

1 **Seasonal dynamics of carbon and nutrients from two**
2 **contrasting tropical floodplain systems in the Zambezi**
3 **River Basin**
4

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21 **Abstract**

22 Floodplains are important biogeochemical reactors during fluvial transport of carbon and nutrient
23 species towards the oceans. In the tropics and subtropics pronounced rainfall seasonality results in
24 highly dynamic floodplain biogeochemistry. Massive construction of dams, however, has
25 significantly altered the hydrography and chemical characteristics of many (sub)tropical rivers. In this
26 study, we compare organic matter and nutrient biogeochemistry of two large, contrasting floodplains
27 in the Zambezi River Basin in Southern Africa, the Barotse Plains and the Kafue Flats. Both systems
28 are of comparable size, but differ in anthropogenic influence: while the Barotse Plains are still
29 relatively pristine, the Kafue Flats are bordered by two hydropower dams.

30

31 The two systems exhibit different flooding dynamics, with a larger contribution of floodplain-derived
32 water in the Kafue Flats and a stronger peak flow in the Barotse Plains. Distinct seasonal differences
33 have been observed in carbon and nutrient concentrations, loads, and export and retention behavior in
34 both systems. Simultaneous retention of particulate carbon and nitrogen, and net export of dissolved
35 organic and inorganic carbon and nitrogen suggested that degradation of particulate organic matter
36 was the dominant process influencing the river biogeochemistry during the wet season in the Barotse
37 Plains, and during the dry season in the Kafue Flats. Reverse trends during the dry season indicated
38 that primary production was important in the Barotse Plains, whereas the Kafue Flats seemed to have
39 both primary production and respiration occurring during the wet season, potentially occurring
40 spatially separated in the main channel and on the floodplain, respectively.

41

42 Carbon to nitrogen ratios of particulate organic matter showed that soil-derived material was
43 dominant year round in the Barotse Plains, whereas the Kafue Flats transported particulate organic
44 matter that had been produced in the upstream reservoir during the wet season. Stable carbon isotopes
45 suggested that inputs from the floodplain to the particulate organic matter pool varied throughout the
46 year in both systems, in opposite patterns. In the Kafue Flats, encroachment of woody plants since the
47 construction of the dams could be responsible for the altered pattern. Additionally, the timing of
48 runoff-driven inputs during the wet season has been changed by the presence of the dams. This study
49 revealed effects of dam construction on organic matter and nutrient dynamics on the downstream
50 floodplain that only become visible after longer periods, highlighting the need for continued
51 monitoring after dam construction.

52

53

54 **Keywords:** Zambezi, tropical floodplain, organic matter, nutrients, yields, dam, Barotse Plains, Kafue
55 Flats

56

57

58 **1. Introduction**

59 In current global budgets of organic matter and nutrients, large rivers (discharge $> 400 \text{ km}^3 \text{ yr}^{-1}$)
60 account for approximately 35% of the total freshwater-related flux to the ocean (Milliman and
61 Farnsworth, 2011). In studies presenting global budgets and models for carbon, nitrogen and
62 phosphorus export via large rivers, tropical systems are often underrepresented (Alvarez-Cobelas et
63 al., 2008; Alvarez-Cobelas et al., 2012; Alvarez-Cobelas et al., 2009). Global extrapolations based on
64 the well-studied temperate and boreal systems are therefore prone to large errors because they neglect
65 the distinct seasonal flooding of extensive tropical floodplain areas (Junk, 1999; Junk et al., 1989).
66 Floodplain systems have been recognized for their potential to alter fluxes of particulate matter,
67 organic carbon, and nutrients transported by rivers (McJannet et al., 2012; Fisher and Acreman, 2004).

68
69 During transport from land to sea, riverine organic matter is modified by processes in biogeochemical
70 reactors, specifically natural and artificial lakes and wetlands or floodplains. In the past decades,
71 increasing energy demands have resulted in the construction of hydropower dams in most of the
72 world's large river systems (Nilsson et al., 2005). These man-made biogeochemical reactors
73 significantly change the characteristics of river flow. Since water flow is restricted in most lakes,
74 particles have time to settle. The water exiting the lake is therefore depleted in particulate matter and
75 its associated organic carbon and nutrients. Lake stratification favors hypoxia or anoxia in the
76 hypolimnion, which can lead to methane outgassing (Barros et al., 2011; Bastviken et al.,
77 2008; DelSontro et al., 2011), low oxygen concentrations and potentially toxic levels of reduced
78 substances in the outflow from turbines (Kunz et al., 2013). In addition to the direct effects of
79 hydropower reservoirs, energy demands often require flow regimes that deviate from the natural
80 tropical situation, changing the hydrography in the downstream reaches of the river (Lu and Siew,
81 2006; Maingi and Marsh, 2002; Rood et al., 2005).

82
83 Floodplains make up a large fraction of all tropical wetlands (which cover about 2.5-3.5% of the
84 Earth's surface), with areas of $>10^6 \text{ km}^2$ in South America and $>10^5 \text{ km}^2$ in Africa (Tockner and
85 Stanford, 2002). Because of the large area, the periodic flooding and corresponding changing redox
86 conditions, the high temperatures, and the intense rates of primary production (Junk and Piedade,
87 1993; Robertson et al., 1999; Ward and Stanford, 1995), the impact of tropical floodplains on riverine-
88 transported organic matter and nutrients can be significant (Hamilton et al., 1997). River-floodplain
89 exchange has been identified as a key process for the ecological and biogeochemical functioning in
90 temperate (Hunsinger et al., 2010; Tockner et al., 2010) and tropical systems [e.g. Melack et al.
91 (2009)]. Lateral exchange between a river and its floodplain was shown to affect sediment erosion and
92 transport (Dunne et al., 1998), the composition of the particulate matter (Devol et al., 1995), carbon
93 fluxes (Pettit et al., 2011), and nutrient supply (Villar et al., 1998).

94

95 The type of organic matter transported by tropical rivers co-varies with discharge. Both the Tana
96 River in Kenya (Tamooh et al., 2014) and the Sanaga River in Cameroon (Bird et al., 1998)
97 transported mainly organic matter from the degradation of C₄ plants during the wet season, while dry
98 season runoff is characterized by organic matter originating from C₃ plants. Spencer et al. (2010) also
99 showed that the properties of organic carbon transported by a tributary of the Congo River vary
100 during different hydrographic phases, with highest dissolved organic carbon and lignin concentrations
101 during peak flow. In the same river, the particulate organic carbon concentration increased when the
102 discharge increased (Mariotti et al., 1991).

103

104 Following the construction of dams, the hydrological and sediment-related changes have been
105 assessed in several systems, including the Tana River in Kenya (Maingi and Marsh, 2002) and the
106 Lower Mekong River in China (Kummu and Varis, 2007;Fu et al., 2008;Lu and Siew, 2006).
107 However, the impacts of these changes in hydrography on the biogeochemistry of tropical floodplain
108 systems have hardly been studied. Considering the importance of floodplains within the catchment of
109 large tropical rivers, changes in flooding and inundation might have pronounced effects on the
110 biogeochemical behavior of floodplains and can have far-reaching consequences for the downstream
111 catchment.

112

113 In this study, we assessed the dynamics and export rates of organic matter and nutrients in two large,
114 understudied floodplains in the Zambezi River Basin, the pristine Barotse Plains and the dam-
115 impacted Kafue Flats, during wet and dry season conditions. This comparative analysis aims at
116 identifying effects of damming on floodplain biogeochemistry and builds on previous studies on
117 river-floodplain interactions in the Kafue Flats (Zurbrügg et al., 2012;Wamulume et al.,
118 2011;Zurbrügg et al., 2013). Based on field campaigns from contrasting seasons, we were able to
119 describe seasonal variability in the two systems. We further quantified the changes in the
120 concentration, speciation, origin, and loads of carbon, nitrogen, and phosphorus along the floodplains
121 in order to assess the implications of river damming and an altered hydrological regime on floodplain
122 biogeochemistry.

123

124

125 2. Study sites

126

127 <<Figure 1>>

128

129 At 1.4×10^6 km², the Zambezi River Basin is the fourth largest in Africa, and the only major African
130 river draining into the Indian Ocean. Due to its geographic location, the catchment experiences a
131 pronounced wet season during the passage of the Inter Tropical Convergence zone (Dec-Mar) and a
132 dry season (Apr-Nov) during the remainder of the year.

133

134 <<Figure 2>>

135

136 The Barotse Plains are a near-pristine floodplain area in the upstream part of the Zambezi River in the
137 Western part of Zambia (Fig. 1). The hydrography in the Barotse Plains clearly reflects the climatic
138 conditions, with peak flow around April/May and low flow between July and November (Fig. 2). The
139 total inundatable area is estimated at around 7,700 km² (Hughes and Hughes, 1992). The Kafue Flats
140 are located along the Kafue River, one of the largest tributary of the Zambezi River. Upstream of the
141 Flats, the Itezhi-Tezhi dam (ITT, closed in 1978) stores a significant part of the wet-season runoff in
142 order to allow for a continuous operation of the power station at Kafue Gorge (dam closed in 1972)
143 downstream of the Kafue Flats. Evaporation from the reservoir changes the water level by 780 mm
144 year⁻¹, according to Beilfuss (2012). The maximum inundated area of the Kafue Flats is slightly
145 smaller than of the Barotse Plains, at 6,000 km² (Hughes and Hughes, 1992). The hydrography of the
146 Kafue Flats has been significantly altered by the presence of the dams (Fig. 2). Over the last decades,
147 peak flow has been reduced (approximately -50%) and base flow has increased (roughly +50%, Fig.
148 2). In consequence, timing and extent of inundation in the Kafue Flats have changed (Mumba and
149 Thompson, 2005). The floodplain area has been reduced by 40% due to permanent inundation, a
150 direct result of elevated base flow sustained by the dam operation.

151

152 The vegetation in the Kafue Flats has been described as a gradient, ranging from open water to
153 floodplain grasslands, water meadows, littoral zones, termitaria grasslands, to woodland areas
154 (Ellenbroek, 1987). After the construction of the dams, the area covered by shrubs has increased
155 (Mumba and Thompson, 2005;Blaser, 2013). For the Barotse Plains a detailed overview of the
156 vegetation zones is lacking, but several sources hint to grasslands, combined with Miombo woodland
157 and deciduous forest patches (Zambezi Society, 2000;Timberlake, 2000).

158

159

160 **3. Methods**

161 **3.1 Sampling**

162 Sampling of the main river channel at multiple locations along the floodplains (Fig. 1) was conducted
163 during peak flow, hereafter called the wet season (April/May; Barotse Plains 2009, 2013; Kafue Flats
164 2008, 2009, 2010) and low flow, referred to as the dry season (October; Barotse Plains 2008, 2013;
165 Kafue Flats 2008). Samples were collected in the middle of the well-mixed channel from surface
166 water (50cm, Barotse Plains), or at mid-depth (Kafue Flats) using a peristaltic pump. The similarity of
167 the results from different years (Zurbrügg et al., 2013; Zurbrügg et al., 2012) allowed combination and
168 averaging of the data sets in order to obtain generalized patterns for the two systems and seasons.
169 Discharge in the main channel was measured using a RiverRay ADCP (for Barotse Plains dry season
170 data from the Zambezi River Authority were used).

171

172 **3.2 Laboratory analyses**

173 Samples for dissolved nutrient concentrations were filtered through 0.45 μm filters. Dissolved
174 inorganic nitrogen (DIN), phosphate, and the sum of nitrate and nitrite were measured by
175 chemoluminescence detection (Antek 9000). Ammonium was determined by standard colorimetric
176 technique. Total dissolved nitrogen and total phosphorus (TDN and TDP) were determined by
177 chemoluminescence detection (Antek 9000) following persulphate oxidation (Solórzano and Sharp,
178 1980; Bronk et al., 2000). Samples for particulate phosphorus concentrations during the wet season
179 were collected onto 0.7 μm GF/F filters (Whatman) and measured using a sequential phosphorus
180 extraction method (SEDEX, Ruttenberg (1992) as modified by Slomp et al. (1996)). Samples for
181 dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) were filtered through 0.7 μm
182 GF/F filters (Whatman) and analyzed on a Shimadzu TOC-L (Barotse Plains) or on a Shimadzu 5050
183 TOC analyzer (Kafue Flats, DOC only). DIC concentrations for the Kafue Flats were calculated from
184 pH and alkalinity measurements (data not shown). Stable oxygen isotopes were determined on filtered
185 water samples (0.45 μm nylon filters) using a Picaro L2120-I Cavity Ringdown Spectrometer
186 (Barotse Plains) or a MultiFlow preparation module connected to a continuous flow IRMS (Isoprime,
187 UK; Kafue Flats) and calibrated against in-house standards ranging from 0 to -22.5‰_{VSMOW}. Riverine
188 suspended matter was collected on pre-weighed GF/F filters (Whatman). After freeze-drying of
189 samples, suspended matter concentrations were determined by weight difference. Particulate organic
190 carbon and nitrogen and their stable isotopic compositions (POC, PN, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively)
191 were determined using EA-IRMS (Thermo-Fischer MAT 253 or ThermoFinnigan FlashEA 1112
192 coupled to a DeltaV Advantage Continuous-Flow IRMS), and calibrated against in-house standards
193 ($\delta^{13}\text{C}$: -15 to -30‰_{V_PDB}, precision 0.1‰; $\delta^{15}\text{N}$: -1.1 to +32.7‰_{air}, precision 0.2‰).

194

195

196

197 **4. Results**

198

199 **4.1 Hydrology and oxygen isotopes**

200

201 << Figure 3>>

202

203 During the wet season, the runoff in the main channel of both floodplains was characterized by a
204 discharge minimum roughly in the middle of both systems (Fig. 3). Located around 100 km and 200-
205 300 km downstream in the Barotse Plains and in the Kafue Flats, respectively, constrictions in the
206 river bed were present, which promoted flooding of the surrounding floodplain area (Zurbrügg et al.,
207 2012). During the dry season, the discharge remained rather constant in both systems with a gain due
208 to tributaries along the Barotse Plain and a slight loss in the dry Kafue Flats. Notice, however, that the
209 peak discharge in the wet season was about four times higher in the Zambezi crossing the Barotse
210 Plains compared to the dammed Kafue River (Fig. 2).

211

212 The intense river-floodplain exchange left a distinct $\delta^{18}\text{O}$ signal in both systems: the rivers lost water
213 to the floodplain during the wet season. Downstream of the stretch where discharge in the river
214 decreased, the $\delta^{18}\text{O}$ of the river water sharply turned towards heavier values (Fig. 3). The overall ^{18}O -
215 enrichment of the channel water between the upstream and downstream sampling locations was more
216 pronounced in the Kafue Flats during the wet season. In the Barotse Plains, the $\delta^{18}\text{O}$ signal showed an
217 overall shift from -2.0‰ in the upstream part to -0.9‰ at the downstream end. In the Kafue Flats a
218 sharp increase towards heavier values was observed downstream of the channel constriction. To
219 correct for different travel distances along the river stretches, the change in $\delta^{18}\text{O}$ per 100 km of river
220 length was estimated: for the Barotse Plains this enrichment was +0.36‰ and for the Kafue +0.56‰
221 per 100 km. During the dry season, no significant increase in isotopic signal of oxygen was observed
222 in the Barotse Plains, while in the Kafue Flats enrichment occurred at +0.17‰ per 100 km.

223

224

225 **4.2 Concentrations and loads**

226

227 <<Figure 4>>

228

229 For comprehensive comparison of the concentrations of carbon, nitrogen, and phosphorus species
230 along the two floodplains during contrasting seasons, all measurements along the floodplain have
231 been considered, irrespective of spatial trends (Fig. 4). The occurrence of large spatial variations

232 along the floodplain, or differences between measurement methods between the different years,
233 resulted in larger ranges.

234

235 The dissolved inorganic fraction dominated the total carbon concentration in both seasons and both
236 systems (Fig. 4). Dissolved organic nitrogen (DON) was always the main nitrogen species. In the
237 Barotse Plains particulate phosphorus (PP) was the dominant form during the wet season, while
238 dissolved inorganic phosphorus (DIP) was generally the prevailing species during the dry season.
239 Phosphorus concentrations were largely close to detection limit in both systems, and were therefore
240 excluded from the calculation of loads.

241

242 While both systems exhibited very low inorganic nutrient concentrations during the dry season, the
243 Barotse Plains were substantially lower in organic carbon and nitrogen species concentration
244 compared to the Kafue Flats. Differences between the dry season and wet season C and N
245 concentrations within both systems are statistically significant (paired analysis, p-values <0.05) for all
246 species, except for the Kafue Flats DOC (p = 0.23), DON (0.084) and DIN (0.284). The differences in
247 concentrations between the Barotse Plains and Kafue Flats in similar seasons are significant
248 (hypothesis testing, p-values <0.05) for all species, except PP (wet season, p = 0.121) and DIP (dry
249 season, p=0.053).

250

251 <<Figure 5>> <<Table 1>>

252

253 Loads were calculated from the discharge and concentration data for the respective species, as the
254 water column was well mixed (see Supplementary Information for details). Total carbon and nitrogen
255 loads increased along the Barotse Plains during the wet season, mainly due to larger contribution by
256 the dissolved organic form (Fig. 5). The increase in total carbon load in the Kafue Flats during the wet
257 season was mainly attributed to the dissolved inorganic fraction. The magnitude of the wet season
258 carbon loads leaving the floodplain area is comparable between the two systems (roughly 1500 t C d⁻¹,
259 Fig. 5), while the nitrogen loads in the Barotse Plains were almost twice as high as those in the Kafue
260 Flats (44 t N d⁻¹ and 20 t N d⁻¹) During the dry season the loads decrease slightly.

261

262 Net export was determined as the difference between the load at the downstream end of the floodplain
263 and the load at the upstream end of the floodplain (Table 1). During the wet season, the Barotse Plains
264 were a sink for all particulate phases, while the Kafue Flats acted as a source (Table 1). Both systems
265 were sources of DOC and DIC. Dissolved organic nitrogen was exported from both floodplains, but
266 the Barotse Plains retained the small DIN flux, while the Kafue Flats were a minor source. During the
267 dry season, the Barotse Plains acted as source of particulate matter. For the Kafue Flats this could not
268 be determined due to lack of POC and PN measurements in the downstream stretches of the river.

269 DOC and DIC were retained by both systems. The Barotse Plains were a minor source of dissolved
270 nitrogen, while the Kafue Flats retained both organic and inorganic nitrogen.

271

272

273 **4.3 C:N ratios and isotopes**

274

275 <<Figure 6>>

276

277 The C:N ratios of particulate organic matter (Fig. 6) remained fairly constant along the floodplain in
278 the Barotse Plains and Kafue Flats during the wet season (10.8 ± 0.7 and 7.5 ± 0.7 , respectively
279 (statistically significant difference at 95% confidence intervals)). During the dry season the along-
280 floodplain variability within each of the floodplains was larger (10.3 ± 1.5 and 10.3 ± 1.8 ,
281 respectively), but no significant difference was observed between the two systems. On average,
282 particulate carbon was more depleted in ^{13}C in the Kafue Flats compared to the Barotse Plains during
283 the wet season ($\delta^{13}\text{C} = -28.5 \pm 0.9$ and -26.9 ± 1.1 ‰, respectively (statistically significant $p < 0.05$)).
284 During the dry season mean $\delta^{13}\text{C}$ values were -28.5 ± 1.0 ‰ in the Barotse Plains and -26.5 ± 1.9 ‰ in
285 the Kafue Flats, again a significant difference. The organic matter in the Barotse Plains became more
286 enriched in ^{13}C during the wet season compared to the dry season, while in the Kafue Flats lower $\delta^{13}\text{C}$
287 values were observed during the wet season than during the dry season (both significant, $p < 0.05$).

288

289 The C:N ratio of the dissolved organic phase was more variable: While the wet season values of 17.5
290 ± 1.9 and 23.7 ± 3.4 were fairly similar for the Barotse Plains and Kafue Flats, respectively, they
291 differed widely during the dry season: 166 ± 20 and 22.7 ± 11.3 . The two systems differed
292 significantly ($p < 0.05$) from each other during a given season.

293

294 Paired analysis showed that there was no statistically significant ($p < 0.05$) difference in particulate
295 C:N ratios in the Barotse Plains between contrasting seasons, while there was a difference in
296 dissolved C:N ratios and C-isotopic signals. In the Kafue Flats, there was a significant decrease in
297 particulate C:N ratio from the dry to the wet season (as previously reported in Zurbrügg et al. (2013)).

298

299

300 **5. Discussion**

301 **5.1 Hydrology and inundation dynamics**

302 The discharge patterns (Fig. 3) showed how the bankfull capacity of the Zambezi and Kafue Rivers
303 varied along the floodplain stretch. In both systems water has moved from the main channel onto the
304 floodplain, roughly 600 and $400 \text{ m}^3 \text{ s}^{-1}$ in the Barotse Plains and the Kafue Flats, respectively. Where

305 the capacity of the channel increases again further downstream, water from the floodplains (and
306 potential tributaries) returned to the main channel at higher rates. On the floodplain, flow velocities
307 were extremely low ($< 1 \text{ mm s}^{-1}$ on the Kafue Flats in May 2008, unpublished data), which led to
308 prolonged residence times of the water on the floodplain, during which evaporation might occur,
309 resulting in heavier $\delta^{18}\text{O}$ signatures in floodplain water.

310

311 Using a mass balance approach based on oxygen isotopic data, Zurbrügg et al. (2012) calculated that
312 $>80\%$ of the water in the Kafue Flats had spent time on the floodplain during the wet season.
313 Logistical constraints prevented the collection of similar remote floodplain samples in the Barotse
314 Plains. Assuming a similar floodplain signal in the Barotse Plains as in the Kafue Flats, a first
315 approximation was made to determine how much water in the Barotse Plains has spent time on the
316 floodplain. This resulted in 50% of the water leaving the pristine floodplain area having spent time
317 outside the channel. This estimate shows that the interaction between river and floodplain was
318 stronger in the Kafue Flats than in the Barotse Plains, and reinforces the observation that a larger
319 fraction of the river discharge in the Kafue Flats was forced onto the floodplain at the constriction
320 location, compared to the Barotse Plains. In the published literature, high contributions of floodplain-
321 derived water are also reported for the Tonle Sap Lake-floodplain system, where water from the
322 Mekong contributed over 50% to the inflows of the lake, and more than 80% of the outflows from the
323 lake returned to the main river channel of the Mekong (Kummu et al., 2014). At peak flow in the
324 Amazon, 97% of the river inflow occurred at overbank flow at the Curuai floodplain, and this water
325 spent on average 19 days on the floodplain, according to the modeling results by Rudorff et al. (2014).

326

327 During the dry season, the increasing discharge along the Barotse Plains is most likely caused by
328 inflow of the Luanginga tributary. By contrast, the decreasing discharge in the Kafue Flats combined
329 with a calculated 16% of the downstream discharge having spent time on the floodplain (Zurbrügg et
330 al., 2012) indicated that there was still exchange between the river channel and some permanently
331 inundated areas in the downstream reaches of the Kafue Flats. In a regional perspective, the along-
332 floodplain increase in the $\delta^{18}\text{O}$ signal in the Barotse Plains and Kafue Flats during the wet (flooding)
333 season ($+0.21\text{‰}_{\text{VSMOV}}$ to $+0.56\text{‰}_{\text{VSMOV}}$ per 100 km) was considerably lower than the increase in the
334 Okavango delta during the dry (flooding) season ($+2.04\text{‰}$ per 100 km) and during wet season
335 ($+0.74\text{‰}_{\text{VSMOV}}$ per 100 km; calculated from Akoko et al. (2013)), indicating that there was
336 significantly less extensive evaporation on the Zambezi catchment floodplains than in the inland
337 Okavango delta.

338

339 **5.2 Seasonality of C and N export and retention**

340 During the wet season, the Barotse Plains were characterized by a net export of dissolved phases and
341 retention of particulate material. Degradation processes or settling of particulate organic matter, either

342 in the main channel or on the floodplain could result in apparent retention of POC and PN. The
343 concurrent export of DOC, DIC, and DON could similarly be a result of degradation, or of leaching of
344 vegetation or soils. During the dry season, the patterns were reversed, indicative of inputs of organic
345 matter from the Plains.

346

347 In contrast, the Kafue Flats were a net source for both particulate and dissolved phases during the wet
348 season, indicating a different balance. The high proportion of DIC to the net dissolved C export
349 suggests that degradation was a dominant process during flooding. While the constant POC:PN ratios
350 contradict large soil inputs, a combination of primary production around the edges of the main
351 channel, and degradation and leaching of soil and vegetation from the inundated floodplain (indicated
352 by low oxygen concentrations of the water from the floodplain (Zurbrügg et al., 2012)) could be
353 responsible for the observed patterns. During the dry season, the retention of DOC, DIC, DON, and
354 DIN pointed towards primary production potentially a minor contribution from sorption of dissolved
355 organic phases onto particulate material.

356

357 The observed net export of particulate organic matter might not have effects beyond the downstream
358 reservoirs of Lake Kariba and Kafue Gorge, respectively (Fig. 1). Both impoundments will trap
359 mobilized particles, and retain 70% and 90% of incoming total N and P within Lake Kariba (Kunz et
360 al., 2011a). Nevertheless, on a catchment scale, mobilization of particulate organic matter from the
361 inundated area of the river-floodplain systems resulted in specific POC and PON yields (net export
362 per inundated area per year; Table 2) from the Barotse Plains, which were close to an order of
363 magnitude higher than previously reported values for the entire Zambezi River (Beusen et al.,
364 2005; Mayorga et al., 2010). Despite the behavior as a sink during the wet season, the normalization to
365 inundated area has resulted in positive annual export from the floodplain. Also, DOC yields from the
366 Barotse Plains were higher than previously estimated for the Zambezi, but comparable to those
367 measured in the Amazon and Orinoco rivers (Table 2; Beusen et al. (2005); Harrison et al. (2005);
368 Lewis and Saunders (1989)). Similarly, DON yields from the pristine floodplain were similar to
369 values measured in the Amazon and Orinoco (Table 2). The Kafue Flats show negative DOC, DON,
370 DIN yields, i.e. are retaining these species. These negative yields show how floodplains can impact
371 the riverine loads in trends opposite to those observed for the whole catchment. Similarly, the high
372 yields from the Barotse Plains underlined the dominant role of floodplains as biogeochemical reactors
373 in riverine transport of organic matter from land to sea.

374

375 <<Table 2>>

376

377 **5.3 Sources of organic matter**

378 **5.3.1 Dissolved organic matter**

379 Based on the export and retention behavior of the two floodplains, degradation of floodplain-derived
380 organic matter may be a large source of DOC in the Barotse Plains during the wet season. During the
381 dry season, organic matter inputs from the floodplain and sorption of dissolved organic phases to
382 particles may have decreased the DOC concentrations. In the Kafue Flats, degradation of organic
383 matter on the floodplain was contributing to in-stream DOC during the wet season, whereas during
384 the dry season, similarly to the Barotse Plains, primary production and sorption of dissolved phases
385 onto particles were lowering DOC and DON concentrations. The high contribution of DON to TDN
386 further indicates that the Zambezi and Kafue Rivers are still relatively pristine, as anthropogenic
387 activities mainly add N in the form of DIN to aquatic systems (Berman and Bronk, 2003).

388
389 The elevated C:N ratio of the dissolved organic matter was indicative of terrestrial origin of the
390 organic material in both systems. The ITT reservoir did not have a pronounced impact on the
391 dissolved phase (C:N around 23 during both seasons), which has previously been attributed to a
392 mostly refractory dissolved organic matter phase (Zurbrügg et al., 2013). The comparison with the
393 Barotse Plains revealed a much larger variability in C:N of the dissolved matter reaching dry season
394 values of 166 compared to the wet season signatures around 18. While DOC concentrations were
395 fairly similar during both seasons, the large decrease in DON concentrations from the wet to the dry
396 season (Fig. 4) has resulted in this shift in dissolved C:N ratio.

397
398 The increase in DOC and DON concentrations during the wet season in the Barotse Plains compared
399 to the dry season also corresponds to the general observation that DOC export increases with runoff,
400 caused by shallowing of the flow paths through organic-rich upper soils (Mulholland,
401 2003; Aitkenhead-Peterson et al., 2003). This seasonal variability in DOC and DON concentrations
402 has been previously shown in Hawaii (Wiegner et al., 2009) and Congo (Spencer et al., 2010). Runoff
403 from inundated soils, such as found in the Zambezi River Basin during the wet season, also tend to
404 have higher DON concentrations (Aitkenhead-Peterson et al., 2003). This (potentially refractory)
405 source of DON might be responsible for the high DON concentrations found in the Barotse Plains
406 during the wet season. For the Kafue Flats, there was no significant seasonal change in DOC and
407 DON concentrations between the wet and dry seasons. This might be due to the fact that an increase
408 in DOC and DON concentration in the upstream catchment would be diluted and delayed by the
409 presence of the Itzhi-Tezhi dam, showing after peak flow. With a residence time of 0.7 years, large
410 fractions of organic carbon ($\pm 16\%$) and nutrient loads (50% N, 60% P) were trapped in the sediments
411 of the reservoir (Kunz et al., 2011b). Monthly measurements showed that the highest TOC
412 concentrations occurred in the main channel in the floodplain area in May/June, after the peak flow

413 (Wamulume et al., 2011). This could be a delayed effect of the increased concentrations at higher
414 runoff during the wet season (November-March).

415

416 **5.3.2 Particulate organic matter**

417 The higher C:N ratio of the suspended matter in the Barotse Plains year-round indicates a soil-derived
418 source in the pristine part of the catchment. In contrast, C:N ratios found in the Kafue Flats during the
419 wet season were indicative of aquatic production (Zurbrügg et al., 2013). This could be attributed to
420 the presence of the ITT reservoir: surface sediments from the reservoir showed an elevated C:N ratio
421 (12.1 ± 0.6 , Supplementary information of Zurbrügg et al. (2013)), similar to the numbers found for the
422 suspended matter in the Barotse Plains. Hence, the presence of the dam significantly affected the
423 chemical composition of the suspended matter, and while soil-derived suspended matter settled in the
424 reservoir, mainly photosynthetically produced organic matter from the reservoir surface waters
425 reached the Kafue Flats and eventually the Kafue-Zambezi confluence. The decrease in C:N ratio
426 along the floodplain in the Kafue Flats during the dry season could be indicative of gradual organic
427 matter input from nitrogen-fixating vegetation. As a consequence of nutrient elimination in the ITT
428 reservoir, widespread encroachment of N-fixing woody plants onto the floodplain has been observed
429 (Blaser, 2013).

430

431 While the C:N ratio showed little variation throughout the year in the Barotse Plains, the stable C-
432 isotopic signatures of the particulate matter further suggest different contributors to the POC in the
433 river. During the wet season, the particulate organic matter in the Barotse Plains is ^{13}C enriched
434 compared to the dry season (-26.9 and -28.5‰, respectively). Organic matter sources on the
435 floodplain (soils on average -18‰, abundant reeds between -12 and -27‰, unpublished data) had
436 distinctly heavier $\delta^{13}\text{C}$ signatures than the permanent vegetation in the area (average of 6 different tree
437 species -28.3 ± 1.22 ‰, unpublished data). Inputs from permanent vegetation were the dominant
438 source of organic matter during the dry season, whereas inputs from the floodplain during the wet
439 season led to more enriched values. Shifts to isotopically heavier organic matter during the wet season
440 as observed in the Barotse Plains, have been described for the Tana River in Kenya (Tamooh et al.,
441 2014), the Sanaga River in Cameroon (Bird et al., 1998), and the Congo River in Central Africa
442 (Mariotti et al., 1991). These studies clearly showed how the source of organic matter transported by
443 tropical rivers is changing with inundation.

444

445 In contrast, the particulate organic matter in the Kafue Flats was more enriched during the dry season
446 compared to the wet season (-26.5 and -28.5‰, respectively). The average dry season $\delta^{13}\text{C}$ value for
447 the Kafue Flats should be interpreted with caution, since there is a clear spatial pattern: values become
448 more depleted towards the end of the floodplain. This spatial pattern has previously been attributed to

449 floodplain-derived particulate organic matter, which would consist of phytoplankton and periphyton
450 material in the permanently inundated area in the downstream reaches of this floodplain (Zurbrügg et
451 al., 2013). In the more typical stretch of the floodplain however, the dry season value was even
452 heavier. The encroaching species have resulted in a vegetation pattern with C₄ species occurring close
453 to the river, and C₃ species growing on the higher grounds that are only seasonally flooded (Blaser,
454 2013;Ellenbroek, 1987). The inputs from these encroaching species can be considered as terrestrial
455 inputs of permanent vegetation.

456

457 The difference in composition and origin between dissolved and particulate phases, i.e. DOM from
458 terrestrial sources, POM more aquatic influence has previously been described for the Amazon
459 (Aufdenkampe et al., 2007;Hedges et al., 1986) and the Fly-Strickland system in Papua New Guinea
460 (Alin et al., 2008). We showed that the interaction of the river with its floodplain is responsible for the
461 changes observed in organic matter characteristics, but that influence of aquatic production in the
462 systems only originated from the reservoir.

463

464

465 **6. Conclusions**

466 << Figure 7 >>

467

468 While the pristine Barotse Plains and dam-impacted Kafue Flats seem to have similar properties in
469 terms of timing and dynamics of seasonal flooding, there are several marked differences between the
470 two systems with respect to hydrology, carbon and nutrient dynamics, and sources of the organic
471 matter (Fig. 7). Based on an oxygen isotope mass balance, a larger fraction of water has spent time on
472 the floodplain at the outflow of the Kafue Flats compared to the Barotse Plains. The two floodplains
473 have significantly different concentrations of dissolved carbon and nutrient species during both wet
474 and dry seasons. Over an annual cycle, the Barotse Plains export more carbon and nutrients
475 normalized to the floodplain area (yields) than previously reported for the Zambezi and other tropical
476 rivers. The Kafue Flats are exhibiting negative yields, effectively retaining and accumulating organic
477 matter and nutrients over a full hydrological cycle. Particulate organic carbon $\delta^{13}\text{C}$ values indicated a
478 larger contribution of floodplain-derived organic matter in the Barotse Plains than in the Kafue Flats
479 during the wet season, and the reversed situation during the dry season. The spatial distribution of C_3
480 and C_4 plants in the floodplains disrupts the signal of floodplain inputs during the wet season in the
481 Kafue Flats.

482

483 Differences between the two systems that can be attributed to the presence of the Itezhi-Tezhi
484 reservoir upstream of the Kafue Flats included a delay of the input of runoff-derived floodplain soil
485 organic matter and altered inputs to the particulate organic matter pool in the Kafue Flats. The
486 difference between sources of organic matter in the two floodplains partly also results from the
487 presence of the Kafue River dams: since the dam construction, woody encroachment onto the Kafue
488 Flats floodplain has increased, contributing to the wet-season signal of permanent vegetation. This is a
489 result of the presence of the dams that only became evident with time, and shows the importance for
490 monitoring after dam construction.

491

492 **Author contributions**

493 A. L. Zuijdgeest, R. Zurbrügg, D. B. Senn, and B. Wehrli were responsible for the study design. A. L.
494 Zuijdgeest, R. Zurbrügg, N. Blank, and R. Fulcri performed the fieldwork and the laboratory analyses.
495 Data analysis was performed by A. L. Zuijdgeest, R. Zurbrügg, and D. B. Senn, and supported by N.
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511

512

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703

704

Tables

Table 1. Net export (in t C d⁻¹ and t N d⁻¹), calculated as the difference between loads at the downstream and upstream ends of the respective floodplain, from the two floodplains during wet and dry seasons. Positive numbers indicate that the floodplain acted as a source (export), negative numbers indicate the floodplain acting as a sink (retention). POC and PN export from the Kafue Flats during the dry season could not be estimated due to lack of measurements at downstream locations.

System		POC	DOC	DIC	PN	DON	DIN
Barotse Plains	<i>Wet season</i>	-38	170	270	-3.7	12	0.0
	<i>Dry season</i>	14	-1.5	-78	1.6	0.0	0.0
Kafue Flats	<i>Wet season</i>	6.5	160	640	0.6	11	0.1
	<i>Dry season</i>	NA	-11	-89	NA	-0.8	-0.2

Table 2. Yields of carbon, nitrogen and phosphorus in kg (C or N) km⁻² yr⁻¹ from large river basins and floodplain yields from the Barotse Plains and Kafue Flats. Yields for this study are calculated assuming 6 months of dry-season export, and 6 months of wet-season export. Inundation areas should be considered conservative estimates (see methods section for how inundation areas were estimated). Dry-season areas were estimated based on river length and width. POC and PN yields from the Kafue Flats during the dry season could not be estimated due to lack of measurements at downstream locations.

Sources: a Beusen et al. (2005), b Bouillon et al. (2014), c Esser and Kohlmaier (1991), d Harrison et al. (2005), e Lewis and Saunders (1989), f Mayorga et al. (2010), g Hall et al. (1977).

River	POC	DOC	PN	DON	DIN
Amazon	2900 ^a	5200 ^d	500 ^a	330 ^d , 180 ^f	170 ^f
Congo	1400 ^a , 400 ^c	3300 ^a , 1600 ^c	200 ^a	92 ^c , 58 ^f	32 ^f
Orinoco	1500 ^e	5600 ^d , 5200 ^e	190 ^e	310 ^d , 190 ^e , 170 ^f	
Oubangui	180-300 ^b	660-1500 ^b	20-29 ^b		
Zambezi	800 ^a	1000-2000 ^f	100 ^a	-	14 ^f , 100-300 ^g
This study:					
Barotse Plains	8000	3000	880	310	0
Kafue Flats	NA	-2700	NA	-200	-110

Figures

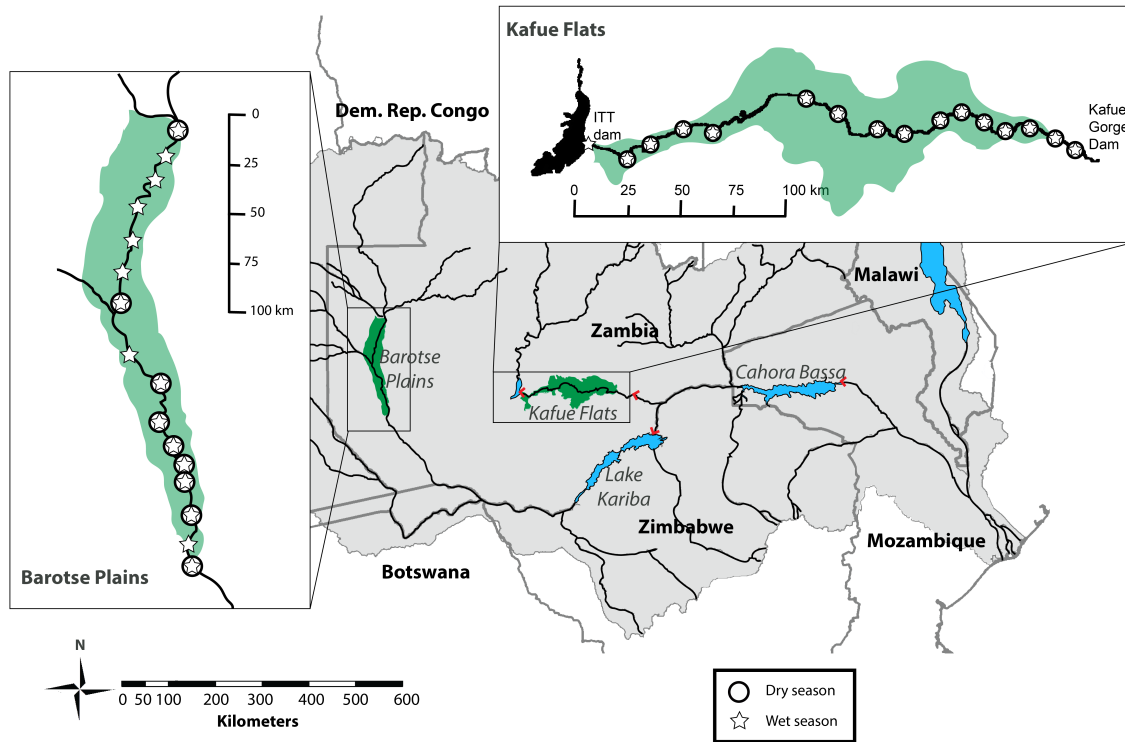


Figure 1. Map of the Zambezi catchment, with floodplains (in green) and large dams (red arrows) marked. Inserts show sampling stations during the dry (circles) and wet season (stars) in the Barotse Plains and Kafue Flats. Sampling stations will be further presented in distance along the river (km).

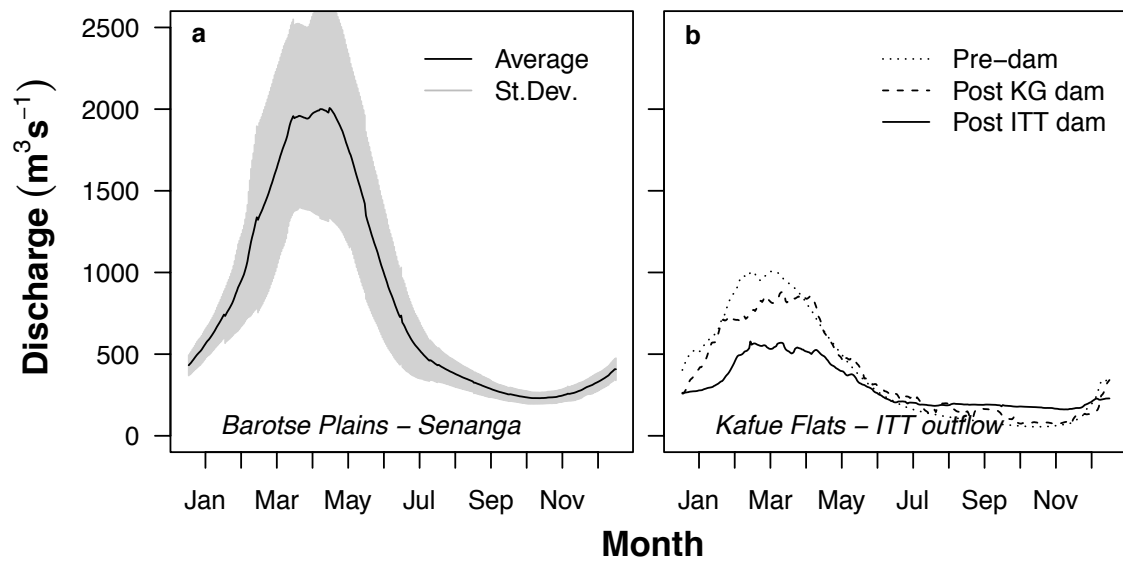


Figure 2. River discharge (a) at Senanga, the downstream boundary of the Barotse Plains (1988-2006 average and standard deviation) and (b) at the outflow of Itezhi-Tezhi (ITT) dam, the upstream boundary of the Kafue Flats. Discharge for the Kafue Flats are means of pre-dam (1960-1971), and post-dam construction (Kafue Gorge dam: 1972-1977; ITT dam: 1978-2010) periods. Data from the Department of Water Affairs and Zambezi River Authority, permission for reprint first granted to Blaser (2013).

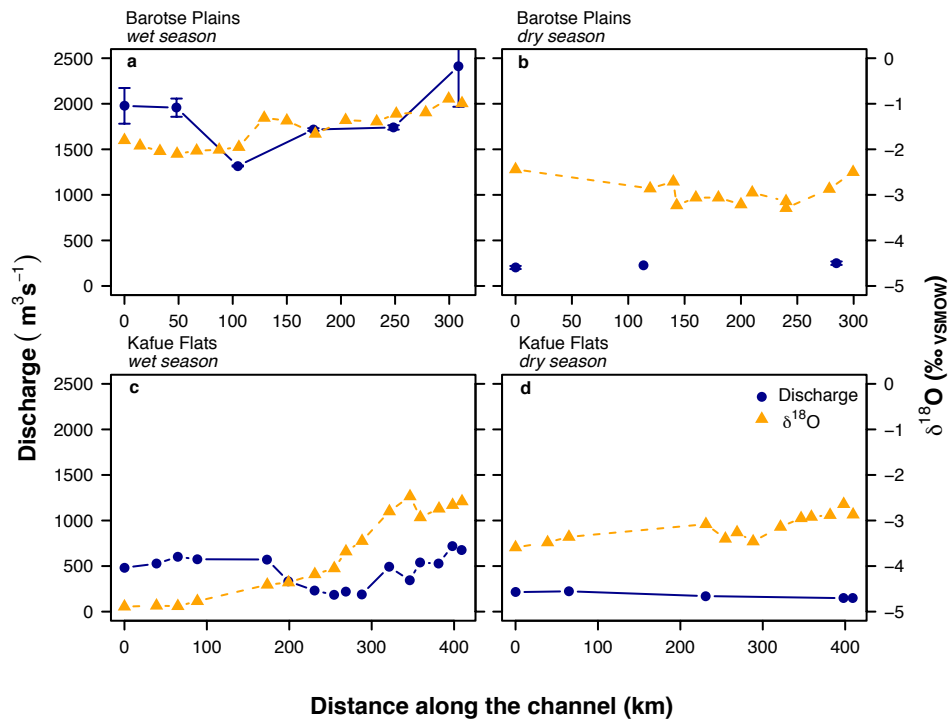


Figure 3. Discharge and stable oxygen isotope signals in the Barotse Plains and the Kafue Flats during wet and dry seasons. Discharge and $\delta^{18}\text{O}$ data for the Kafue Flats have been published previously in Zurbrügg et al. (2012).

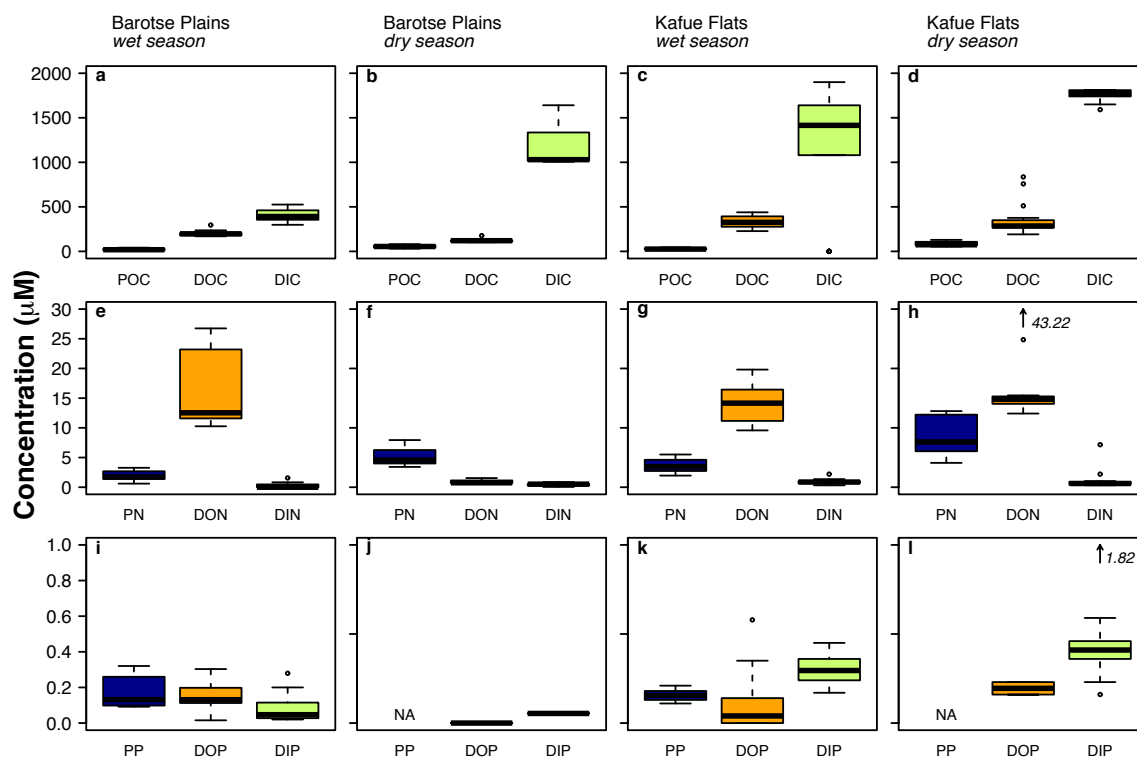


Figure 4. Boxplots of the concentrations of dissolved and particulate carbon, nitrogen and phosphorus species along the Barotse Plains and the Kafue Flats during wet and dry seasons along the floodplain. The boxes represent the first and third quartiles, and the median. No measurements of particulate phosphorus were made on samples from the dry seasons. Carbon and nitrogen data of the Kafue Flats have been previously published in Zurbrügg et al. (2013).

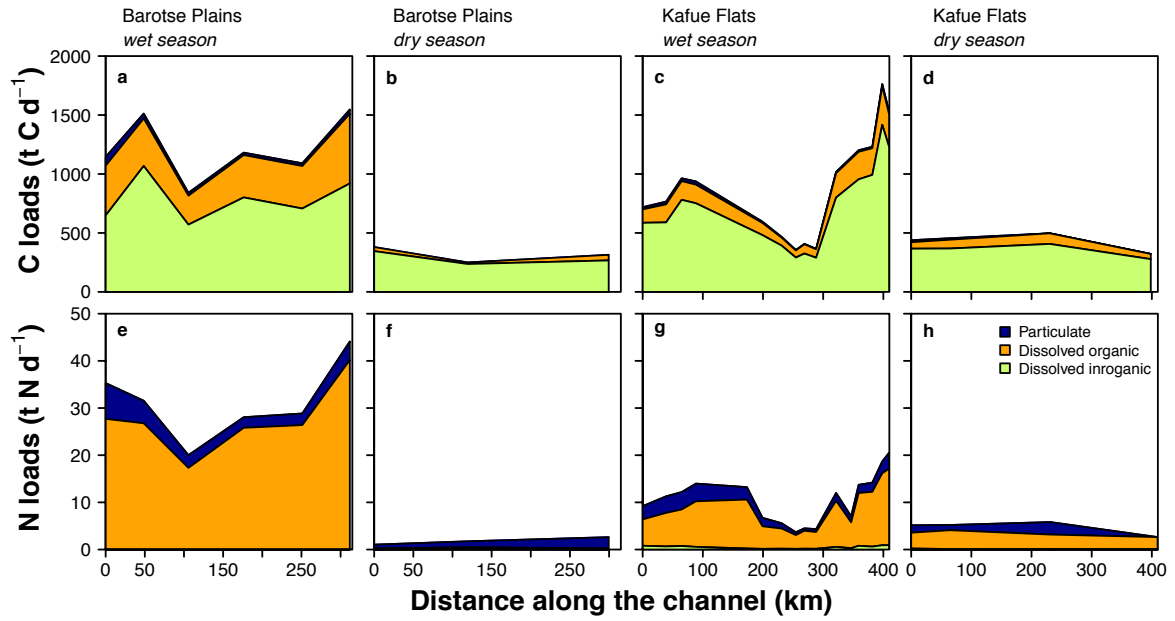


Figure 5. Dissolved and particulate carbon and nitrogen loads along the Barotse Plains and the Kafue Flats during wet and dry seasons. The loads of particulate carbon and nitrogen at the two most downstream locations in the Kafue Flats could not be determined for the dry season due to lack of POC and PN measurements.

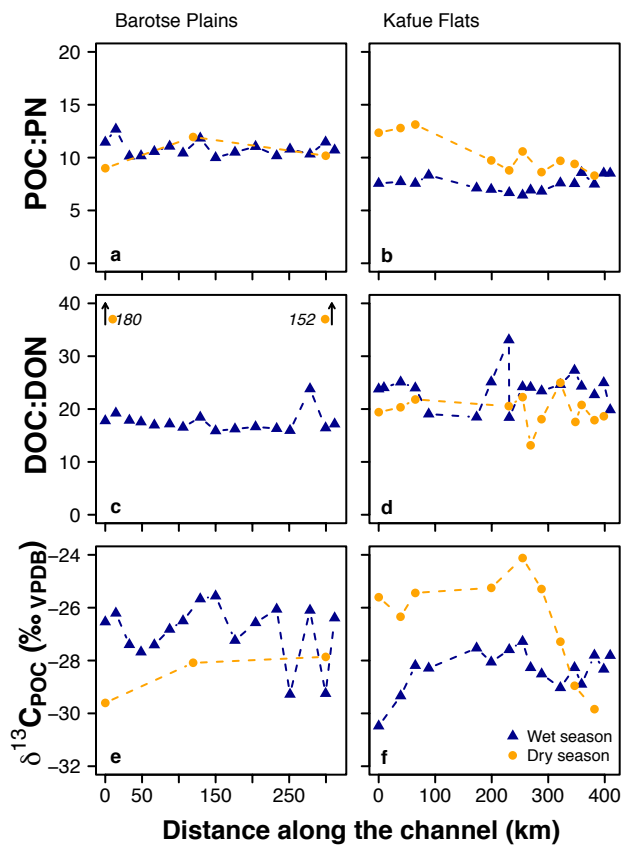


Figure 6. Carbon to nitrogen (C:N) ratios of particulate and dissolved organic matter as well as carbon isotopic signatures of particulate organic matter during wet (blue triangles) and dry (orange circles) seasons. The Kafue Flats data have been previously published in Zurbrügg et al. (2013).

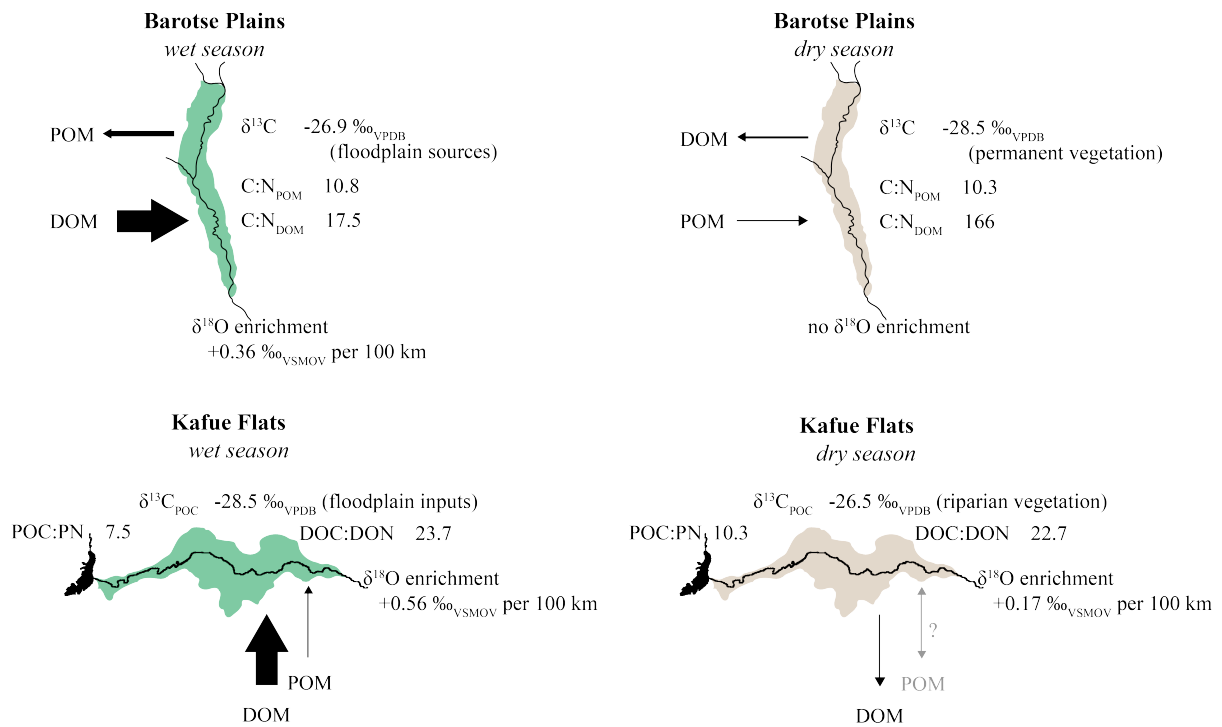


Figure 7. Summary of the organic matter characteristics ($\delta^{13}\text{C}$, POC:PN, DOC:DON), oxygen isotopic enrichment along the floodplain, and proportional arrows for net export and removal rates of POM (POC+PN) and DOM (DOC+DON) in the Barotse Plains and Kafue Flats during the wet and dry season.