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Seasonal dynamics of carbon and nutrients from two contrasting tropical floodplain systems in the Zambezi River Basin

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Seasonal dynamics of carbon and nutrients

A. Zuijgeest et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



Abstract

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

While the Barotse Plains retain particles during the wet season, annual yields of particulate organic carbon and nitrogen are higher than previously reported for the Zambezi and other tropical rivers. Enhanced wet-season runoff adds soil-derived dissolved organic carbon and nitrogen to the Zambezi River, with a corresponding increase in the Barotse Plains. Soil-derived organic matter dominates the particulate phase year-round in the Barotse Plains, and a varying influence of C_3 - and C_4 -plant vegetation can be observed throughout the year.

In contrast to the Barotse Plains, net export of particulate matter from the Kafue Flats has been observed during the wet season, but over an annual cycle, the Kafue Flats are effectively accumulating dissolved carbon and nutrients. In the Kafue Flats, the runoff-induced increase in dissolved organic carbon and nitrogen concentrations is delayed by the upstream dam operation. The dam reservoir also causes a shift in the source of the particulate organic matter – from soil-derived during the dry season to aquatically produced in the wet season – in the downstream Kafue Flats. Spatial zonation in vegetation and temporal flooding dynamics in the Kafue Flats result in mostly C_3 -derived particulate organic matter during wet season, and a dominance of C_4 -derived material during dry season. This pattern results from dam-induced changes in vegetation,

BGD

12, 10545–10578, 2015

Seasonal dynamics of carbon and nutrients

A. Zuijdeest et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



as dam construction along the Kafue River has led to encroachment of woody plant species onto the Kafue Flats.

The two systems exhibit different flooding dynamics, with a larger contribution of floodplain-derived water in the Kafue Flats and a stronger peak flow in the Barotse Plains. Differences in the biogeochemistry of the two systems that can be linked to the dams are the timing of the runoff-driven dissolved organic carbon and nitrogen pulses in the wet season and the origin and inputs of particulate organic matter. This study reveals clear effects of dam construction on organic matter and nutrient dynamics on the downstream floodplain. Man-made reservoirs alter the origin of organic matter, and change the timing of precipitation-driven carbon and nitrogen pulses. Environmental assessments of dam impacts should therefore consider changes in water quality.

1 Introduction

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

During transport, riverine organic matter is modified by processes in biogeochemical reactors, specifically natural and artificial lakes and wetlands or floodplains. In the past decades, increasing energy demands have resulted in the construction of hydropower dams in most of the world's large river systems (Nilsson et al., 2005). These man-made biogeochemical reactors significantly change the characteristics of river flow. Since wa-

BGD

12, 10545–10578, 2015

Seasonal dynamics of carbon and nutrients

A. Zuijdeest et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



ter flow is restricted in most lakes, particles have time to settle. The water exiting the lake is therefore depleted in particulate matter and its associated organic carbon and nutrients. Lake stratification favors hypoxia or anoxia in the hypolimnion, which can lead to methane outgassing (Barros et al., 2011; Bastviken et al., 2008; DelSontro et al., 2011), low oxygen concentrations and potentially toxic levels of reduced substances in the outflow from turbines (Kunz et al., 2013). In addition to the direct effects of hydropower reservoirs, energy demands often require flow regimes that deviate from the natural tropical situation, changing the hydrography in the downstream reaches of the river (Lu and Siew, 2006; Maangi and Marsh, 2002; Rood et al., 2005).

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

The type of organic matter transported by tropical rivers depends on their discharge. Both the Tana River in Kenya (Tamooh et al., 2014) and the Sanaga River in Cameroon (Bird et al., 1998) transport mainly C₄-derived organic matter during the wet season, while dry season runoff is characterized by organic matter originating from C₃ plants. Spencer et al. (2010) also showed that the properties of organic carbon transported by a tributary of the Congo River vary during different hydrographic phases, with highest dissolved organic carbon and lignin concentrations during peak flow. In the same river,

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

the particulate organic carbon concentration increased when the discharge increased (Mariotti et al., 1991).

Following the construction of dams, the hydrological and sediment-related changes have been assessed in several systems, including the Tana River in Kenya (Maingi and Marsh, 2002) and the Lower Mekong River in China (Kummu and Varis, 2007; Fu et al., 2008; Lu and Siew, 2006). However, the impacts of these changes in hydrography on the biogeochemistry of tropical floodplain systems have hardly been studied. Considering the importance of floodplains within the catchment of large tropical rivers, changes in flooding and inundation might have pronounced effects on the biogeochemical behavior of floodplains and can have far-reaching consequences for the downstream catchment. Decreased sediment supply from previously flooded areas would affect erosion processes along the river corridor and in the coastal zone, and altered nutrient export could affect riparian and coastal ecosystems (Friedl and Wüest, 2002).

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

2 Study sites

At $1.4 \times 10^6 \text{ km}^2$, the Zambezi River Basin is the fourth largest in Africa, and the only major African river draining into the Indian Ocean. Due to its geographic location, the

BGD

12, 10545–10578, 2015

Seasonal dynamics of carbon and nutrients

A. Zuijdeest et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[◀](#)

[▶](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



catchment experiences a pronounced wet season during the passage of the Inter Tropical Convergence zone (December–March) and a dry season (April–November) during the remainder of the year.

The Barotse Plains are a near-pristine floodplain area in the upstream part of the 5 Zambezi River in the Western part of Zambia (Fig. 1). The hydrography in the Barotse Plains clearly reflects the climatic conditions, with peak flow around April/May and low flow between July and November (Fig. 2). The total inundatable area is estimated at around 7700 km² (Hughes and Hughes, 1992). The Kafue Flats are located along the 10 Kafue River, one of the largest tributary of the Zambezi River. Upstream of the Flats, the Itezhi-Tezhi dam (ITT, closed in 1978) stores a significant part of the wet-season runoff in order to allow for a continuous operation of the power station at Kafue Gorge (dam closed in 1972) downstream of the Kafue Flats. The maximum inundated area 15 of the Kafue Flats is slightly smaller than of the Barotse Plains, at 6000 km² (Hughes and Hughes, 1992). The hydrography of the Kafue Flats has been significantly altered by the presence of the dams (Fig. 2). Over the last decades, peak flow has been reduced (approximately –50 %) and base flow has increased (roughly +50 %). In consequence, timing and extent of inundation in the Kafue Flats have changed (Mumba and Thompson, 2005). The floodplain area has been reduced by 40 % due to permanent inundation, a direct result of elevated base flow sustained by the dam operation.

20 The vegetation in the Kafue Flats has been described as a gradient, ranging from open water to floodplain grasslands, water meadows, littoral zones, termitaria grasslands, to woodland areas (Ellenbroek, 1987). After the construction of the dams, the area covered by shrubs has increased (Mumba and Thompson, 2005; Blaser, 2013). For the Barotse Plains a detailed overview of the vegetation zones is lacking, but several 25 sources hint to grasslands, combined with Miombo woodland and deciduous forest patches (Zambezi Society, 2000; Timberlake, 2000).

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

3 Methods

3.1 Sampling

Sampling of the main river channel in the floodplain areas was conducted during peak flow (April/May; Barotse Plains 2009, 2013; Kafue Flats 2008, 2009, 2010) and low flow (October; Barotse Plains 2008, 2013; Kafue Flats 2008). Samples were collected in the middle of the well-mixed channel from surface water (50 cm, Barotse Plains), or at mid-depth (Kafue Flats) using a peristaltic pump (Eijkelkamp). Discharge in the main channel was measured using a RiverRay ADCP (for Barotse Plains dry season data from the Zambezi River Authority were used).

10 3.2 Laboratory analyses

Samples for dissolved nutrient concentrations were filtered through 0.45 μm filters. Dissolved inorganic nitrogen (DIN), phosphate, and the sum of nitrate and nitrite were measured by chemoluminescence detection (Antek 9000). Ammonium was determined by standard colorimetric technique. Total dissolved nitrogen and total phosphorus (TDN and TDP) were determined by chemoluminescence detection (Antek 9000) following persulphate oxidation (Solórzano and Sharp, 1980; Bronk et al., 2000). Samples for particulate phosphorus concentrations during the wet season were collected onto 0.7 μm GF/F filters (Whatman) and measured using a sequential phosphorus extraction method (SEDEX, Ruttenberg, 1992, as modified by Slomp et al., 1996). Samples for dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) were filtered through 0.7 μm GF/F filters (Whatman) and analyzed on a Shimadzu TOC-L (Barotse Plains) or on a Shimadzu 5050 TOC analyzer (Kafue Flats, DOC only). DIC concentrations for the Kafue Flats were calculated from pH and alkalinity measurements (data not shown). Stable oxygen isotopes were determined on filtered water samples (0.45 μm nylon filters) using a Picarro L2120-I Cavity Ringdown Spectrometer (Barotse Plains) or a MultiFlow preparation module connected to a continuous flow

BGD

12, 10545–10578, 2015

Seasonal dynamics of carbon and nutrients

A. Zuijdeest et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



IRMS (Isoprime, UK; Kafue Flats) and calibrated against in-house standards ranging from 0 to $-22.5\text{‰}_{\text{vSMOW}}$. Riverine suspended matter was collected on pre-weighed GF/F filters (Whatman). After freeze-drying of samples, suspended matter concentrations were determined by weight difference. Particulate organic carbon and nitrogen and their stable isotopic compositions (POC, PN, $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively) were determined using EA-IRMS (Thermo-Fischer MAT 253 or ThermoFinnigan FlashEA 1112 coupled to a DeltaV Advantage Continuous-Flow IRMS), and calibrated against in-house standards ($\delta^{13}\text{C}$: -15 to $-30\text{‰}_{\text{VPDB}}$; $\delta^{15}\text{N}$: -1.1 to $+32.7\text{‰}_{\text{air}}$).

4 Results

10 4.1 Hydrology

During the wet season, the runoff in the main channel of both floodplains was characterized by a discharge minimum at a constriction of the river roughly in the middle of both systems (Fig. 3). These constrictions were located around 100 km and 200–300 km downstream in the Barotse Plains and in the Kafue Flats, respectively, and 15 promoted flooding of the surrounding floodplain area (Zurbrügg et al., 2012). During the dry season, the discharge remained rather constant in both systems with a gain due to tributaries along the Barotse Plain and a slight loss in the dry Kafue Flats. Notice, however, that the peak discharge in the wet season was about four times higher in the upstream Zambezi compared to the dammed Kafue River (Fig. 2).

20 The intense river-floodplain exchange left a distinct $\delta^{18}\text{O}$ signal in both systems: the rivers lost water to the floodplain during the wet season. Downstream of the stretch where discharge in the river decreased, the $\delta^{18}\text{O}$ of the river water sharply turned towards heavier values (Fig. 3). The overall ^{18}O -enrichment of the channel water between the upstream and downstream sampling locations was more pronounced in 25 the Kafue Flats, during the wet season. In the Barotse Plains, the water O-isotopic signal showed an overall shift from -2.0‰ in the upstream part to -0.9‰ at the

BGD

12, 10545–10578, 2015

Seasonal dynamics of carbon and nutrients

A. Zuijgeest et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



downstream end. In the Kafue Flats a sharp increase towards heavier values was observed downstream of the channel constriction. To correct for different travel distances along the river stretches, the change in $\delta^{18}\text{O}$ per 100 km of river length was estimated: for the Barotse Plains this enrichment was +0.36‰ and for the Kafue 5 +0.56‰ (100 km) $^{-1}$. At low flow conditions, no significant increase in isotopic signal of oxygen was observed in the Barotse Plains, while in the Kafue Flats enrichment occurred at +0.17‰ (100 km) $^{-1}$.

4.2 Concentrations and loads

The dissolved inorganic fraction dominated the total carbon concentration in both seasons and both systems (Fig. 4). DON was always the main nitrogen species. In the 10 Barotse Plains particulate phosphorus (PP) was the dominant form during the wet season, while dissolved inorganic phosphorus (DIP) was generally the prevailing species during the dry season. Phosphorus concentrations were largely close to detection limit in both systems, and were therefore excluded from the calculation of loads.

15 While both systems have very low inorganic nutrient concentrations during the dry season, the Barotse Plains are a lot lower in organic nutrient species concentration compared to the Kafue Flats. Differences between the dry season and wet season C and N concentrations within both systems are statistically significant (paired analysis, p values < 0.05) for all species, except for the Kafue Flats DOC ($p = 0.23$), DON (0.084) 20 and DIN (0.284). The differences in concentrations between the Barotse Plains and Kafue Flats in similar seasons are significant (hypothesis testing, p values < 0.05) for all species, except PP (wet season, $p = 0.121$) and DIP (dry season, $p = 0.053$).

Total carbon and nitrogen loads increased along the Barotse Plains during the wet season, mainly due to larger contribution by the dissolved organic form (Fig. 5; Table 1). 25 The increase in total carbon load in the Kafue Flats during the wet season was mainly attributed to the dissolved inorganic fraction. During the dry season the loads decrease slightly. Net export for particulate phases from the Kafue Flats could not be determined due to lack of POC and PN measurements at the downstream end of the floodplain.

4.3 C : N ratios and isotopes

The C : N ratios of particulate organic matter (Fig. 6) remained fairly constant along the floodplain in the Barotse Plains and Kafue Flats during the wet season (10.8 ± 0.7 and 7.5 ± 0.7 , respectively, statistically significant difference at 95 % confidence intervals). During the dry season the along-floodplain variability within each of the floodplains was larger (10.3 ± 1.5 and 10.3 ± 1.8 , respectively), but no significant difference was observed between the two systems. On average, particulate carbon was more depleted in ^{13}C in the Kafue Flats compared to the Barotse Plains during the wet season ($\delta^{13}\text{C} = -28.5 \pm 0.9$ and $-26.9 \pm 1.1 \text{‰}_{\text{VPDB}}$, respectively, statistically significant $p < 0.05$). During the dry season mean $\delta^{13}\text{C}$ values were $-28.5 \pm 1.0 \text{‰}_{\text{VPDB}}$ in the Barotse Plains and $-26.5 \pm 1.9 \text{‰}_{\text{VPDB}}$ in the Kafue Flats, again a significant difference. The organic matter in the Barotse Plains became more enriched in ^{13}C during the wet season, while in the Kafue Flats lower $\delta^{13}\text{C}$ values were observed (both significant, $p < 0.05$).
The C : N ratio of the dissolved organic phase was more variable: while the wet season values of 17.5 ± 1.9 and 23.7 ± 3.4 were quite similar for the Barotse Plains and Kafue Flats, respectively, they differed widely during the dry season: 166 ± 20 and 22.7 ± 11.3 . The two systems differed significantly ($p < 0.05$) from each other during a given season.
Paired analysis showed that there was no statistically significant ($p < 0.05$) difference in particulate C : N ratios in the Barotse Plains between contrasting seasons, while there was a difference in dissolved C : N ratios and C-isotopic signals. In the Kafue Flats, there was a significant decrease in particulate C : N ratio from the dry to the wet season (as previously reported in Zurbrügg et al., 2013).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



5 Discussion

5.1 Hydrology and inundation dynamics

Using a mass balance approach based on oxygen isotopic data, Zurbrügg et al. (2012) calculated that > 80 % of the water in the Kafue Flats had spent time on the floodplain during the wet season. Based on the same approach but without a remote sample of floodplain water a first approximation for the Barotse Plains was made using the evaporative isotope value of floodplain water from the Kafue Flats. This resulted in 50 % of the water leaving the pristine floodplain area having spent time outside the channel. This estimate shows that the interaction between river and floodplain was stronger in the Kafue Flats than in the Barotse Plains, even though the Kafue flood peak was mitigated by Itezhi-Tezhi dam. In the published literature, high contributions of floodplain-derived water are also reported for the Tonle Sap Lake-floodplain system, where water from the Mekong contributed over 50 % to the inflows of the lake, and more than 80 % of the outflows from the lake returned to the main river channel of the Mekong (Kummu et al., 2014). At peak flow in the Amazon, 97 % of the river inflow occurred at overbank flow at the Curuai floodplain, and this water spent on average 19 days on the floodplain, according to the modeling results by Rudorff et al. (2014).

During the dry season, the increasing discharge along the Barotse Plains could be explained by the inflow of the Luanginga tributary. By contrast, the decreasing discharge in the Kafue Flats combined with a floodplain contribution of 16 % (Zurbrügg et al., 2012) indicated that here there was still exchange between the river channel and some permanently inundated areas. In addition, increasing $\delta^{18}\text{O}$ values towards the lower end of in the Kafue Flats during the dry season could also be a consequence of lower flow velocities, prolonged the travel times and stronger evaporation without any floodplain interaction. At present, the data is not sufficient to discriminate between the two mechanisms, but based on the larger ^{18}O enrichment in the Kafue Flats, we can conclude that more evaporation occurs along the Kafue Flats compared to the Barotse Plains. In a regional perspective, the along-floodplain increase in the

BGD

12, 10545–10578, 2015

Seasonal dynamics of carbon and nutrients

A. Zuijdeest et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



$\delta^{18}\text{O}$ signal in the Barotse Plains and Kafue Flats during the wet (flooding) season (+0.21 to +0.56 ‰_{vsMOV} (100 km)⁻¹) was considerably lower than the increase in the Okavango delta during the dry (flooding) season (+2.04 ‰ (100 km)⁻¹) and during wet season (+0.74 ‰_{vsMOV} (100 km)⁻¹; calculated from Akoko et al., 2013), indicating that 5 there was significantly less extensive evaporation on the Zambezi catchment floodplains than in the inland Okavango delta.

5.2 Export and retention behavior

During the wet season, the Barotse Plains were a sink for all particulate phases, while the Kafue Flats acted as a source (Table 1). Both systems were sources of DOC and

10 DIC. During the wet season, the Barotse Plains showed markedly different concentrations from the dry season and year-round values in the Kafue Flats. The upstream catchments of both the Zambezi and the Kafue River exhibit the same Late Precambrian geological formations (Geological Map Zambia, Geological Survey Department), 15 after which the Zambezi flows through the Kalahari sands. Therefore, it seems unlikely that erosional processes in the headwaters result in significantly different concentrations during contrasting seasons, and the low concentration of DIC leaving the Barotse Plains was most likely the result of dilution by the high discharge. Dissolved organic nitrogen was exported from both floodplains, but the Barotse Plains retained the small DIN flux, while the Kafue Flats were a minor source. The magnitude of the wet season 20 carbon loads leaving the floodplain area is comparable between the two systems (roughly 1500 t C d⁻¹, Fig. 5), while the nitrogen loads in the Barotse Plains were almost twice as high as those in the Kafue Flats (44 and 20 t N d⁻¹); here the upstream ITT reservoir removed most of the nitrogen (Kunz et al., 2011b).

During the dry season, the Barotse Plains acted as source of particulate matter, most 25 likely caused by aeolian transport of dry floodplain soil material. For the Kafue Flats this could not be determined due to lack of POC and PN measurements in the downstream stretches of the river. DOC and DIC were retained by both systems, potentially con-

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	

verted to particulate phases by primary production. The Barotse Plains were a minor source of dissolved nitrogen, while the Kafue Flats retained both organic and inorganic nitrogen. The general decrease in C loads during the dry season in the Barotse Plains could probably be explained by the slightly higher discharge at the downstream end of the floodplain, due to lower concentrations flowing in from the Luanginga tributary (no data).

Specific POC and PON yields (export per area; Table 2) from the Barotse Plains are close to an order of magnitude higher than previously reported values for the entire Zambezi River (Beusen et al., 2005; Mayorga et al., 2005), highlighting the importance of floodplains as biogeochemical reactors on the catchment scale. Note that these yields should be seen as conservative estimates, as they are based on maximum inundatable areas. DOC yields from the Barotse Plains are higher than previously estimated for the Zambezi, but comparable to those measured in the Amazon and Orinoco rivers (Table 2; Beusen et al., 2005; Harrison et al., 2005; Lewis and Saunders, 1989). Similarly, DON yields from the pristine floodplain resemble values measured in the Amazon and Orinoco. The Kafue Flats show negative DOC, DON, DIN yields, i.e. are retaining these species.

For downstream ecosystems the different particle organic matter dynamics of both floodplains is of limited consequence: since the pristine Barotse Plains are located in the upstream part of the catchment, it is likely that a lot of the particulate matter mobilized in the floodplain will end up in the sediments of Lake Kariba and the same is true for the export of the Kafue flats which will be deposited in the Cahorra Bassa reservoir (Fig. 1). Mass balance calculations have shown that 70 and 90 % of incoming total N and P, respectively, are removed from the water column within Lake Kariba (Kunz et al., 2011a). Hence, while large amounts of organic matter and nutrients are mobilized from (pristine) floodplains, only a small fraction thereof will eventually reach the coastal ocean due to the presence of downstream lakes and reservoirs.

BGD

12, 10545–10578, 2015

Seasonal dynamics of carbon and nutrients

A. Zuijgeest et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



5.3 Sources of organic matter

5.3.1 Dissolved organic matter

The increase in DOC and DON concentrations during the wet season in the Barotse Plains corresponds to the general observation that DOC export increases with runoff, 5 caused by shallowing of the flow paths through organic-rich upper soils (Mulholland, 2003; Aitkenhead-Peterson et al., 2003). This seasonal variability in DOC and DON concentrations has been previously shown in Hawaii (Wiegner et al., 2009) and Congo 10 (Spencer et al., 2010). Runoff from inundated soils, such as found in the Zambezi River Basin during the wet season, also tend to have higher DON concentrations 15 (Aitkenhead-Peterson et al., 2003). This (potentially refractory) source of DON can explain the high DON concentrations found in the Barotse Plains during peak flow.

For the Kafue Flats, there was no significant seasonal change in DOC and DON concentrations between peak and lowest flows. This might be due to the fact that an increase in DOC and DON concentration in the upstream catchment would be diluted 20 and delayed by the presence of the Itezhi-Tezhi dam, showing after peak flow. With a residence time of 0.7 years, large fractions of organic carbon ($\pm 16\%$) and nutrient loads (50 % N, 60 % P) were trapped in the sediments of the reservoir (Kunz et al., 2011b). Monthly measurements showed that the highest TOC concentrations occurred in the main channel in the floodplain area in May/June, after the peak flow (Wamulume et al., 2011). This could be a delayed effect of the increased concentrations at higher runoff during the wet season (November–March).

5.3.2 Terrestrial or aquatic sources of particulate organic matter

The higher C : N ratio of the suspended matter in the Barotse Plains year-round indicates a more terrestrial, specifically soil-derived source in the pristine part of the catchment. In contrast, C : N ratios found in the Kafue Flats during the wet season were 25 indicative of (mostly) aquatic production (Zurbrügg et al., 2013), which could be attributed

BGD

12, 10545–10578, 2015

Seasonal dynamics of carbon and nutrients

A. Zuijdeest et al.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
 	 
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	



to the presence of the ITT reservoir: surface sediments from the reservoir showed an elevated C : N ratio (12.1 ± 0.6 , Supplement of Zurbrügg et al., 2013), similar to the numbers found in the Barotse Plains. Hence, the presence of the dam significantly affected the chemical composition of the suspended matter, and while soil-derived suspended matter settled in the reservoir, mainly photosynthetically produced OM from the reservoir surface waters reached the Kafue Flats and eventually the Kafue-Zambezi confluence.

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

The difference in composition and origin between dissolved and particulate phases (DOM from terrestrial sources, POM more aquatic influence) has previously been described for the Amazon (Aufdenkampe et al., 2007; Hedges et al., 1986) and the Fly-Strickland system in Papua New Guinea (Alin et al., 2008). The constant C : N ratios observed along the floodplain indicate that aquatic production on the inundated floodplains is of limited importance during peak flow. The high contribution of DON to TDN further indicates that the Zambezi and Kafue Rivers are still relatively pristine, as anthropogenic activities mainly add N in the form of DIN to aquatic systems (Berman and Bronk, 2003).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



5.3.3 Vegetation contributions

The stable C-isotopic signatures of the particulate matter further suggest different POC sources. During the wet season, the organic matter in the Barotse Plains is ^{13}C enriched compared to the Kafue Flats, indicating a C_4 -plant-dominated source in the pristine system ($\delta^{13}\text{C}-\text{C}_3$ approx. $-26\text{\textperthousand}_{\text{VPDB}}$, vs. $\delta^{13}\text{C}-\text{C}_4$ approx. $-13\text{\textperthousand}_{\text{VPDB}}$, as in Zurbrügg, et al., 2013). In contrast, during the dry season the situation is reversed, and the organic matter in the Kafue Flats shows higher C_4 contribution than in the Barotse Plains. The average dry season $\delta^{13}\text{C}$ value for the Kafue Flats should be treated with caution, since there is a clear spatial pattern: values become more depleted towards the end of the floodplain. This has previously been attributed to floodplain-derived particulate organic matter, which would consist of phytoplankton and periphyton material in the permanently inundated area in the downstream reaches of this floodplain (Zurbrügg et al., 2013).

Shifts to more C_4 -derived organic matter during the wet season as observed in the Barotse Plains, have been described for the Tana River in Kenya (Tamooh et al., 2014), the Sanaga River in Cameroon (Bird et al., 1998), and the Congo River in Central Africa (Mariotti et al., 1991). These studies clearly showed how the source of organic matter is changing with inundation.

The contrasting trend in vegetation source in the Kafue Flats compared to other tropical rivers could be explained by the spatial distribution of C_3 and C_4 grasses: most of the C_4 species occur close to the river, while C_3 grasses and plants are found on the higher grounds that are only seasonally flooded (Blaser, 2013; Ellenbroek, 1987). This spatial variation could explain why the wet season organic matter in the Kafue Flats shows a higher contribution of C_3 -derived organic matter, whereas during low water conditions only C_4 plants are inundated. Since the construction of the dams in the Kafue catchment, encroachment of woody plants onto the floodplain has been observed (Blaser, 2013). The encroaching species most likely contribute to the C_3 signal observed during the wet season. The regulation of water flow through the Kafue

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Flats has therefore had an indirect effect on the type of the particulate organic matter transported downstream by the river.

6 Conclusions

While the pristine Barotse Plains and dam-impacted Kafue Flats seem to have similar properties in terms of timing and dynamics of seasonal flooding, there are several marked differences between the two systems with respect to hydrology, carbon and nutrient dynamics, and sources of the organic matter (Fig. 7). Based on an oxygen isotope mass balance, a larger fraction of water has spent time on the floodplain at the outflow of the Kafue Flats compared to the Barotse Plains. The two floodplains have significantly different concentrations of dissolved carbon and nutrient species: while the Barotse Plains retain particles during the flooding season, in the Kafue Flats the load of particulate phases increases along the floodplain. Retention of particles occurs when flow velocities drop on the floodplain, but due to the very low inputs of particulate matter to the Kafue Flats, any material mobilized will easily contribute to a positive yield. Annually, the Barotse Plains yields more carbon and nutrients than previously reported for the Zambezi and other tropical rivers, but in a basin-wide perspective it should be noted that a significant fraction thereof is trapped in the downstream Kariba reservoir. The Kafue Flats are exhibiting negative yields, effectively retaining and accumulating organic matter and nutrients over a full hydrological cycle. Particulate organic carbon $\delta^{13}\text{C}$ values indicate a larger contribution of C_4 plants in the Barotse Plains vs. a C_3 -dominated vegetation in the Kafue Flats during the wet season, and the reversed situation during the dry season. These differences in plant source of the organic matter owe to the spatial distribution of C_3 and C_4 plants in the floodplains.

The difference between vegetation source in the two floodplains partly also results from the presence of the Kafue River dams: since their construction, woody encroachment onto the Kafue Flats floodplain has increased, contributing to the wet-season C_3 signal. Further differences between the two systems can be attributed to the presence

BGD

12, 10545–10578, 2015

Seasonal dynamics
of carbon and
nutrients

A. Zuijdeest et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



of the Itezhi-Tezhi reservoir upstream of the Kafue Flats: a delay of the input of runoff-derived organic matter and altered origin of the particulate organic matter in the Kafue Flats. In the Kafue Flats the C : N ratio of particulate organic matter shifts from a terrestrial to an aquatic signal during the wet season, due to a prolonged retention time in the reservoir (Zurbrügg et al., 2013). In contrast, the C : N ratio of the particulate organic matter in the Barotse Plains indicates that soil organic matter is the dominant source year-round. The concentrations of DOC and DON in the Kafue Flats do not change significantly between dry and wet season. Typically, increased precipitation and overland runoff result in higher concentrations of soil-derived organic matter. However, based on previous year-round measurements (Wamulume et al., 2011), the increase in dissolved organic species is likely delayed by the reservoir, and occurs after peak flow. In the Barotse Plains on the other hand, increased export of DOC and DON during the wet season corresponds to the typical trends of increased export with increased precipitation and runoff.

We have shown that dam construction not only affected the hydrological regime but also the sources and concentrations of OM and nutrients within downstream (floodplain) systems, since the presence of a reservoir altered the origin of the particulate organic matter, and changed the timing of a precipitation-driven pulse of dissolved organic carbon and nitrogen. Therefore, environmental assessments of dams should explicitly analyze the potential changes in water quality and their effects on downstream ecosystems.

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BGD

12, 10545–10578, 2015

Seasonal dynamics of carbon and nutrients

A. Zuijgeest et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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12, 10545–10578, 2015

Seasonal dynamics of carbon and nutrients

A. Zuijgeest et al.

Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	



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BGD

12, 10545–10578, 2015

Seasonal dynamics of carbon and nutrients

A. Zuijdegeest et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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Title Page	
Abstract	Introduction
Conclusions	References
Tables	Figures
◀	▶
◀	▶
Back	Close
Full Screen / Esc	
Printer-friendly Version	
Interactive Discussion	



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Seasonal dynamics of carbon and nutrients

A. Zuijdegeest et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

◀

▶

◀

▶

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



Seasonal dynamics
of carbon and
nutrients

A. Zuijdgeest et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)



[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



Table 1. Net export from the two floodplains during peak and base flow. Units are $t\text{Cd}^{-1}$ and $t\text{Nd}^{-1}$. 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	Wet season	-38	170	270	-3.7	12	0.0
	Dry season	14	-1.5	-78	1.6	0.0	0.0
Kafue Flats	Wet season	6.5	160	640	0.6	11	0.1
	Dry season	NA	-11	-89	NA	-0.8	-0.2

Seasonal dynamics
of carbon and
nutrients

A. Zuijdeest et al.

Table 2. Yields of carbon, nitrogen and phosphorus in kg (C or N) $\text{km}^{-2} \text{yr}^{-1}$ 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 are 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.

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

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. (2005), ^g Yasin et al. (2010).

- [Title Page](#)
- [Abstract](#) [Introduction](#)
- [Conclusions](#) [References](#)
- [Tables](#) [Figures](#)
- [◀](#) [▶](#)
- [◀](#) [▶](#)
- [Back](#) [Close](#)
- [Full Screen / Esc](#)
- [Printer-friendly Version](#)
- [Interactive Discussion](#)



Seasonal dynamics
of carbon and
nutrients

A. Zuijdegeest et al.

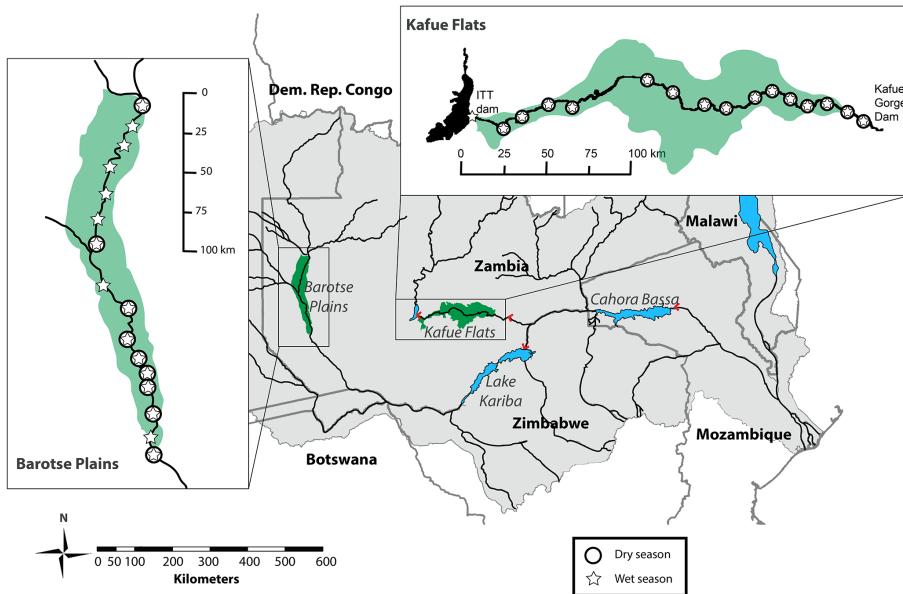


Figure 1. Map of the Zambezi catchment. Inserts show sampling stations during the dry (circles) and wet season (stars) in the Barotse Plains and Kafue Flats.

Seasonal dynamics
of carbon and
nutrients

A. Zuijdegeest et al.

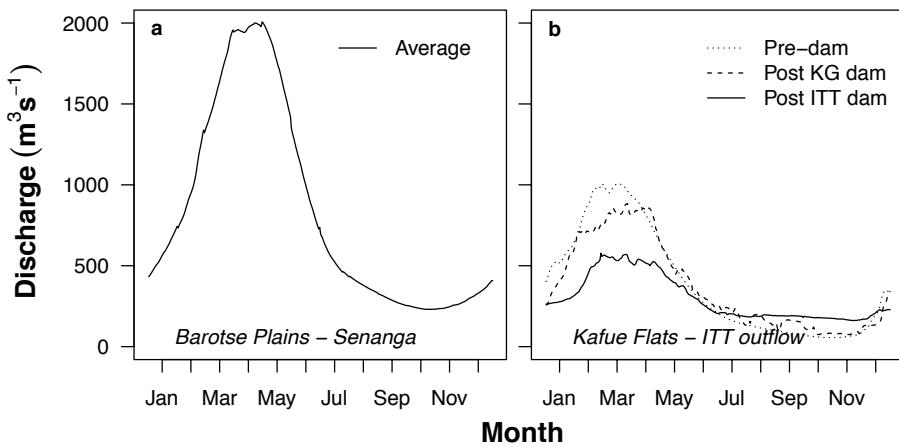


Figure 2. River discharge **(a)** at Senanga, the downstream boundary of the Barotse Plains (1988–2006 average) and **(b)** at the outflow of Itezhi-Tezhi (ITT) dam, the upstream boundary of the Kafue Flats. Discharge for the Kafue Flats are means of pre-dam (1960–1971), and post-dam construction (Kafue 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).

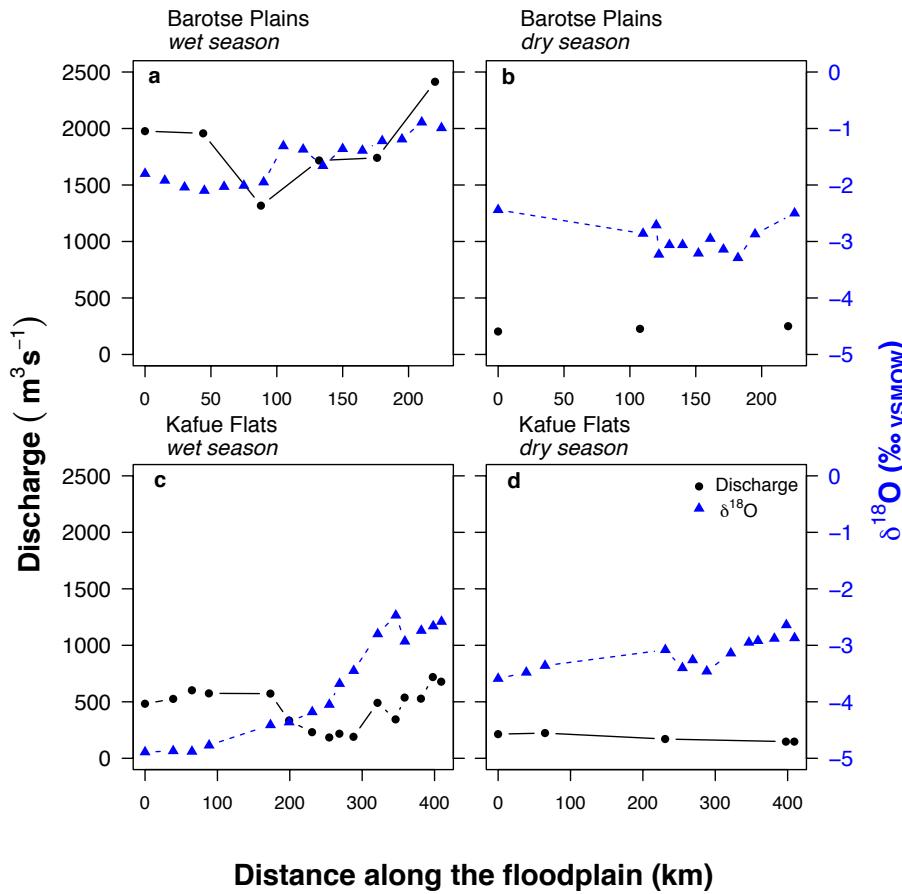


Figure 3. Discharge and stable oxygen isotope signals in the Barotse Plains and the Kafue Flats during wet and dry seasons. Discharge and $\delta^{18}\text{O}$ data for the Kafue Flats have been published previously in Zurbrügg et al. (2012).

Seasonal dynamics
of carbon and
nutrients

A. Zuijdgeest et al.

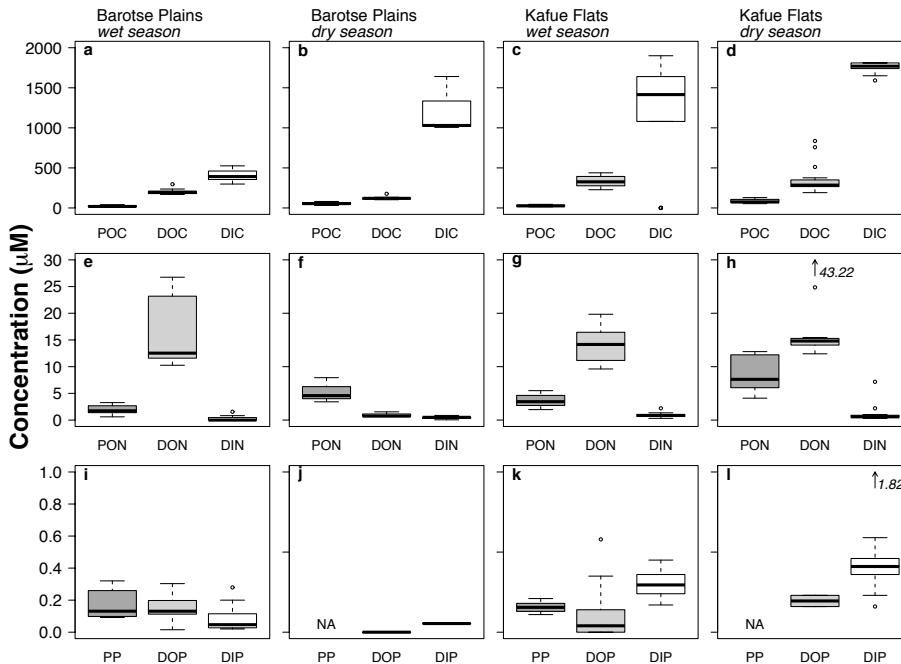


Figure 4. Concentrations of dissolved and particulate carbon, nitrogen and phosphorus species along the Barotse Plains and the Kafue Flats during wet and dry seasons. No measurements of particulate phosphorus were made on samples from the dry seasons. Carbon and nitrogen data of the Kafue Flats have been previously published in Zurbrügg et al. (2013).

Seasonal dynamics
of carbon and
nutrients

A. Zuijdegeest et al.

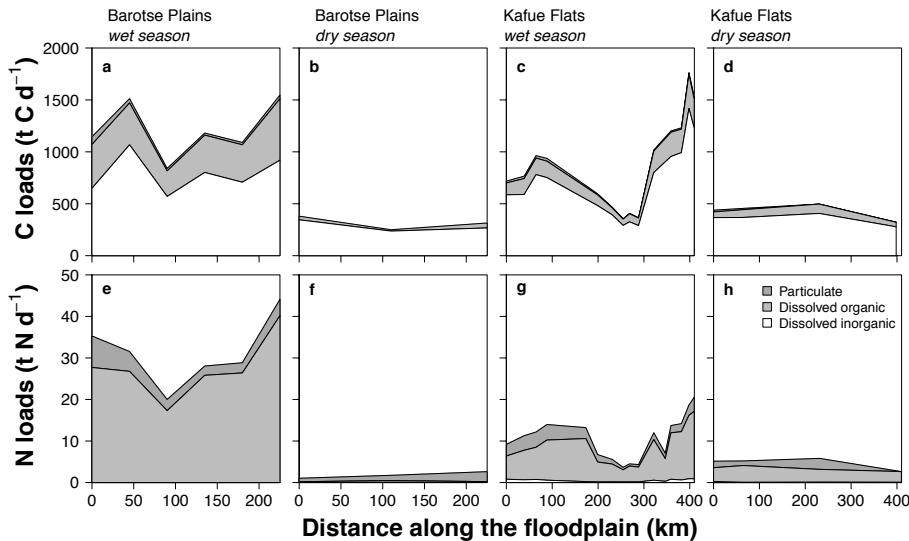


Figure 5. Dissolved and particulate carbon and nitrogen loads along the Barotse Plains and the Kafue Flats during wet and dry seasons. The loads of particulate carbon and nitrogen at the two most downstream locations in the Kafue Flats could not be determined for the dry season due to lack of POC and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

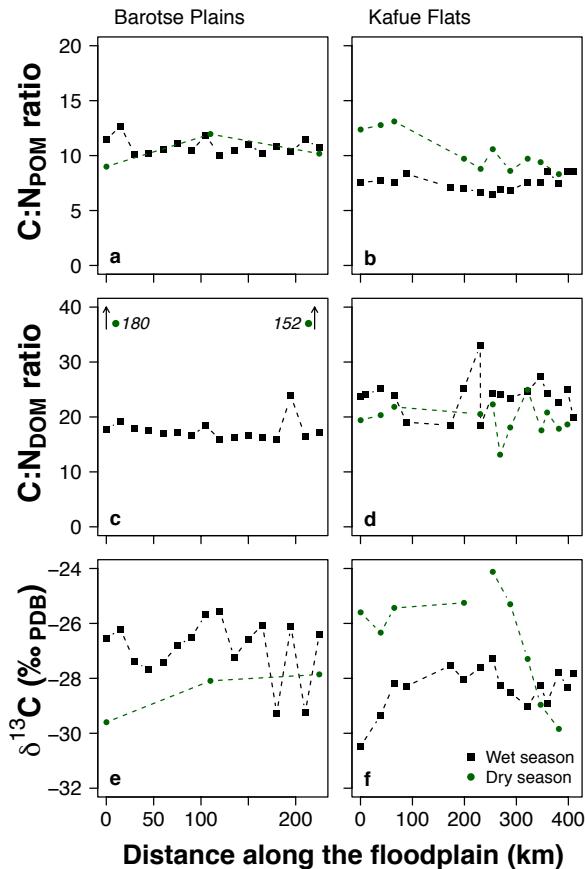


Figure 6. Carbon to nitrogen (C : N) ratios of particulate and dissolved organic matter as well as carbon isotopic signatures of particulate organic matter during wet (black squares) and dry (green circles) seasons. The Kafue Flats data have been previously published in Zurbrügg et al. (2013).

Seasonal dynamics of carbon and nutrients

A. Zuidgeest et al.

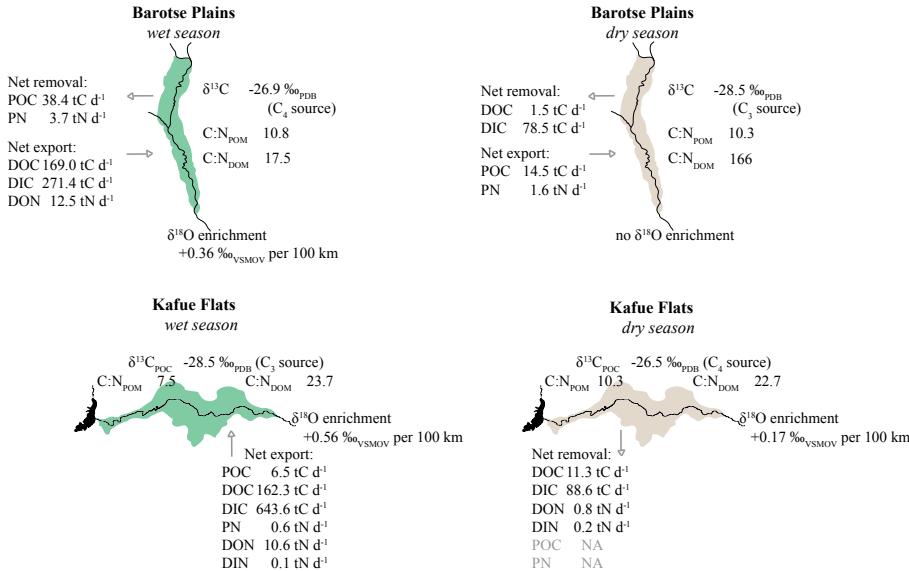


Figure 7. Summary of the organic matter characteristics ($\delta^{13}\text{C}$, C:N_{POM} , C:N_{DOM}), oxygen isotopic enrichment along the floodplain, and net export and removal rates in the Barotse Plains and Kafue Flats during the wet and dry season.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

[Printer-friendly Version](#)

Interactive Discussion

