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Organic carbon and nitrogen export from a tropical dam-impacted floodplain system

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Abstract. Tropical floodplains play an important role in organic matter transport, storage, and transformation between headwaters and oceans. However, the fluxes and quality of organic carbon (OC) and organic nitrogen (ON) in tropical river-floodplain systems are not well constrained. We explored the quantity and characteristics of dissolved and particulate organic matter (DOM and POM, respectively) in the Kafue River flowing through the Kafue Flats (Zambia), a tropical river-floodplain system in the Zambezi River basin. During the flooding season, $> 80\%$ of the Kafue River water passed through the floodplain, mobilizing large quantities of OC and ON, which resulted in a net export of 69–119 kg OC km^{-2} d^{-1} and 3.8–4.7 kg ON km^{-2} d^{-1}, 80 % of which was in the dissolved form. The elemental C : N ratio of ~ 20, the comparatively high δ^{13}C values of -25 ‰ to -21 ‰, and its spectroscopic properties (excitation-emission matrices) showed that DOM in the river was mainly of terrestrial origin. Despite a threefold increase in OC loads due to inputs from the floodplain, the characteristics of the riverine DOM remained relatively constant along the sampled 410-km river reach. This suggests that floodplain DOM displayed properties similar to those of DOM leaving the upstream reservoir and implied that the DOM produced in the reservoir was relatively short-lived. In contrast, the particulate fraction was ^{13}C-depleted (-29 ‰) and had a C : N ratio of ~ 8, which indicated that POM originated from phytoplankton production in the reservoir and in the floodplain, rather than from plant debris or resuspended sediments. While the upstream dam had little effect on the DOM pool, terrestrial particles were retained, and POM from algal and microbial sources was released to the river. A nitrogen mass balance over the 2200 km^2 flooded area revealed an annual deficit of 15 500–22 100 t N in the Kafue Flats. The N isotope budget suggests that these N losses are balanced by intense N-fixation. Our study shows that the Kafue Flats are a significant local source of OC and ON to downstream ecosystems and illustrates how the composition of riverine OM can be altered by dams and floodplains in tropical catchments.

1 Introduction

Floodplains can act as major sources or sinks for riverine carbon (C) and nitrogen (N), regulating the organic matter (OM) transport from headwaters to downstream systems such as lakes and oceans. Numerous studies in temperate floodplains have quantified their function as efficient particle and nutrient sinks (e.g. Noe and Hupp, 2009; Hoffmann et al., 2011; Olde Venterink et al., 2003), while only a few studies have examined tropical systems (e.g. McJannet et al., 2012). Despite the importance of wetlands in the global C cycle, the role of floodplains for riverine C storage, transformation and export has not been well constrained (Battin et al., 2009). This is particularly true for the large wetlands in the tropics, which are among the most productive and valuable ecosystems worldwide.

Previous studies have investigated the biogeochemistry of dissolved organic carbon (DOC) in different tropical river-floodplain systems (e.g. Alin et al., 2008; Aufdenkampe et al., 2007; Spencer et al., 2010), and identified large

differences in age, origin, chemical structure and bioavailability within the DOC pool and between DOC and particulate organic C (POC). While POC in forested catchments has frequently been associated with plant debris, the source allocation of DOC is more complex and often inconclusive (Tremblay and Benner, 2009). The organic N fraction, in particular the analysis of dissolved organic N (DON), however, has seldom been used as a means of dissolved OM (DOM) characterization in tropical systems, despite the fact that DON accounts for 50–90 % of total dissolved N (TDN), and generally high DON export from tropical catchments (Berman and Bronk, 2003; Wiegner et al., 2009).

Hydrological interaction between rivers and floodplains has been identified as a primary factor governing OM mobilization and nutrient dynamics in temperate systems (Hunsinger et al., 2010). In the tropical floodplains of the Amazon basin, river-floodplain exchange has been shown to affect particle distribution and storage (Aalto et al., 2003), cause shifts in the composition of riverine OM due to the injection of floodplain-derived OM to rivers (Richey et al., 1990), and foster in-stream mineralization of OM (Mayorga et al., 2005).

In this study we examined the changes in loading and quality of riverine OC and ON during passage through highly productive floodplains. We characterized POM and DOM in the Kafue Flats (Fig. 1a), a floodplain system along the Kafue River, the largest tributary of the Zambezi River in southern Africa. The hydrology of the Kafue River shows a distinct seasonality, with more than 80 % of the river discharge during the wet season (600–800 $m^3 s^{-1}$) passing through the floodplain (Zurbrügg et al., 2012). For comparison, only ∼ 30 % of the Amazon stream flow travels through floodplains (Richey et al., 1989). During the dry season, the discharge is rather constant and the exchange with the floodplain strongly reduced. Intense river-floodplain exchange exerts a strong influence on river biogeochemistry of the Kafue River, as evidenced by pronounced hypoxia over the last 150 km-long river reach dominated by lateral inflows from the inundated floodplain (Zurbrügg et al., 2012).

The case of the Kafue Flats illustrates how a pristine tropical floodplain system can be affected by water resources development. Two large dams built in the 1970s have altered the hydrological regime (Zurbrügg et al., 2012), and the flooding patterns in the Kafue Flats (Mumba and Thompson, 2005; Meier et al., 2010). The associated changes in downstream flooding modified the hydrological connectivity between river and floodplain, and could eventually affect the quality and fluxes of OM (Bouillon et al., 2009). Biogeochemical impacts of dam operation in this system have been addressed recently (Zurbrügg et al., 2012; Kunz et al., 2011) as part of an effort to quantify the effect of damming on fluvial ecosystems in the tropics.

The goals of this study were (1) to quantify retention or leaching and export of OC and ON from the floodplain to the river, and the net export from the Kafue Flats; (2) to determine source, quality and fate of the exported OM during the flooding and dry season; (3) describe how intense river-floodplain exchange affects the sources of OM transported by the Kafue River; and (4) to explore changes in OM mobilization, transport, and quality that are related to dam operation. We hypothesized that intense river-floodplain exchange and the backflow from the floodplain carries large OM loads with terrestrial characteristics to the river and alter the composition of the riverine OM. In addition, we hypothesized that dam operation would affect the source and quality of OM in the downstream Kafue Flats.

2 Methods

2.1 Study site – Kafue Flats

The Kafue Flats are a floodplain system along the Kafue River in Zambia (Fig. 1a). The total area of the floodplain is 6500 km^2, whereof up to 3300 km^2 are seasonally inundated (Köck, personal communication). The annual flooding occurs from January to August and is caused by direct precipitation (November–April; mean 800 mm), the peak flows of the Kafue River (up to 1900 $m^3 s^{-1}$; Fig. 1b), and seasonal tributaries, creating an extensive wetland area and rich wildlife habitat. The floodplain vegetation fringing the river channel consists of highly productive C_4 grasses, with a net primary production of 800–2000 $g C m^{-2} yr^{-1}$, while water meadows with less productive C_3 vegetation prevail in the more distant areas (Ellenbroek, 1987). During the dry season from June-October, river discharge drops to < 100 $m^3 s^{-1}$ (Fig. 1b) and the floodplain dries up almost completely. The land use in the immediate catchment is traditional, that is, small-scale cattle farming and fisheries, and large areas remain unutilized. Sugar cane plantations are located along the last 60 river-km, leaving large sections of the Kafue Flats relatively pristine.

The hydrology of the Kafue River ($Q_{avg} \sim 300 m^3 s^{-1}$) has been influenced by two large dams at Itezhi-Tezhi (ITT; closed in 1978) immediately upstream of the flats, and Kafue Gorge (closed in 1972), immediately downstream of the flats (Fig. 1c). At ITT dam, water is currently released to the floodplain via spillways, draining the reservoir's epilimnion. A recent study by Kunz et al. (2011) showed that ITT reservoir (with a hydraulic residence time of ∼ 0.7 yr) efficiently traps particles and removes 50 % of N and 60 % of P inputs from the Kafue River.

Intense hydrological exchange between river and floodplain has been identified as a major feature in the Kafue Flats (Zurbrügg et al., 2012). A constriction of the river channel forced 70 % of the stream flow into the floodplain between 180 and 225 km downstream of ITT dam (Fig. 2). The backflow from the wetlands caused a seasonally recurring steep decline in dissolved oxygen (DO) concentration down to < 1 $mg l^{-1}$ and low DO levels (< 2 $mg l^{-1}$) along a 150-km river reach.
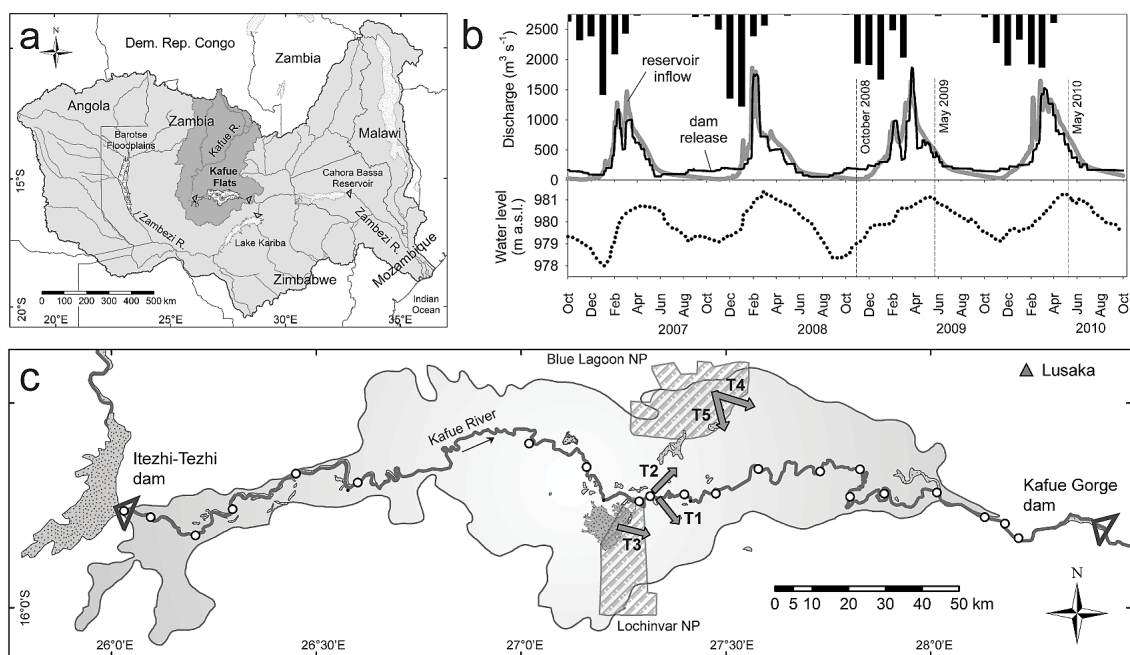
Fig. 1. (a) Kafue Flats in the Kafue River basin (dark shaded), a sub-basin of the Zambezi River basin (light gray). **(b)** The hydrograph from 2007–2010 shows the reservoir inflow (gray line), dam release (black line), rainfall (bars), and the water level in the middle of the floodplain (dotted line, lower panel). The three sampling campaigns are marked by vertical lines. **(c)** Map of the Kafue Flats. Dams are marked with triangles, white dots indicate sampling stations along the main channel, arrows T1–T5 depict transects into the floodplain.

The extent of river-floodplain exchange during inundation was quantified in a mixing model using natural tracers such as specific conductivity and δ^{18}O-H$_2$O (stable oxygen isotope composition of water; Zurbrügg et al., 2012). The tracer levels in ITT reservoir and along transects into the floodplain served as end members to calculate the fractions of floodplain and reservoir water to the river discharge for the 410 km longitudinal transect (Fig. 2). Intense lateral exchange was observed after $\sim$ 230 km, by monitoring the increasing contribution of floodplain water to river discharge (Fig. 2). As a net result, more than 80 % of the water leaving the Kafue Flats had passed through the floodplain. A comparison of the 2008–2009 exchange regime with historical discharge data showed that the magnitude river-floodplain exchange has been reduced by 50 % since the construction of the two dams in the 1970s (Zurbrügg et al., 2012). In addition, dam operation also changed the timing and extent of inundation in the Kafue Flats (Mumba and Thompson, 2005).

2.2 Sampling campaigns

After a pilot campaign in May 2008, three spatially intensive sampling campaigns were carried out during the dry season (October 2008), and the flooding seasons in May 2009 and May 2010 (Fig. 1b). Sampling was conducted along the Kafue River at $\sim$ 20 km resolution from downstream of the spillways at ITT dam (0 km) until the end of the floodplain (410 km; Fig. 1c). To characterize floodplain waters, addi-
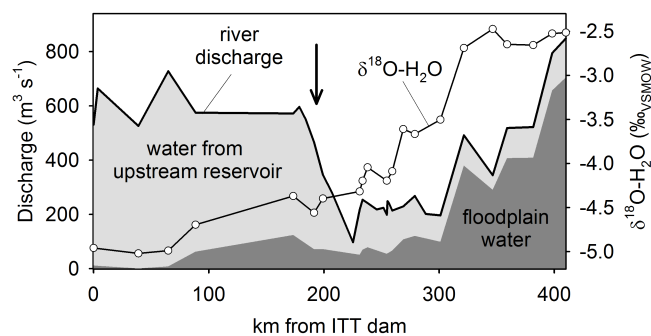
Fig. 2. Evidence of river-floodplain exchange in May 2010, indicated by an increasing proportion of floodplain-derived water (dark gray shading) to the river discharge (solid line) relative to water from the upstream reservoir (light gray shading). The contribution of floodplain water was calculated by a mixing model based on δ^{18}O-H$_2$O along the river (full circles). For details see Zurbrügg et al. (2012). The arrow marks the steep decline in discharge (180–225 km) caused by a constriction in the river channel.

tional samples were taken along 2–7 km transects perpendicular to the Kafue River into the floodplain (T1–T3), and from the wetland boundaries towards the floodplain in Blue Lagoon National Park (T4–T5; Fig. 1c) in May 2010. Water samples were pumped from mid-depth in the middle of the well-mixed river channel through hydrochloric acid (HCl) and MilliQ-washed polyethylene and teflon tubing, using a

peristaltic pump (Ejikelkamp, 12 VDC Standard). The tubing was flushed repeatedly before taking samples, and the contact time was minimized to avoid contamination. Samples for DOC and DON, and spectroscopic analyses were filtered in the field through 0.7 µm glass fiber (GF) filters (Whatman) into glass bottles and LDPE bottles for DON. Samples for spectroscopic analyses were kept at 4 °C in the dark and analyzed within 3–4 weeks after sampling. Replicate measurements were done after different storage times after sampling and no effect of storage was detected. Water samples for elemental and isotope analyses were acidified to pH 2.5 and frozen until further analysis. For POC and particulate N (PN) characterization, particles from ~ 2 L of water were collected on 0.7 µm GF filters (Whatman) and frozen until analysis. All sampling equipment was 2 M HCl / MilliQ-washed, glassware and filters were, in addition, pre-combusted (6 h at 450 °C). For comparative purposes, δ^{13}C, δ^{15}N and C and N contents were also analyzed in floodplain vegetation, soil OM, river sediment, and dry deposition (see Supplement for details).

2.3 Laboratory analyses

2.3.1 Concentrations and stable isotopic composition of DOC, POC and PN

DOC concentration was measured on a Shimadzu 5050 TOC analyzer. For POC and PN concentration and C and N isotope measurements (δ^{13}C-POC and δ^{15}N-PN, respectively), GF filters were dried (3 h at 40 °C), and cut into subsamples. POM samples were not acidified because the sediments of ITT reservoir contained only negligible amounts of inorganic carbon (Kunz et al., 2011) and the epilimnion was undersaturated with respect to calcium carbonate ($CaCO_3$; data not shown). POM aliquots were enclosed in tin capsules and measured on a FlashEA 1112 coupled to a DeltaV Adantage Continuous-Flow Isotope Ratio Mass Spectrometer (FlashEA-CF-IRMS; ThermoFinnigan). In-house ethylenediaminetetraacetic acid (EDTA; δ^{13}C $= -30.25$ ‰$_\text{VPDB}$; δ^{15}N $= -1.1$ ‰$_\text{air}$) and ammonium oxalate standards (δ^{13}C $= -17.02$ ‰$_\text{VPDB}$; δ^{15}N $= +32.7$ ‰$_\text{air}$) were used for calibration, with a precision of ± 0.1 ‰$_\text{VPDB}$ for δ^{13}C and ± 0.2 ‰$_\text{air}$ for δ^{15}N. The isotopic ratios are reported using the delta notation, that is, δ^{13}C or δ^{15}N $= (R_\text{sample} - 1) \times R_\text{standard} \times 1000$ ‰ , where R is the isotopic ratio (^{13}C : ^{12}C or ^{15}N : ^{14}N) of the sample (R_sample) and the standards (R_standard), i.e. Vienna Pee Dee Belemnite (VPDB) for C and atmospheric N_2 for N.

For the C-isotope analysis of DOC (δ^{13}C-DOC), 1 ml of 5 g l^{-1} high-purity, precombusted potassium sulfate (K_2SO_4) was added to 40 ml of sample and the acidic samples were purged for 2 min with argon to remove inorganic C (HCl had been added in the field), refrozen and freeze-dried (Schwendenmann and Veldkamp, 2005). The precipitate was measured on the same FlashEA-CF-IRMS using IAEA-CH6 su-

crose (δ^{13}C $= -10.45$ ‰$_\text{VPDB}$), EDTA and ammonium oxalate as standards at an analytical precision of ± 0.1 ‰$_\text{VPDB}$. The analytical precision is based on replicate measurements of untreated standards of sucrose ($n = 7$) and ammonium oxalate ($n = 7$), and standards that were processed as samples ($n = 6$ and $n = 8$, respectively).

2.3.2 Concentrations of DIN and DON, and δ^{15}N-TDN

For dissolved inorganic N (DIN), ammonium (NH_4^+) and nitrite (NO_2^-) were measured using standard colorimetric techniques. The sum of nitrate (NO_3^-) and NO_2^- was determined by reduction to nitrous oxide (Braman and Hendrix, 1989) in an acidic vanadium (III) solution in an Antek 745 preparation module followed by chemoluminescence detection (Antek 9000), and NO_3^- was calculated by difference.

TDN was measured according to Solórzano and Sharp (1980) and Bronk et al. (2000) by oxidizing 12 ml of filtered sample to NO_3^- with 2 ml of persulfate oxidizing reagent (POR), which consisted of 6 g potassium peroxydisulfate ($K_2S_2O_8$) and 6 g sodium hydroxide (NaOH; both ACS-grade) per 100 ml MilliQ water (Knapp et al., 2005). In order to reduce the nitrogen blank of POR, the peroxydisulfate salt was recrystallized 3–5 times according to Grasshoff et al. (1999) and stored under argon atmosphere. Samples with POR were autoclaved in 30 ml Pyrex vials (acid washed, precombusted, teflon-lined lids) for 55 min and the NO_3^- concentration was measured as described above. IAEA-N2 (ammonium sulfate (NH_4)$_2SO_4$; $+20.3$ ‰$_\text{air}$), USGS-41 (L-glutamic acid; $+47.6$ ‰$_\text{air}$), urea ($+0.24$ ‰$_\text{air}$), and EDTA were used as processing and isotopic standards, and were oxidized with the samples over the expected concentration range (Fig. S1, Supplement). The oxidation yield was 95–106 % after blank correction. Duplicates of pure POR solution were oxidized with every run to determine the contribution of POR to the N blank. The POR blank contribution was generally 0.5 ± 0.3 µM per sample, which is equal to ~ 3 % of the sample TDN. DON concentrations were calculated as $DON = TDN - NO_3^- - NO_2^- - NH_4^+$.

The δ^{15}N ratio of TDN-derived NO_3^- (δ^{15}N-TDN) was measured according to Knapp et al. (2005) and Bourbonnais et al. (2009), combining persulfate oxidation and the denitrifier method (Casciotti et al., 2002; Sigman et al., 2001) where NO_3^- is bacterially converted to N_2O. After microbial reduction of NO_3^-, N_2O was measured on a modified GasBench II with a GC PAL autosampler coupled to a Delta Plus XP Continuous Flow IRMS (all instruments ThermoFinnigan). IAEA-NO3 ($+4.7$ ‰$_\text{air}$) and in-house UBN1 ($+14.2$ ‰$_\text{air}$) were used as δ^{15}N-NO_3^- standards. DON dominated TDN in all samples (generally > 94 %), therefore, δ^{15}N-TDN can be considered a reasonable approximation to δ^{15}N-DON and no large changes from NO_3^- in δ^{15}N-TDN were expected.

2.3.3 Concentrations of total suspended solids

Total suspended solids (TSS) were measured in October 2008 and May 2009 by gravimetry, that is, weighing 47 mm pre-combusted 0.7 μm GF filters (Whatman) before and after filtration of ∼ 2 l of water sample and subsequent drying (3 h at 40 °C).

2.3.4 Spectroscopic analyses

To constrain the source and chemical character of DOM we measured specific UV absorption at 254 nm (SUVA$_{254}$), which is a measure of the aromaticity of the DOM (Weishaar et al., 2003). UV absorption from 200–700 nm was measured in a 1 cm quartz cuvette using a UV-VIS spectrophotometer (Varian Cary 100Bio) and SUVA$_{254}$ was calculated as

$$\text{SUVA}_{254} = \frac{\text{Abs}_{254}}{[\text{DOC}]} \ [\text{lmg}^{-1}\text{m}^{-1}], \tag{1}$$

whereby Abs$_{254}$ is the absorption measured at 254 nm and [DOC] is the DOC concentration. Excitation-emission matrices (EEMs; Coble, 1996; McKnight et al., 2001) were obtained for each of the 45 filtered whole water samples from May 2010 over an excitation range from 240 to 450 nm in 5 nm increments and an emission range from 320 to 550 nm in 2 nm increments on a Fluoromax-4 spectrofluorometer (Horiba Jobin Yvon). All matrices were corrected for the inner-filter effect, using measured UV absorbance (Lakowicz, 2006), for lamp decay (Stedmon et al., 2003), and normalized by the Raman peak area. Parallel factor analysis (PARAFAC) was used to identify the underlying fluorescence components following the procedures of Stedmon et al. (2003) and Stedmon and Bro (2008). A series of PARAFAC models with two to eight components were fitted to the data and we found that a four-component model gave the best representation of the EEMs' fluorescence signal. More details on PARAFAC modeling are given in the Supplement.

In order to characterize the origin of DOM, the fluorescence index (FI) was calculated as:

$$\text{FI} = \frac{\text{Em}_{470}}{\text{Em}_{520}}. \tag{2}$$

Em$_{470}$ and Em$_{520}$ are the emission intensities at wavelengths of 470 nm and 520 nm, respectively, at an excitation wavelength of 370 nm (Cory et al., 2010). The FI was originally developed to distinguish fulvic acids from "terrestrial" (e.g. from decomposition and leaching of plant and soil organic matter) and "microbial" sources (autochthonous; e.g. from extracellular release and leachate of algae and bacteria; McKnight et al., 2001) and has widely been applied for bulk DOM samples (e.g. Johnson et al., 2011; Mladenov et al., 2005; Miller and McKnight, 2010). The range of FI is confined by end member fulvic acids from terrestrially dominated (river draining a swamp) and microbially dominated

sources (lakes in the Antarctica). The end member values are ∼ 1.2 for terrestrial and, ∼ 1.6 for the microbial sources, whereby values of > 1.4 indicate rather microbial and < 1.4 mainly terrestrial origin (Cory et al., 2010).

2.4 Statistical analyses

Correlations between normally distributed parameters were determined by linear regression, and by Spearman's correlations for non-normally distributed data. To evaluate differences between pooled data, we used ANOVA if normally distributed, otherwise we used non-parametric Kruskal–Wallis tests, both at a critical level of 0.05. Averaged data are given as mean ±SD. Statistical analyses were done with SigmaPlot 11. The full concentration and stable isotope data set is available as an electronic supplement.

3 Results

3.1 Organic carbon and nitrogen concentrations along the Kafue River

Longitudinal profiles of dissolved and particulate organic matter revealed significant differences between the two flooding season campaigns in May 2009 and May 2010 compared to the data set from the dry season in October 2008 (Fig. 3). Wet season DOC increased from ∼ 250 μM immediately downstream of ITT dam (0 km) to ∼ 400 μM at end of the floodplain (410 km; Fig. 3a). Most of the DOC increase occurred after 230 km, where a large influx of floodplain-derived water began entering the river (Fig. 2). Dry season DOC concentrations remained relatively constant at 280 ± 50 μM along the river reach, with the exception of lower concentrations at 240 km and 270 km.

Flooding season DON concentrations showed a similar twofold increase, from ∼ 10 μM at the dam site to maximum concentrations of ∼ 20 μM at 410 km. In the dry season, DON was found at fairly constant concentrations of 14 ± 1.2 μM. For all three campaigns, ON was the dominant form of N, representing 93–97 % of total N while DIN, mainly in form of NO_3^- and NH_4^+, was generally < 1.5 μM (data not shown). As a logic consequence of the similar increase of the DOC and DON concentrations for all three campaigns, the molar DOC : DON ratio remained relatively invariant along the river (May 2010: 19.7 ± 2.4; May 2009: 23.2 ± 2.3; October 2008: 19.8 ± 3.5; Fig. 3a). In May 2010, DOC tended to be higher in the inundated floodplain than at the adjacent river stations, reaching up to 600 μM, while the DON concentrations were comparable to those measured in the river (Fig. 3a).

In contrast to the dissolved OM fraction, flooding season POC and PN concentrations were highest over the first 90 km after the dam (Fig. 3b), and decreased by factor of 2–3 between 200 and 300 km before rebounding towards the end of the Kafue Flats. Maximum concentrations were 40–65 μM

for POC and 6.6 µM for PN, respectively. For the dry season, pronounced peaks to 130 µM POC and 13 µM PN were evident between 200 and 300 km (Fig. 3b), while for the remaining reaches the concentrations of both parameters were comparable to values observed during flooding. As observed for the dissolved fraction, the molar ratio of POC and PN was uniform during the flooding period (May 2010: 7.9±0.9; May 2009: 8.6 ± 0.7). For the dry season, POC : PN was elevated at the dam site but decreased to the levels found in May when passing the Kafue Flats (Fig. 3b).

TSS measurements from May 2009 and October 2008 generally followed the POC and PN concentration data (Fig. 3c). However, for both campaigns, the C and N content of the particles revealed that particles leaving the ITT reservoir were highly enriched in C (36–42 wt %) and N (4.0–4.7 wt %) relative to the downstream reaches, but C and N contents increased again between 200–300 km.

3.2 Carbon and nitrogen stable isotopes

δ^{13}C-DOC values in the river were confined to a narrow range of −21.0 ‰ to −24.7 ‰ during all three sampling campaigns (Fig. 4). Nonetheless, some systematic variations were evident. During the May 2010 campaign, δ^{13}C-DOC exhibited a distinct increase from −23.9 ‰ to −21.7 ‰ over the first 90 km, and during both flooding season campaigns δ^{13}C-DOC decreased by 2.5 ‰ after 250 km. Along the floodplain transects, ^{13}C-enrichment in DOC tended to co-occur with high DOC concentrations, mostly in the more distant areas from the river channel. During the dry season, δ^{13}C-DOC did not show any systematic variation along the river channel and the negative peaks corresponded to the DOC concentration minima.

Across all sampling campaigns, POC at the river stations was systematically depleted in ^{13}C relative to the corresponding DOC (mean difference = 5.1 ± 1.7 ‰; Fig. 4). During both flooding seasons, δ^{13}C-POC increased by ∼ 2.5 ‰ over the first 100 km downstream of ITT dam. The δ^{13}C-POC of floodplain samples varied substantially, covering a range of −33.7 ‰ to −23.4 ‰. In the dry season, δ^{13}C-POC initially remained constant at −26 ‰, that is, enriched by > 1 ‰ relative to the co-located flooding season data. After 250 km, δ^{13}C-POC sharply declined to almost −30 ‰ which essentially is the ^{13}C signature of the POC leaving the Kafue Flats.

δ^{15}N-TDN values during the May 2010 and May 2009 campaigns exhibited limited variability along the river (2.1 ± 0.4 ‰ and 1.4 ± 0.5 ‰, respectively), as well as small differences between river and adjacent floodplain stations (Fig. 4). Dry season δ^{15}N-TDN was characterized by a 3 ‰ increase over the first 65 km after the dam followed by a net decline of δ^{15}N-TDN to 2.5 ‰ at the end of the floodplain. For the particulate fraction, δ^{15}N-PN at ITT dam in May 2010 and 2009 was elevated by ∼ 2 ‰ relative to δ^{15}N-TDN, and gradually approximated values comparable to δ^{15}N-TDN further downstream (Fig. 4). Floodplain δ^{15}N-PN in May 2010 cov-
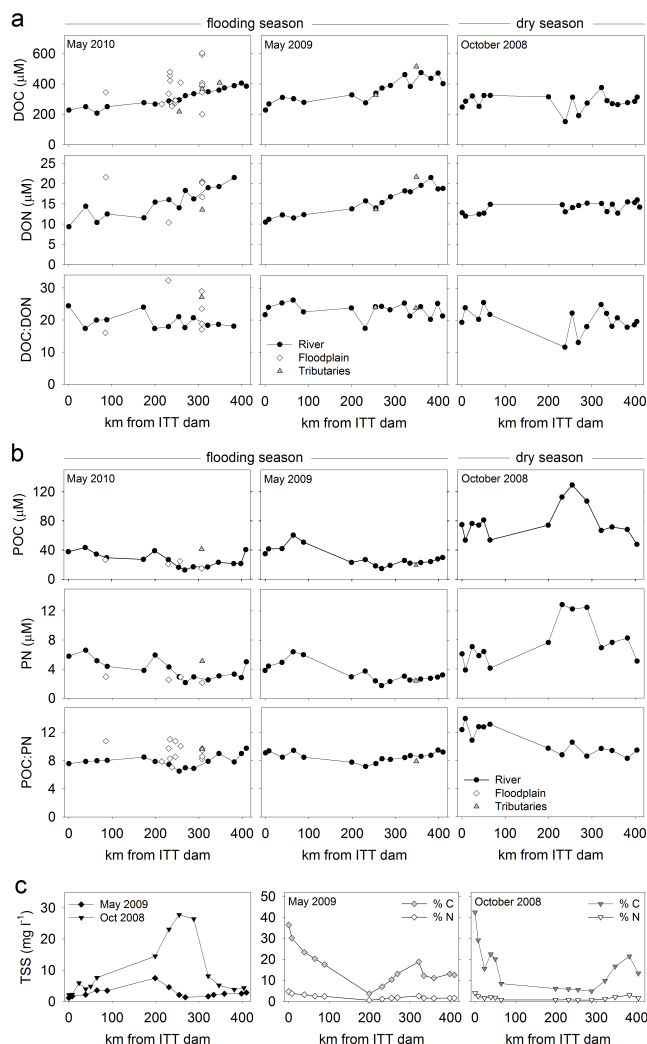

Fig. 3. (a) Concentrations of DOC and DON, and molar DOC : DON ratio, **(b)** concentrations of POC and PN, and molar POC : PN ratio for the flooding season (May 2010 and May 2009), and the dry season (October 2008) along the Kafue River channel (black dots and lines), at floodplain stations (empty diamonds) and tributaries (gray triangles). **(c)** TSS concentration and C and N content of the particles in the Kafue River for May 2009 and October 2008.

ered a considerably wider range than observed in river samples (0.3 ‰ to 5.7 ‰). High variation in δ^{15}N-PN was also measured in the dry season, however, without obvious trend.

3.3 Spectroscopic analyses of dissolved organic matter

SUVA$_{254}$ was $3.5 \pm 0.3 \, \mathrm{l \, mg^{-1} \, m^{-1}}$ (Fig. 5a) and did not change significantly along the river ($P = 0.077$), remaining unaffected by emerging river-floodplain exchange after 230 km. Floodplain and tributary samples showed smaller but more variable values than the adjacent river reach. Similar to SUVA$_{254}$, FI values along the main channel fell in
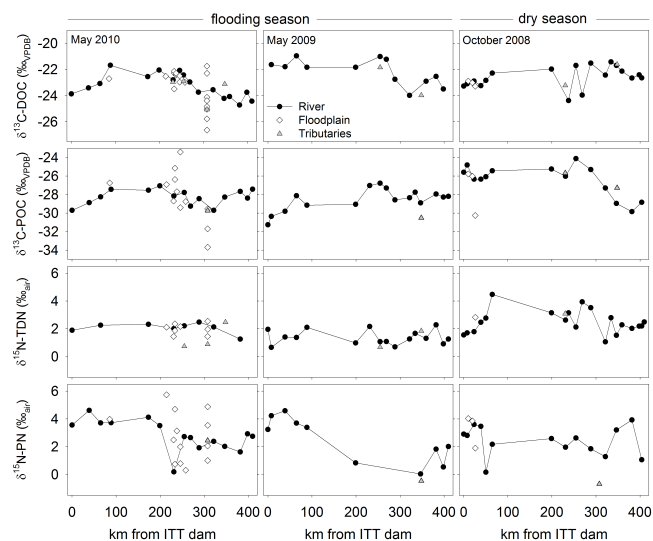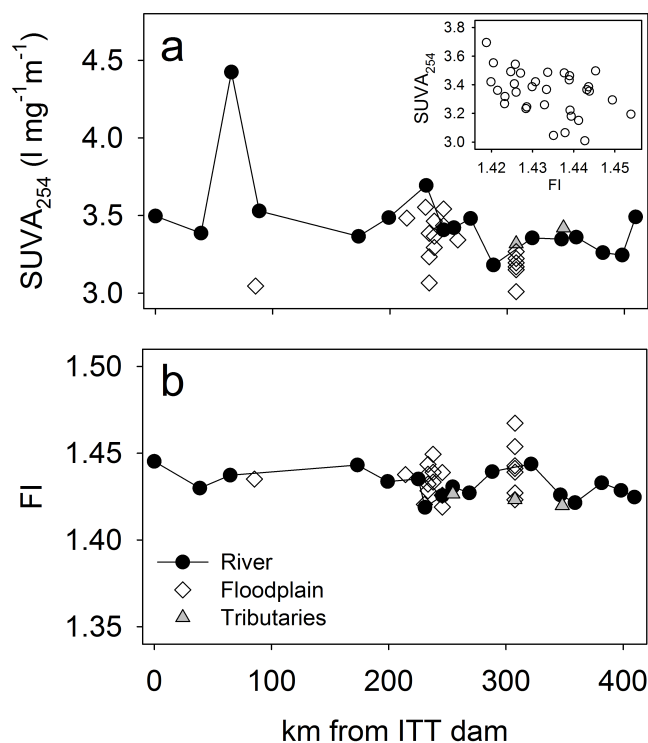
Fig. 4. Stable isotope signatures of dissolved and particulate organic carbon and nitrogen for the flooding seasons and dry season (symbols as indicated in Fig. 3).

Fig. 5. (a) Specific UV absorption at $254\,\mathrm{nm}$ ($\mathrm{SUVA_{254}}$), and **(b)** fluorescence index (FI) along the river (black circles), in the floodplain (empty diamonds), and in tributaries (gray triangles) in May 2010. The insert in **(a)** shows the negative correlation of the pooled $\mathrm{SUVA_{254}}$ and FI data ($P < 0.001$). Samples with $\mathrm{SUVA_{254}} > 4.01\,\mathrm{mg^{-1}\,m^{-1}}$ were removed for clarity.

a very narrow range between 1.42 and 1.47 and exhibited only minor, non-significant ($P = 0.117$) variation along the river (Fig. 5b). The EEMs showed a high degree of similarity among the stations along the river (Fig. 6a) and floodplain transects (Fig. 6b). Two main fluorescence peaks were detected at excitation/emission wavelengths of 345/440 nm, and 240/430 nm. These peaks are common features in natural DOM and have been named Peak A and Peak C (Coble, 1996), respectively.

4 Discussion

4.1 Net export of organic matter from the Kafue Flats

The Kafue River's channel morphology is conducive to intense exchange with the floodplain, yet this exchange is highly variable along the river (Fig. 2). During high flows, a large fraction of the stream flow was diverted into the floodplain between 180 and 225 km, while downstream of the 300 km mark, water returned from the floodplain into the river, resulting in a $\sim$ fourfold discharge increase (Fig. 2). The average water residence time on the floodplain of ~ 2 months was deduced from the evaporative signal of water isotopes (Zurbrügg et al., 2012). Most of the discharge and the chemical loads of the lower Kafue River in May 2010 and May 2009 originated in, or passed through, the floodplain. Comparable levels of exchange occur every year when flow rates substantially exceed ~ 200–$300\,\mathrm{m^3\,s^{-1}}$ (December–July; Zurbrügg et al., 2012). During low-flow periods (August–November), the exchange with the floodplain was substantially reduced.

We combined discharge measurements with concentration data to quantify mass loads of OC and ON along the river (Fig. 7; Table 1). In May 2010, the minimum discharge and minimum DOC and DON loads were observed at $\sim 230\,\mathrm{km}$ (Fig. 2), after $\sim 85\,\%$ of the flow and loads had been forced into the floodplain (Fig. 7). Downstream of 230 km, discharge and concentrations of dissolved organic matter increased, resulting in a threefold increase in loading (Table 1). As DOC and DON mass loads at 410 km were 2.7 and 2.3 times larger than at the dam, and some of the dissolved organic matter entering the floodplain may have been metabolized before reentering the river, a minimum of 82 % of DOC and 75 % of DON in the river originated from the floodplain. Load patterns in May 2009 were, overall, similar to those in May 2010, indicating that the large export pulses of DOC and DON from the Kafue Flats are a recurring seasonal phenomenon (Fig. 7). During the flooding period, the Kafue Flats were a net source of 108–214 t DOC d^{-1} and 6.0–7.6 t DON d^{-1}. This stands in contrast to the dry season when loads were reduced in general, and decreased along the river and when the Kafue Flats acted as net sink for dissolved organic matter.
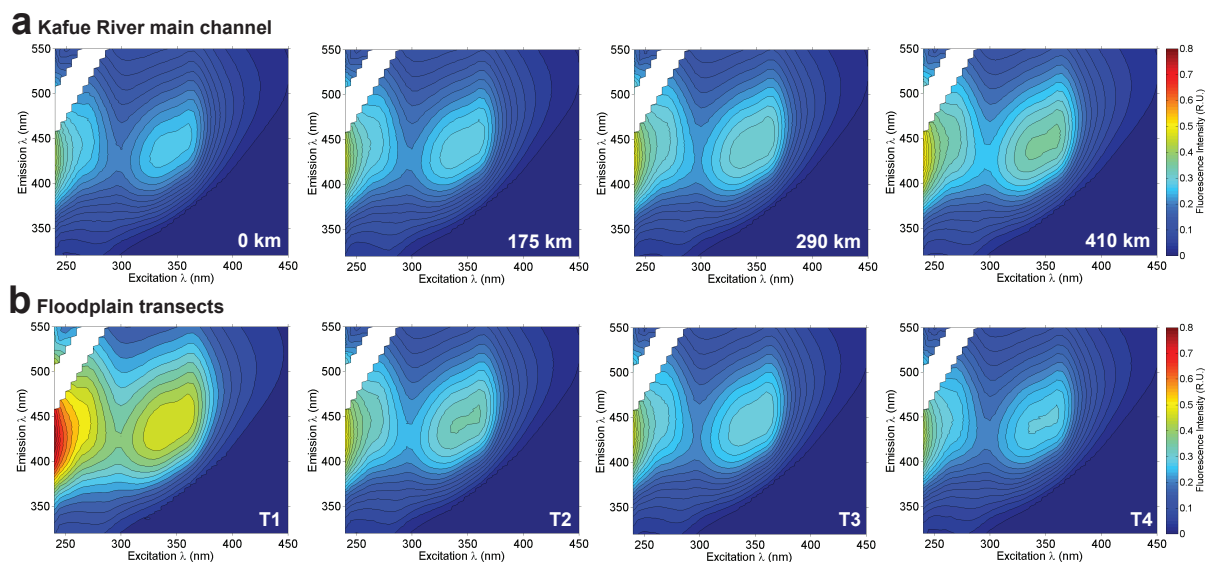
Fig. 6. Excitation-emission matrices (EEMs) for **(a)** four river samples indicated with distance from ITT dam, and **(b)** four floodplain samples along different floodplain transects. The two main fluorescence peaks are at excitation/emission wavelengths of 240/430 nm and 345/440 nm, and have been named by Coble (1996) as Peak A and Peak C, respectively.

In contrast to the clear pattern of dissolved organic matter, the Kafue Flats were a net POM source only in May 2010, not in 2009. During inundation, the contribution of POC to the total OC declined threefold along the flow path from $\sim 15\,\%$ to $\sim 5\,\%$, and the PN fraction of total N from $\sim 30\,\%$ to $\sim 10\,\%$ (Fig. S2, Supplement). Concentration and load data show that some fraction of POM must have been deposited or degraded during the transit through the inundated floodplain. The floodplain had no net effect on the particle transport during the dry season, as the Kafue River was flowing through the flats with little floodplain interaction. The short travel times of 1.5 weeks along the river (average velocity of $\sim 0.5\,\mathrm{m\,s^{-1}}$) and relatively constant flows for several weeks around the sampling time period (Zurbrügg et al., 2012) allowed for a comparison of upstream and downstream loads. Strictly speaking, our results represent "snapshots" in time, which may not represent the average annual conditions. However, results from a bi-monthly sampling campaign that was carried out over one year at several stations along the river indicate a net export of OM predominating for several months. Integrated over an annual cycle, net exports from the Kafue Flats were estimated as $\sim 60\,000\,\mathrm{t\,OC\,yr^{-1}}$ and $\sim 1800\,\mathrm{t\,ON\,yr^{-1}}$, respectively (Wamulume et al., 2011).

The sources and sinks of a floodplain can be compared among different systems by scaling the fluxes to the active area. We assumed that the OC and ON export resulted from the total inundated area at a given time and used the inundation model of Meier et al. (2010) to retrieve flooded areas and calculate area-specific export rates (or yields). The monthly mean flooded surfaces for May 2010, May 2009
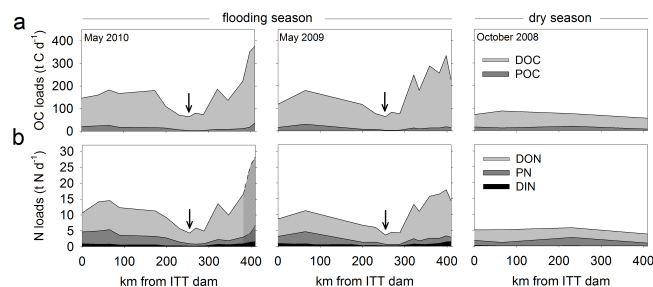
Fig. 7. Organic carbon **(a)** and nitrogen **(b)** loads (t C or N d^{-1}) calculated as discharge ×concentration for the flooding and dry season. For the hatched areas in May 2010, N loads were calculated with extrapolated concentrations using the regression between DOC and DON ($\rho = 0.901$, $P < 0.001$), due to missing DON data. Arrows indicate the discharge minimum due to a channel constriction from Zurbrügg et al. (2012).

and October 2008 were 1930 km^2, 1560 km^2 and 270 km^2 (Köck, personal communication). Flooding in the dry season was restricted to the actual river channel and the permanently flooded areas after 320 river-km. Based on the net OC and ON export for the 2010 and 2009 flooding periods and the respective area, OC yields were 119 and 69 kg C km^{-2} d^{-1} (annual average 43 and 25 g C m^{-2} yr^{-1}) for May 2010 and 2009, respectively. The ON exports from the Kafue Flats were on the order of 6–9 t N d^{-1}, which corresponds to area normalized yields of 3.8–4.7 kg N km^{-2} d^{-1} (1.4–1.7 g N m^{-2} yr^{-1}) for May 2009 and 2010, respectively (Table 1).

Table 1. Organic carbon and nitrogen loads, net exports and yields from the Kafue Flats.

	Export from Kafue Flats[a] (t C or N d^{-1})	Load increase after $\sim$230 km[b] ($\times$)	Floodplain contribution to export[c] (%)	Net export[d] (t C or N d^{-1})	Yields[e] (kg C or N km^{-2} d^{-1})
May 2010 – flooding season, flooded area = 1930 km^2					
DOC	339	3.3	82	214	111
POC	35.7	3.0	92	14.9	7.7
DON	13.6	4.6	75	7.6	3.9
PN	5.1	11	88	1.4	0.8
DIN	1.6	7.6	85	0.6	0.3
May 2009 – flooding season, flooded area = 1560 km^2					
DOC	210	2.5	72	108	69
POC	15.6	4.0	80	−0.2	−0.1
DON	11.5	3.0	75	6.0	3.8
PN	2.0	3.5	78	0.0	0
DIN	0.9	4.1	80	−0.2	−0.1
October 2008 – dry season, flooded area = 270 km^2					
DOC	48.1	n.a.	n.a.	−6.9	−26
POC	7.4	n.a.	n.a.	−9.3	−34
DON	2.9	n.a.	n.a.	−0.5	−1.7
PN	0.9	n.a.	n.a.	−0.7	−2.5
DIN	0.1	n.a.	n.a.	−0.2	−0.7

[a] Calculated as discharge $\times$ concentration at the outflow (410 km).

[b] Flooding season C and N loads were minimum at $\sim$230 km due to a channel constriction and reduced river discharge (marked with arrows in Fig. 7). The increase in C and N loads thereafter was assumed to originate from the floodplain.

[c] The floodplain contribution to the exported OM was calculated assuming negligible in-stream production of DOM or POM.

[d] Calculated as the difference of discharge $\times$ concentration between 0 km and 410 km.

[e] The export per area was calculated using modeled monthly mean flooded areas from the model of Meier et al. (2010; F. Köck, personal communication, 2012).

The OC yields from the Kafue Flats correspond to 3–17 % of the floodplain's annual mean estimated primary production of 260–800 g C m^{-2} yr^{-1} (Ellenbroek, 1987; Blaser, unpublished). For the overall carbon budget, other processes like burial, mineralization, burning and particularly grazing are important. For example, burial in the open water areas was estimated to be 25–42 g C m^{-2} yr^{-1} (Zurbrügg, unpublished), and may be as high as 60–90 g C m^{-2} yr^{-1} in the vegetated floodplain (Mitsch and Gosselink, 2007).

Comparable OC yields of 8–19 g DOC m^{-2} yr^{-1} were found in subcatchments of the Amazon basin (Waterloo et al., 2006; Johnson et al., 2006). A model study by Alvarez-Cobelas (2012) estimated C exports for over 500 catchments ranging from 1.2–57 g DOC m^{-2} yr^{-1} and 0.4–74 g POC m^{-2} yr^{-1}. The Zambezi river basin is at the lower end of this range at 1–2 g DOC m^{-2} yr^{-1} (Harrison et al., 2005) and 0.3–0.5 g POC m^{-2} yr^{-1} (Mayorga et al., 2010). Both, the Zambezi model predictions of OC and for ON of 0.14–0.27 kg DON km^{-2} d^{-1} (Harrison et al., 2005) and 0.30–0.49 kg ON km^{-2} d^{-1} (Mayorga et al., 2010), show that the yields from the Kafue Flats are very high and that the system represents a substantial local source of OM to the Kafue and the Zambezi Rivers.

4.2 Source of organic matter

Analogous to the river discharge, the OM transported in the Kafue River can, to a first approximation, come from reservoir or floodplain sources, or from in-stream processes such as aquatic primary production or river bed erosion. If there were distinct differences in OM characteristics, a shift from reservoir to floodplain OM could be expected, as suggested by the relative contributions of the water masses (Fig. 2).

Floodplain-derived DOM can, in principle, originate from three main sources which have different chemical signatures and bioavailability: (1) mobilization from floodplain soils during drainage (aged OM; Mladenov et al., 2005), Eq. (2) leaching from floodplain vegetation, or (3) exudates from phytoplankton, periphyton or microbial biomass (Ziegler and Brisco, 2004). POM could originate from relatively fresh plant debris, previously deposited and re-suspended aged POM or eroded soils (Hedges et al., 2000), or phytoplankton and detached periphyton (Wiegner et al., 2009). Along the sampled river reach, our data showed significant differences

between the C : N ratios of DOM and POM ($P < 0.05$) and between δ^{13}C of DOC and POC across all campaigns (Fig. 8). This indicates that DOM and POM derived from distinctly different sources.

There are several lines of evidence indicating a planktonic source of particulate organic matter: POM had a substantially lower C:N elemental ratio (~ 8) than DOM (~ 21), soil OM and river sediments (both ~ 20; Table S1, Supplement). The relative elemental N-enrichment and ^{13}C-depletion suggest that POM along the river consisted mainly of phytoplankton sources (Hamilton and Lewis, 1992; Ellis et al., 2012). This finding is consistent with the high C content of the suspended material leaving the ITT reservoir (30–40 wt % C; Fig. 3c). Profiles taken in ITT reservoir between May 2008 and June 2009 (Fig. S4, Supplement) showed epilimnetic δ^{13}C-POC signatures closely matching riverine POC in October 2008 and May 2009. Over an annual cycle, δ^{13}C-POC in the reservoir varied between -25 and -30 ‰ , indicating that some minor terrestrial contribution of fine POM cannot be excluded. In summary, however, there is strong evidence that the POM downstream of the dam originated mainly from the primary production of the reservoir.

By contrast, the composition of dissolved organic matter suggests primarily terrestrial sources: The consistently elevated DOC : DON (range 19–23; Fig. 3a) observed during all sampling campaigns and across all sites indicates an N-poor DOM pool, indicating a terrestrial origin, given its elevated δ^{13}C compatible with a mix of C_3 vegetation and soil/sedimentary OM (Table S1, Supplement). DOM does not indicate any significant contribution from the C_4 vegetation fringing the Kafue River (Ellenbroek, 1987), which has a distinct C isotopic signature of -13 ‰ . Several studies in the Amazon River have documented high DOC : DON in refractory, degraded DOM from lowland reaches of Amazon tributaries (Aufdenkampe et al., 2007), dominated by fulvic and humic substances (Hedges et al., 2000), or soil-derived DOM (Bernardes et al., 2004). In some of the investigated systems like the Tana River in Kenya (Bouillon et al., 2007) or the Amazon (Raymond and Bauer, 2001), POC was enriched in ^{13}C relative to DOC, and DOC could thus originate from POC degradation. In the Kafue Flats this is unlikely, because of the consistently isotopically heavier DOC (Fig. 7).

Spectroscopic results supported the chemical findings that DOM was primarily of terrestrial origin, but they also revealed a microbially derived contribution. The SUVA$_{254}$ values for the Kafue River of $\sim 3.51\,\text{mg}^{-1}\,\text{m}^{-1}$ are characteristic for humic substances of ~ 25 % aromaticity (Weishaar et al., 2003). Similarly, the two peaks detected in the EEMs, fall in the range of "humic acid-like" DOM (Peak A), and "fulvic acid-like" and "hydrophobic acid-like" DOM (Peak C), respectively (Chen et al., 2003). However, the FI of ~ 1.43 is a median between the terrestrial and microbial end members and indicates contributions of mixed sources to DOM (Cory et al., 2010). Because of the relative stability of terrestrial DOM, the FI is often negatively correlated with DOC con-
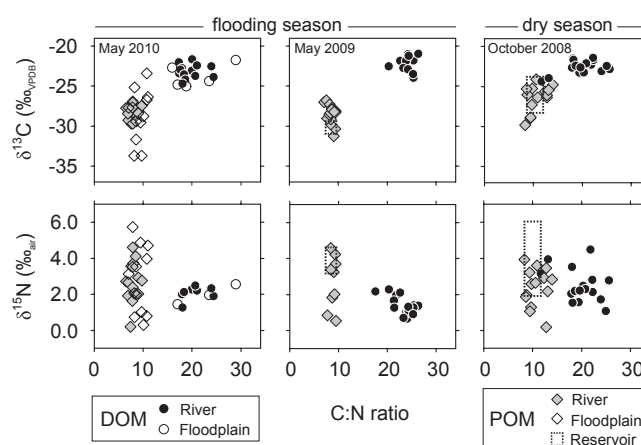
Fig. 8. δ^{13}C and δ^{15}N values of dissolved and particulate organic matter, relative to their C : N ratio. Dashed rectangles in May 2009 and October 2008 indicate the ranges measured in the epilimnion of the upstream ITT reservoir at the time of river sampling (Fig. S4, Supplement). Significant differences ($P < 0.05$) were found between C : N ratios and δ^{13}C of DOM and POM, throughout all sampling campaigns, but not for δ^{15}N.

centration (Johnson et al., 2011; Petrone et al., 2011), but no significant correlation between FI or SUVA$_{254}$ and DOC was found in the Kafue ($P > 0.05$). In other tropical systems, FI ranged from 1.21–1.41 on the Guayana Shield in Venezuela (Yamashita et al., 2010a) and 1.3–3.0 in the lower Amazon basin (Johnson et al., 2011), and in subtropical systems from 1.28–1.47 in the Everglades (Yamashita et al., 2010b) to 2.0–2.3 in the Yangtze River basin (Chen and Zheng, 2012). The microbial signal in the FI of the Kafue River DOM could be associated with the onset of microbial degradation of mobilized terrestrial OM after the peak flow (Johnson et al., 2011; Mladenov et al., 2005) or with the aquatic primary production in the floodplain.

The four components C1–C4 derived from the PARAFAC analysis provided additional evidence for terrestrial DOM with some minor microbial contribution. All components had been identified in previous studies (Fig. S6 and Table S2, Supplement) and were found characteristic for humic-like substances (Stedmon and Markager, 2005). The components C1 and C3 are exclusively from terrestrial sources while C2 and C4 can also have microbial origin. A detailed evaluation of components C2–C4 is given in Ishii and Boyer (2012).

Based on spectroscopic data (SUVA$_{254}$, EEMs and FI), DOM sampled even directly after the dam spillways showed a strong terrestrial signature (C : N, δ^{13}C, δ^{15}N), which only moderately shifted with the addition of a large proportion of floodplain-derived DOM. This suggests that the largely refractory, terrestrial DOM pool leaving ITT reservoir originated from upstream wetlands and transited the reservoir basically unchanged. Such aged terrestrial OM was found to be a dominant source of C exported from the Ganges–Brahmaputra system (Galy and Eglinton, 2011). Studies in the Amazon have identified both a modern and an

old (> 1000 yr) OM fraction (Raymond and Bauer, 2001), whereby young OM was found to be preferably mineralized (Mayorga et al., 2005). Large wetlands that are hydrologically connected to the Kafue River upstream of ITT reservoir (Lukanga and Busanga Swamps; total area $= 4600$ km^2) are a potential source of this floodplain-like DOM.

In summary, DOM in the Kafue River was mainly of terrestrial origin with some microbial contribution, while POM had a distinct phytoplankton signature. Nevertheless, some variation in the chemical characteristics along the channel and between seasons was evident, which is discussed in the next section.

4.3 Longitudinal and seasonal changes in organic matter characteristics

Contrary to our hypotheses, OM quality indicators showed only small variation along the river, even along reaches of intense river-floodplain exchange and elevated C and N concentrations and loads. For POM, C : N ratios were rather invariant along the river even after the 3 to 10-fold increase in POC and PN loads from floodplain contributions downstream of 300 km (Fig. 7), which caused some variation in the isotopic signatures of riverine POM. We propose that floodplain-derived POM and reservoir POM had similar δ^{13}C-POC and C : N, and suggest that floodplain-derived POM was thus dominated by microbial sources, such as phytoplankton or periphyton from the floodplain. While the in-stream production was limited (2–5 µg l^{-1} chlorophyll a; Zurbrügg, unpublished), the consistently ^{13}C-depleted POC in the river and along some floodplain transects (Fig. 4) suggest that floodplain primary production substantially contributed to riverine POM, e.g. from open lagoons on the floodplain, which can be sites of high primary production, even under low nutrient conditions (Cotner et al., 2006).

The small changes in OM characteristics along the river illustrated a complex interplay of terrestrial and microbial sources to the riverine OM pool, which has been observed in other studies (e.g. Tamooh et al., 2012). For example, δ^{13}C-POC and POC:PN between 200 and 300 km showed opposite trends for May 2009 and May 2010 (Fig. 4). Along this reach, the contribution of floodplain water was steadily rising (Fig. 2) and C and N loads, and the distinct increase in the C content of TSS in 2009 (Fig. 3a) imply that floodplain POM entered the river. Based on the δ^{13}C-POC and POC : PN, the floodplain inflows can be attributed to an increasing contribution of ^{13}C-depleted and N-rich microbial POM in 2010, and ^{13}C-enriched and N-poor POM in 2009 which could originate from terrestrial sources, e.g. plant debris or eroded soils. During both flooding campaigns, δ^{13}C-POC increased by 2.5 ‰ over the first 90 km, which could similarly be explained by erosion of ^{13}C-enriched terrestrial matter of lower C content (Fig. 3c). Terrestrial inputs could also cause the concurrent 2 ‰ increase in δ^{13}C-DOC in May 2010. On the other hand, the decrease in δ^{13}C-DOC after

~ 250 km during flood season (Fig. 4) requires an inflow of DOC with an average δ^{13}C of -30.2 ‰, based on a two end-member mixing calculation. This suggests a relative increase in the abundance of isotopically light DOM, produced from microbial sources.

Results from fluorescence spectroscopy revealed further changes in DOM composition along the river transect beginning at ~ 230 km. The PARAFAC component's peak fluorescence intensity (F$_{max}$) sharply increased ($P < 0.001$) between 230 and 280 km for all four components (Fig. S7, Supplement). For each component, F$_{max}$ was moderately to strongly correlated with DOC concentration ($R^2 = 0.68 - 0.87$), with C3 ("terrestrial-humic") showing the highest correlation. To detect changes in the DOM fluorescence properties along the river, while correcting for the influence of varying DOC concentrations (Stedmon et al., 2003), we present the F$_{max}$ ratios of C1, C2 and C4 relative to C3 (Fig. 9). The sharp decrease in C2 after 230 km coincides with the decline in DO (Zurbrügg et al., 2012), which implies that C2-type DOM is preferentially degraded in the floodplain. Along the floodplain transects, C1 and C4 increased with increasing distance from the river or the shore into the floodplain (Fig. S9, supplement), indicating higher abundance or production of DOM with C1- and C4-like fluorophores in the floodplain.

More pronounced differences in the OM characteristics than along the longitudinal sampling transects were detected between wet and dry seasons. The absence of lateral exchange during the dry season was evident as relatively constant DOC and DON concentrations and loads (Fig.7). The differences between wet and dry season δ^{13}C-POC were consistent with the POM reservoir profiles (Fig. S4, Supplement). The marked peak in POC, PN and TSS concentrations between 200 km and 300 km could be explained by resuspension of river sediment because of the small organic fraction in TSS and the lack of floodplain inflows in this area.

4.4 Dam effects on organic matter composition

In the Kafue River basin, terrestrial POM is efficiently retained in the ITT reservoir upstream of the Kafue Flats, as indicated by the high sedimentation rates (Kunz et al., 2011) and the elevated δ^{13}C and C : N in sediments relative to epilimnetic POM (Table S1, Fig. S4, Supplement). This effective particle retention is reflected in the high abundance of DOC (> 80 %) relative to total OC, compared to tropical (61 %) or subtropical (70 %) catchments (Alvarez-Cobelas et al., 2012).

The observed injection of authigenic, ^{13}C-depleted POM from the reservoir's primary production to the river has also been documented in the Beijiang River in China (Chen and Jia, 2009) and in the Tana River in Kenya (Bouillon et al., 2009). In the study of Bouillon et al. (2009), ^{13}C-depleted POM with a C content of 33 % was measured in the river after a large reservoir. The microbial POC was rapidly mineralized after the dam, which resulted in a rebound in δ^{13}C-POC from

−29‰ to −22‰. Our flooding season data from the first 90 km showed a less distinct rebound to values of −28‰, accompanied by a concentration increase (Fig. 3b), which suggests inputs of POM from the floodplain rather than significant in-stream mineralization of POM.

Contrary to the particulate fraction, the primary production in the reservoir had limited influence on the riverine δ^{13}C-DOC, which is consistent with the study from Bouillon et al. (2009), where river and reservoir δ^{13}C-DOC were indifferent. This supports the notion that the DOM from the upstream catchment was refractory and not mineralized in significant quantities before entering the Kafue Flats. The lack of a strong microbial DOM signal downstream of ITT dam further suggests that DOM produced in the reservoir was mineralized in situ.

Finally, we observed a 4‰ decline in δ^{13}C-POC (Fig. 4) and a concurrent enrichment in C and N of TSS (Fig. 3c) after ∼ 320 km in the dry season. This lowest section of the Kafue Flats is permanently inundated due to the backwaters of the downstream Kafue Gorge reservoir. As the Kafue was flowing through this area, δ^{13}C-POC declined to values typical for the flooding period, (−29‰) which may be the result of hydrological exchange with the permanent wetlands and the supply of POM from phytoplankton-dominated sources.

4.5 Processes affecting the nitrogen budget in the Kafue Flats

The nitrogen cycle in tropical floodplains is poorly constrained compared to temperate systems (e.g. Hoffmann et al., 2011; Olde Venterink et al., 2003). Our data indicate a large annual N export from the Kafue Flats mostly in the form of refractory DON. We hypothesized that high N-fixation rates are required to compensate the N losses. Combining N fluxes and δ^{15}N signatures, completed by flux estimates from the literature, we obtained a putative N budget over the flooded area and constrained the N-fixation rates required to balance the N deficit. The N fluxes were calculated using our own data and literature values for the Kafue Flats. Denitrification was approximated using conservative rates from a wide range of rivers and floodplains (of 1–4 g N m^{-2} yr^{-1}, Table S3, Supplement). For the upstream reservoir, the fluxes have been described by Kunz et al. (2011), who proposed N-fixation rates of 12 g N m^{-2} yr^{-1} to account for the N losses through export, sediment accumulation and denitrification in the reservoir (Fig. 10a).

For the Kafue Flats, budget calculations revealed an N deficit of 15 500–22 100 t N yr^{-1}, which was 5–7 times higher than the N input from the reservoir and equal to areal rates of 58–82 µmol N m^{-2} h^{-1} or 7–10 g N m^{-2} yr^{-1}, respectively (Fig. 10b). Previous studies in tropical floodplains found N-fixation rates of several g N m^{-2} yr^{-1} (Cleveland et al., 1999), through symbiotic or asymbiotic fixation by free-floating or attached cyanobacteria (Kern and Darwich, 2003). The ^{15}N isotope mass balance of the Kafue
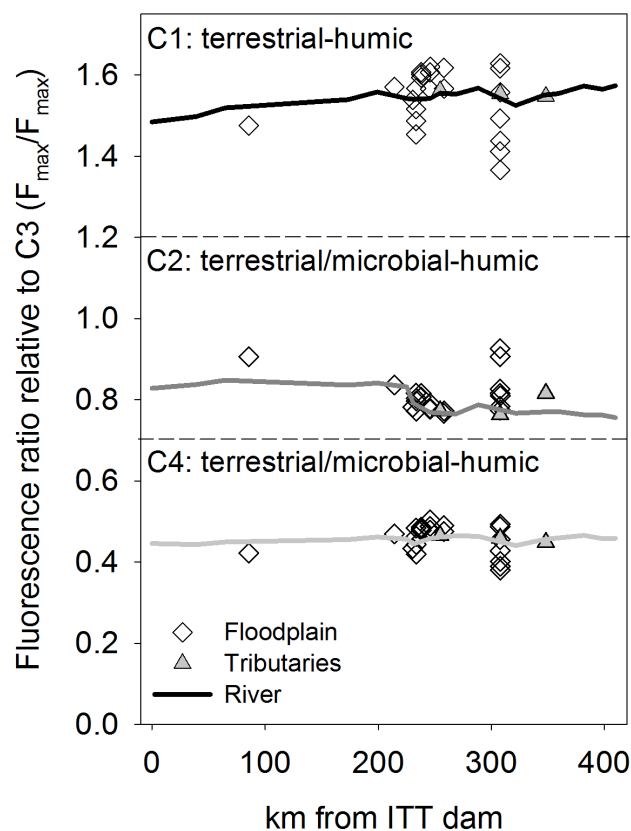

Fig. 9. Ratios of components identified by PARAFAC analysis. Components C1, C2, and C4 are shown relative to C3 along the river, in floodplain and tributaries, measured in May 2010.

Flats supports the hypothesis of N-fixation being the main N source (Fig. 10b). The isotope balance requires a δ^{15}N of 0.8–1.2‰ for the calculated N deficit, which are values close to the 0‰ expected from the fixation of atmospheric N (Martinelli et al., 1992).

The N stable isotope data from the dissolved and particulate fraction provide additional evidence for N-fixation in the Kafue Flats. For the flooding campaigns, δ^{15}N-PN after the dam reflected the epilimnetic signature of ∼ 4‰. During the floodplain transit, δ^{15}N-PN gradually approximated the fairly constant δ^{15}N-TDN signal of ∼ 2‰ (Fig. 4). This shift towards 0‰ could imply the increasing contribution of non-symbiotic N-fixers along the river (Gu and Alexander, 1993; Rejmankova et al., 2004), even though the floodplain δ^{15}N-PN showed considerable heterogeneity (Fig. 4). The δ^{15}N-PN of ∼ 2‰ also persisted during the dry season.

The narrow range of δ^{15}N-TDN (Fig. 4) did not allow to further discriminate between floodplain DOM and reservoir DOM (1.9 ± 0.4‰; Table S1, Supplement), but is consistent with the δ^{13}C-DOC and DOM spectroscopic data, and supports the paradigm that riverine DON in general originates from terrestrial sources (Berman and Bronk, 2003). Intense cycling of DON would affect the δ^{15}N-TDN, as shown by
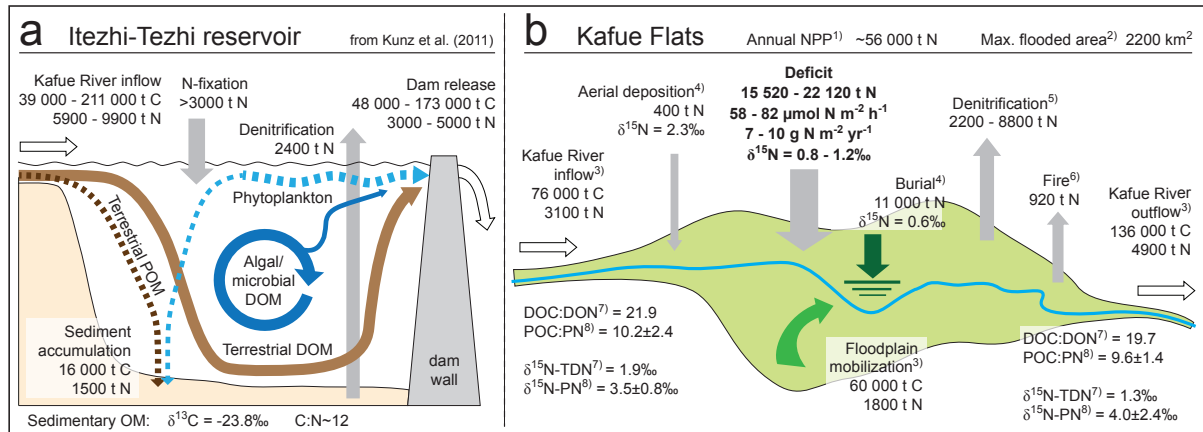
Fig. 10. (a) Schematic illustration of the annual C and N fluxes in ITT reservoir from Kunz et al. (2011). **(b)** System-scale N balance of the Kafue Flats based on our own data from 2008–2010 and literature values: (1) Estimated based on Ellenbroek (1987); (2) data from the inundation model of Meier et al. (2010); (3) data from Wamulume et al. (2011); (4) deposition based on trap data, burial from sediment cores (Zurbrügg, unpublished); (5) estimated from literature data (Table S3, Supplement); (6) burnt areas from Munyati (2000); (7) data from October 2008, May 2009, and May 2010; (8) mean ±SD from annual sampling campaign (Fig. S3, Supplement).

Schlarbaum et al. (2011) who found variation of more than 10 ‰ due to release and uptake of DON in a temperate estuary. Compensating N isotopic fractionation that would result in no net change in δ^{15}N-TDN, e.g. from concomitant release, uptake, and degradation along the main channel cannot be completely excluded, but is considered unlikely (Knapp et al., 2005).

The high abundance of periphyton on inundated vegetation and the high diversity and spreading of N-fixing plants in the floodplain (Ellenbroek, 1987) indicate that N-fixation also occurred through attached and symbiotic fixers. N that was fixed through trees and shrubs outside the flooded area, and deposited through seasonal tributaries could be an additional N source to the floodplain. Complementary measurements of N pools across the Kafue Flats fell in a relatively narrow range (−1 to 4 ‰; Table S1, Supplement). This range is within the data range reported for the Amazon floodplains (Aufdenkampe et al., 2007; Hedges et al., 2000; Bernardes et al., 2004) and might be characteristic for such systems.

5 Conclusions

Intense river-floodplain exchange during the flooding period caused a net export of 69–111 kg C km^{-2} d^{-1} in the form of DOC from the Kafue Flats, which exceeded specific export rates predicted for the Amazon or the Congo River basins by a factor of 5 or more (5–14 kg C km^{-2} d^{-1}; Harrison et al., 2005; Mayorga et al., 2010). During the dry season, the Kafue Flats were a net sink of OM, but during the wet season and over an annual cycle, C and N export exceeded import. Significant N losses through export, burial and denitrification caused an annual N deficit of 15 500–22 100 t N which must

be balanced by high N-fixation rates of 7–10 g N m^{-2} yr^{-1} (Fig. 10b).

Stable isotope and spectroscopic analyses showed that DOM in the Kafue River was dominated by terrestrial sources along the entire reach, despite several months residence time in the upstream reservoir. River DOM characteristics did not vary substantially as floodplain waters increased the DOC and DON loads by a factor of 3, which indicates that DOM leaving the reservoir was likely from refractory terrestrial sources. The exported POM was clearly distinguishable from DOM by its overall lower C : N ratio and more negative δ^{13}C. Both indicators suggest planktonic or microbial sources for POM from the reservoir and floodplain primary production. Marked differences between the flooding and the dry season showed that the in-stream processes were small compared to the organic matter pulses from the floodplain.

Our study underlines how intense river-floodplain exchange fosters high DOM exports to a tropical river basin. In contrast to forested systems like the Amazon, in the flooded grassland ecosystem of the Kafue Flats, the aquatic primary production from the floodplain was a more important POM source than plant debris or soil/sedimentary OM. Finally, the upstream reservoir had a strong effect on the quality of POM by replacing terrestrial particles with OM from autochthonous sources, while its impact on the DOM pool was small.

Supplementary material related to this article is available online at: http://www.biogeosciences.net/10/23/2013/bg-10-23-2013-supplement.pdf.

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