the PCA (63,1 % of variance) by variables (a) and by observation (b) for the
602 different sampled water types.

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Figure 6: (a) Dependence of $^{206}\text{Pb}/^{207}\text{Pb}$ ratio on Pb concentrations for the different water samples. (b) Relationship between $^{206}\text{Pb}/^{207}\text{Pb}$ ratio and $^{208}\text{Pb}/^{206}\text{Pb}$ ratio.