

DISS. ETH No. 20309

Biogeochemistry of a large tropical floodplain system
(Kafue Flats, Zambia): River-floodplain exchange and dam impacts

A dissertation submitted to

ETH ZÜRICH

for the degree of

Doctor of Sciences

presented by

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Dipl. Umwelt-Natw. ETH

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2012

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Summary

Floodplains are among the most valuable ecosystems on the planet because they provide important ecosystem services such as flood mitigation, water purification, and habitat formation. Floodplains also act as biogeochemical reactors that impact particle, nutrient and carbon (C) transport between headwaters and oceans. However, the effect of floodplain carbon and nutrient cycling on river biogeochemistry is not well constrained, particularly in the tropics. The functioning of floodplains strongly depends on alternating water levels that cause water flows from the river to the floodplain and back. This hydrological river-floodplain exchange is a key process for deposition and mobilization of organic matter (OM) and nutrients, and the migration of biota. Any changes in the hydrology can thus compromise the natural functioning of such systems. Dams built along rivers with floodplains, whether for hydropower generation or irrigation, have the potential to impact the flooding regime and nutrient cycles. Ultimately, dam impacts on floodplains in temperate and boreal systems have been studied in much greater detail than in the tropics, but the increasing number of dams in tropical catchments requires better understanding of these processes.

The Zambezi River basin (1.4×10^6 km²) in southern Africa is a catchment that includes both, dams, and valuable wetlands along the Kafue and the Zambezi Rivers. The studies presented in this thesis investigated biogeochemical processes in the Kafue Flats (6,500 km²), a dam-impacted floodplain along the Kafue River, the Zambezi's largest tributary. The following research questions were addressed: (1) What are the characteristics of river-floodplain exchange in the Kafue Flats, and how is it affected by dam operation? (2) How do river-floodplain exchange and dam operation influence the loads and bioavailability of organic C (OC) and organic nitrogen (ON)? (3) Are the Kafue Flats a source or sink of inorganic N and phosphorus (P) and how could dam operation have changed the nutrient and carbon cycling in the Flats? To answer these questions, four spatially intense sampling campaigns and a one-year monitoring campaign were conducted between 2008 and 2010 covering 410 km of the Kafue River flowing through the Kafue Flats. Sampling included detailed discharge surveys along with measurements of natural tracers, nutrients, and OC and ON species and their chemical properties.

The general flood-pulse concept of gradual flooding and receding phases poorly describes the conditions in the Kafue Flats. Instead, high resolution measurements of discharge and natural tracers along the river revealed substantial spatial variations in both the magnitude and direction of river-floodplain exchange. During peak discharge, a constriction in the river channel diverted as much as 70% of the river discharge into the floodplain. Downstream expansions in channel capacity allowed water flowing back from the floodplain and into the main channel. As a result, >80% of water exiting the Kafue Flats via the river passed through the floodplain. River-floodplain exchange had considerable influence on river water quality, evidenced by a seasonally-recurring sharp decline in

dissolved oxygen levels to $<50 \mu\text{M}$ that persisted for 150 km. Box-model estimates suggest that lateral exchange with low-oxygen water from the floodplain caused up to 90% of the dissolved oxygen deficit with only a small contribution from in-stream respiration. A comparison with historical flow data indicates that similar spatial and temporal variations in river-floodplain exchange existed prior to dam construction in the 1970s, but dam operation has reduced the water flows between river and floodplain by ~50%.

During the floodplain transit, river waters mobilized substantial amounts of organic carbon and organic nitrogen, causing net exports of $110\text{-}220 \text{ t OC d}^{-1}$ and $6\text{-}9 \text{ t ON d}^{-1}$ from the Kafue Flats. ON accounted for $>95\%$ of the total N, and a system-scale N budget showed that high N-fixation rates of $>50 \mu\text{M N m}^{-2} \text{ h}^{-1}$ are needed to balance the high ON exports. Stable isotopes, C:N ratios and excitation-emission spectroscopy measurements showed that the dissolved OM (DOM) along the Kafue River was mainly terrestrially-derived, despite travelling through the large upstream reservoir. The particulate OM (POM) and DOM elemental composition and C and N stable isotopic signature differed considerably along the entire river with POM displaying much lower $\delta^{13}\text{C}$ (-29‰ vs. -22‰) and C:N (~ 8 vs. ~ 20) than DOM. This suggested that POM consisted of phytoplankton and was relatively bioavailable. While the reservoir had little impact on the DOM properties, it efficiently trapped terrestrial POM and, instead, phytoplankton-derived POM was discharged to the downstream Kafue Flats.

The large exports of OM from the Kafue Flats were accompanied by a net export of limiting nutrients (130 t N yr^{-1} and 76 t P yr^{-1}) from the system. We compared the nutrient export with the amount of OM respiration in the Kafue Flats, which was estimated by quantifying the dissolved oxygen deficit and CO_2 production along the river. Over an annual cycle, $58,000\text{-}97,000 \text{ t C}$ was respired in the Kafue Flats, whereof $\sim 20,000 \text{ t C}$ may have been through sulfate reduction. The outgassing of CO_2 from the Kafue Flats accounted for $48,000 \pm 19,000 \text{ t C}$ per year. Only 2% of N and 7% of P that was released during mineralization was actually exported via the river. This suggests considerable loss and uptake in the floodplain, which was confirmed by low N:P ratios of <4 along reaches of intense river-floodplain exchange. Despite reduced nutrient inputs due to dam operation and efficient N and P retention in the floodplain, the Kafue Flats are a net local source of nutrients to downstream systems.

These results in this thesis show that hydrological river-floodplain exchange is a crucial process for the biogeochemistry of the Kafue Flats. The floodplain systems represents a hotspot for nutrient and carbon cycling, ultimately resulting in high exports of C, N, and P and low oxygen levels in the Kafue River during the flooding season. The upstream dam has impacted the floodplain by retaining nutrients and changing the flooding patterns and thus river-floodplain exchange in the Kafue Flats, which may have reduced the overall productivity of the system.

Zusammenfassung

Die nützlichen Funktionen von Flussauen wie Hochwasserschutz, Wasserreinigung, oder Lebensraum machen diese zu äusserst wertvollen Ökosystemen. Auengebiete beeinflussen auch den Partikel, Nähr- und Kohlenstoff (C)-Transport zwischen Oberläufen von Flüssen und Ozeanen. Dieser Einfluss ist bislang wenig erforscht, vor allem in tropischen Gebieten. Auen sind auf sich ändernde Wasserstände angewiesen, die dazu führen, dass Wasser vom Fluss in die Aue und wieder zurück fliesst. Dieser hydrologische Austausch ist ein wichtiger Prozess für die Ablagerung und Mobilisierung von organischem Material (OM), Nährstoffen und für die Migration von Lebewesen. Veränderungen der Hydrologie, zum Beispiel durch Staudämme (für Wasserkraft oder Bewässerung) oberhalb von Auengebieten, können daher die natürlichen Funktionen von Auen beeinträchtigen und dabei Nährstoffkreisläufe beeinflussen. Die Auswirkungen von Staudämmen auf Auengebiete wurden bisher vor allem in gemässigten und borealen Systemen erforscht, aber die zunehmende Anzahl von Staudämmen verlangt nach einem besseren Verständnis dieser Prozesse in tropischen Gebieten.

Das Einzugsbiet des Sambesi ($1.4 \times 10^6 \text{ km}^2$) im südlichen Afrika ist ein fragmentiertes System mit vier grossen Staudämmen und wertvollen Feuchtgebieten. In dieser Arbeit wurden biogeochemische Prozesse in den „Kafue Flats“, einem $6'500 \text{ km}^2$ grossen Auengebiet zwischen zwei Staudämmen entlang des Kafue, dem grössten Zufluss des Sambesi mit Hinblick auf folgende Forschungsfragen untersucht: (1) Was sind die Eigenschaften des Wasseraustauschs zwischen Fluss und Aue und wie wurde dieser durch die Staudämme verändert? (2) Wie beeinflussen Staudämme und das hydrologische Regime die Mobilisierung von organischem Kohlenstoff (OC) und organischem Stickstoff (ON)? (3) Sind die Kafue Flats eine Quelle oder eine Senke für die anorganischen Nährstoffe Stickstoff (N) und Phosphor (P) und wie könnten die Staudämme Nährstoff- und Kohlenstoff-Kreislauf beeinflusst haben? Um diese Fragen zu beantworten wurden vier hoch auflösende Feldkampagnen und eine einjährige Monitoring-Kampagne durchgeführt. Die Probenahmen beinhalteten detaillierte Abflussmessungen, Messungen von natürlichen Tracern, Nährstoffen und OC und ON Spezies und deren chemischen Eigenschaften.

Das einfache Konzept einer jährlichen Dynamik einer Überflutung gefolgt von einer Entwässerungsphase der Auengebiete beschreibt die Hydrologie in den Kafue Flats nur unzureichend. Stattdessen wurden durch hoch aufgelöste Abflussmessung starke räumliche Veränderungen des Wasseraustauschs zwischen Fluss und Aue sichtbar. Während des Abflussmaximums leitete eine Verengung im Flusslauf $>70\%$ des Abflusses von $700 \text{ m}^3 \text{ s}^{-1}$ in die Aue. Weiter flussabwärts führte eine Verbreiterung des Flusslaufs zur Entwässerung von grossen Teilen des Feuchtgebiets, was zu einem Anstieg des Abflusses führte. Als Folge wurden $>80\%$ des Gesamtabflusses des Kafue durch das Auengebiet geleitet. Dieser intensive Austausch hatte beträchtliche Auswirkungen auf die Gewässerchemie des Kafue und verursachte einen starken Abfall der Sauerstoffkonzentration bis <50

μM , der über 150 km anhielt und jedes Jahr beobachtet wurde. Modellberechnungen zeigten, dass dieser Abfall zu 90% durch den starken Fluss-Auen Austausch mit sauerstoffarmem Wasser aus dem Feuchtgebiet verursacht wurde und nur zu einem kleinen Teil durch Respiration im Fluss. Ein Vergleich der heutigen Situation mit historischen Abflussdaten zeigte, dass der Betrieb der Dämme den Austausch um bis zu 50% verringert hat.

Während der Passage durch das Auengebiet mobilisierte das Flusswasser grosse Mengen an OC und ON, was zu einem netto Export von 110-220 t OC d^{-1} und 6-9 t ON d^{-1} führte. Der N-Pool bestand zu >95% aus ON und ein Stickstoff-Budget der Kafue Flats zeigte, dass hohe N-Fixierungsraten ($>50 \mu\text{M N m}^{-2} \text{h}^{-1}$) benötigt werden um den hohen ON Verlust auszugleichen. Stabile Isotope, C:N-Verhältnisse und spektroskopische Messungen zeigten, dass das gelöste OM (DOM) im Kafue vorwiegend aus terrestrischen Quellen kam, trotz des Durchflusses durch den Stausee. Entlang des Flusses wiesen die Elementzusammensetzung sowie die C und N-Isotopensignaturen grosse Unterschiede zwischen DOM und partikulärem OM (POM) auf: POM zeigte tiefere Werte für $\delta^{13}\text{C}$ (-29‰ vs. -22‰) und im C:N-Verhältnis (~8 vs. ~20) als DOM, was auf planktonische Quellen und hohe Bioverfügbarkeit von POM deutet. Während das DOM den Stausee beinahe unverändert passierte, wurde terrestrisches POM effizient zurückgehalten und stattdessen gelangte POM in Form von Phytoplankton in die Kafue Flats.

Dank des ausgeprägten hydrologischen Austauschs zwischen Fluss und Aue war es möglich, die Mineralisation vom OM im ganzen System durch Messungen des Sauerstoffdefizits und der CO_2 -Produktion im Fluss abzuschätzen. Während einem Jahr wurden in den Kafue Flats 58'000-97'000 t organischer Kohlenstoff mineralisiert, davon entwichen etwa $48'000 \pm 19'000$ t C den Kafue Flats in Form von CO_2 . Nur etwa 2% des N und 7% des P, die bei der Mineralisation von OM freigesetzt wurden, wurden aus dem System exportiert, was auf hohe Verluste und effiziente Wiederaufnahme im Feuchtgebiet schliessen lässt. Tatsächlich wurde entlang Flussabschnitten mit hohem Wasseraustausch neben einem beträchtlichen Anstieg der CO_2 -Konzentration auch tiefe N:P-Verhältnisse von <4 gemessen. Trotz geringerer Nährstoffzufuhr durch den Betrieb der Staudämme und effizienten Nährstoffrückhalt in der Aue, sind die Kafue Flats eine netto Quelle von 130 t anorganischem N und 76 t P pro Jahr.

Wie diese Resultate zeigen, ist der Wasseraustausch zwischen Fluss und Aue ein entscheidender Faktor für die biogeochemischen Prozesse in den Kafue Flats. Der Austausch verursachte einen Abfall der Sauerstoffkonzentration und erhöhte die OM- und Nährstofffrachten im Kafue. Trotz den tiefen Nährstoffkonzentrationen zeigten hohe C, N und P Exportraten, dass die Kafue Flats ein „Hotspot“ für den C- und Nährstoffumbau des gesamten Einzugsgebiets sind. Die Staudämme beeinträchtigten das Auengebiet durch tiefere Nährstoffzuflüsse und ein verändertes hydrologisches Regime, was wohl die Produktivität der Kafue Flats verringert hat.

Introduction

Introduction

Dynamics of floodplain ecosystems

Floodplain ecosystems are among the most valuable biomes worldwide, providing ecosystem services equivalent to 20,000 USD ha⁻¹ yr⁻¹ (Costanza et al. 1997; Mitsch & Gosselink 2000). These ecosystem services include water purification and storage, flood attenuation, food production, and habitat formation, most of which are essential for both humans and animals (Keddy et al. 2009). Since many floodplains have recreational, cultural and aesthetic values, they are protected by the Ramsar Convention on wetlands, an intergovernmental treaty on the conservation of wetlands of international importance (Ramsar 2012).

Floodplains are periodically inundated areas along rivers or lakes and thus transition zones between the aquatic and the terrestrial environment (Junk et al. 1989). The periodic nature of the flooding is the unique feature of river-floodplain systems, which has been described as “flood pulses” (Junk et al. 1989; Tockner et al. 2000). By definition, flooding occurs when the river discharge exceeds the channel carrying capacity, or by lateral inflows and direct precipitation (Baker et al. 2009). The hydrological connection between the river and floodplain enables exchange of solutes and solids and the migration of biota and the periodic disturbance through flooding shapes the floodplain’s morphology and vegetation zones. In addition, flood pulses are responsible for intense nutrient turnover, and foster high biological productivity and high biodiversity (Tockner & Stanford 2002).

Over the last centuries, most floodplains in industrialized regions have fallen victim to drainage or channelization for land reclamation or flood control. Anthropogenic disturbance has resulted in degradation of up to 90% of Europe’s floodplains (Tockner et al. 2009) and losses in total wetland area of 53% in Europe and 60% in North America over the past 60 years. For comparison, in Africa only 2% of the wetland area has been lost (Mitsch & Gosselink 2007). Because of the dependence on periodic flooding, hydrological alterations have a particularly strong impact on these ecosystems. Hydrological changes frequently result in a reduction in flood peaks, leading to less inundation and a smaller flooding frequency in the flooded areas (Ward & Stanford 1995a). The ecological consequences of flow alterations are system-specific (Carlisle et al. 2011; Tockner et al. 2010), and include an overall decline in biodiversity (Bunn & Arthington 2002), shifts in riparian vegetation zones (Nislow et al. 2002; Toner & Keddy 1997), changes in sediment erosion and distribution (Heath & Plater 2010), changes in nutrient cycling (Gergel et al. 2005), or enhanced salinization (Nilsson & Berggren 2000).

Tropical floodplains – susceptible ecosystems in a changing environment

Tropical floodplains are among the most productive ecosystems worldwide with primary production rates of $>2,000 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Junk & Piedade 1993), compared to $<700 \text{ g C m}^{-2} \text{ yr}^{-1}$ found in temperate floodplains (Mekonigal et al. 1997; Spink et al. 1998). Many tropical systems are in hydrologically intact catchments (Nilsson et al. 2005) with low anthropogenic disturbance that thus provide particularly high value ecosystem services like water supply and water purification (Zedler & Kercher 2005). Moreover, tropical floodplains are hotspots of biodiversity (Junk 2002). Their extent cannot easily be assessed (Lehner & Döll 2004), but they were estimated $>10^6 \text{ km}^2$ in South America and $>1.5 \times 10^5 \text{ km}^2$ in Africa (Tockner & Stanford 2002).

Many tropical and subtropical floodplains are currently facing or are likely to face increasing anthropogenic disturbance that will compromise natural functioning (Tockner & Stanford 2002). This includes hydrological alteration through water abstraction for hydropower or irrigation, expansion of agricultural areas (Downing et al. 1999), or increased climatic variability affecting the thermal and hydrological regime (Hamilton 2010). Hydropower development might primarily affect the floodplains along the Amazon (Junk 2002) and in southern African river basins (The World Bank 2010), that is, areas where local populations particularly depend on floodplain ecosystem services (e.g. fisheries, water supply) (Schuyt 2005). Assessing and predicting the impacts of such human disturbance, and maintaining or restoring vital floodplain functions requires in-depth understanding of the relevant hydrological, ecological, and biogeochemical processes in tropical floodplains.

Biogeochemistry of tropical floodplains

Floodplains as biogeochemical reactors

Tropical floodplains are often situated along large rivers, which are known to export substantial amounts of sediments and solutes to the coastal oceans (Ludwig et al. 1996). In this context, floodplains can act as biogeochemical reactors that regulate transport of sediments and dissolved organic matter (DOM) and nutrients as illustrated in studies from the Congo River basin (Vangriesheim et al. 2009), the Ganges/Brahmaputra delta (Galy et al. 2008), or the Amazon (e.g., Aalto et al. 2003). Tropical river-floodplain systems play an important role in the global carbon (C) cycle through burial or C emissions as CO_2 or CH_4 (Aufdenkampe et al. 2011; Melack et al. 2004). The respiration of organic C (OC) may contribute substantially to the overall metabolism of river ecosystems (Battin et al. 2009a). However, both floodplain OC burial and mineralization are still poorly constrained on a global scale (Cole et al. 2007).

Because of the global relevance, biogeochemical research on tropical floodplains has mostly focused on their role in the C cycle of large catchments. The floodplains of the Amazon River have an inundated area of $91,000 \text{ km}^2$ (Sippel et al. 1998) and are the most intensely studied tropical wetlands.

In the Amazon basin, the source and quality of the OC (Aufdenkampe et al. 2007; Hedges et al. 2000; Tremblay & Benner 2009), OC respiration and CO₂ emission (Bouchez et al. 2010; Richey et al. 1980; Richey et al. 1988; Richey et al. 2002), and methane emissions from wetlands (Bastviken et al. 2010; Devol et al. 1988) have been studied for more than three decades. Recent biogeochemical studies outside the Amazon basin focused on the Okavango Delta (Mladenov et al. 2007a; Mladenov et al. 2007b; Mladenov et al. 2005), the Congo River (Spencer et al. 2010; Stubbins et al. 2010), the Ganges and Brahmaputra (Galy et al. 2007; Galy et al. 2008), the Fly River in Papua New Guinea (Alin et al. 2008), the Tonle Sap as a lacustrine floodplain (Kummu & Sarkkula 2008) or floodplains in northern Australia (Pettit et al. 2011).

Many vital ecosystem services like habitat provision or water purification depend on the availability of limiting nutrients and are thus jeopardized by land use changes that alter nutrient supply (Junk 2002). The respiration of OM is a large source of inorganic N and P, however, in many tropical systems, the underlying nutrient dynamics enabling high productivity are still poorly defined on the scale of entire ecosystems (Villar et al. 1998). Catchment-scale models have been established to estimate nutrient yields from tropical catchments (e.g. He et al. 2011; Yasin et al. 2010) but they hardly reflect the importance of floodplains in nutrients cycles, e.g., by considering only denitrification in reservoirs, neglecting floodplain nutrient storage and their focus on anthropogenic nutrient loads, rather than natural conditions.

Hydrology and river-floodplain exchange

Like their temperate counterparts, tropical floodplains are dependent on the flood-induced changes in water level. However, in contrast to episodic floods after storm events in temperate systems, tropical systems typically experience one or two main floods after the rainy season (Junk 1999). These annual floods mobilize organic matter and nutrients (Mladenov et al. 2005) and fuel respiration in the draining river (Devol et al. 1995). The alterations between wet and dry conditions in soils fosters intense nutrient turnover (Baldwin & Mitchell 2000; Olde Venterink et al. 2002). Flood pulses also force water to flow laterally from river to floodplain during the onset of the flood and to recede at falling water levels (Junk et al. 1989). This hydrological exchange between river and floodplain has been identified as also an important exchange pathway for C and nutrients in temperate systems (e.g. Hunsinger et al. 2010; Tockner et al. 1999; Tockner et al. 2010), but remains poorly described in the tropics. River-floodplain exchange was found to promote channel erosion and sediment deposition on the river banks (Aalto et al. 2003; Dunne et al. 1998) and might thus also influence C burial, mineralization and nutrient availability. A recent study from Australia showed that river-floodplain exchange indeed governs C fluxes and productivity in floodplains (Pettit et al. 2011). Lateral exchange was also associated with oxygen depletions rivers draining the tropical wetlands (Hamilton et al. 1997; Hamilton et al. 1995), which indicated a strong connection between C cycling and river biogeochemistry.

Impact of dams on downstream floodplains

Almost half of the world's large rivers ($Q > 1,000 \text{ m}^3 \text{ s}^{-1}$) are impacted by dams (Lehner et al. 2011). The ecological and biogeochemical changes in downstream floodplains due to dam operation has been widely studied in temperate systems (e.g. Ward & Stanford 1995b), but dam impacts may be different in tropical zones. Water quality changes can occur before and after the dam due to reservoir internal processes, which include removal of particles and nutrients, depletion of dissolved oxygen and changes in OM characteristics (Friedl & Wüest 2002). Additionally, dams modify the hydrology of rivers which alters the extent and duration of downstream flooding. While the changes in water chemistry before and after the dam has been studied in different tropical systems (Chen & Jia 2009; Kummu & Varis 2007; Kunz et al. 2011a), changes in flooding patterns have mostly been addressed in ecological studies (Kingsford 2000; Leigh & Sheldon 2008).

Study site – The Kafue Flats

Zambezi River basin

The Zambezi River basin (Figure 1) is the fourth largest river basin in Africa and drains an area of $1.4 \times 10^6 \text{ km}^2$, corresponding to 5% of the continent (Vörösmarty & Moore 1991). Approximately 40% of the total catchment area is in Zambia. From its source in northern Zambia, the Zambezi River runs over 2,600 km through eight riparian countries before reaching the Indian Ocean in Mozambique. To meet the emerging regional energy demand, four large dams have been built over the past 50 years, on the Zambezi River and its major tributary, the Kafue River. In the Western Province in Zambia, the Zambezi River flows through the Barotse Plains (Figure 1), a $9,000 \text{ km}^2$ floodplain which is still in a near-natural state. After the Victoria Falls and the gorges along the Zambia-Zimbabwe border the Zambezi enters Lake Kariba ($5,360 \text{ km}^2$) reservoir for a 1,320 MW hydropower plant (SADC 2007). After the confluence with the Kafue and the Luangwa River it reaches Cahora Bassa reservoir ($2,740 \text{ km}^2$) and finally reaches its mouth to the Indian Ocean in Mozambique at a mean discharge of $3,200 \text{ m}^3 \text{ s}^{-1}$ (Vörösmarty et al. 2003).

The potential for hydropower expansion in the Zambezi River basin is still large (SADC 2007). To meet the increasing energy demand, the riparian countries aim to increase power production by installing new hydropower schemes over the next decades (Figure 1). In order to address environmental effects and conflicts in water use, the Zambezi River Basin Action Plan (ZACPLAN) was initiated in the 1980s as a first step towards an integrated water resources management.

The Kafue River basin

The Kafue River basin ($152,000 \text{ km}^2$) is an important subbasin of the Zambezi River basin (Figure 1). It covers only 20% of Zambia but almost half of the Zambian population lives in the basin

(Schelle & Pittock 2005), and the Kafue supplies drinking water for more than 40% of the Zambian population (Kambole 2003). At its headwaters, the Kafue River flows through the Copperbelt area, where copper and cobalt mining cause substantial pollution by heavy metals (Norrgren et al. 2000; Pettersson & Ingri 2001; von der Heyden & New 2005). After transiting Itezhi-Tezhi (ITT) reservoir, the Kafue River meanders for 425 km through the Kafue Flats before entering Kafue Gorge reservoir.

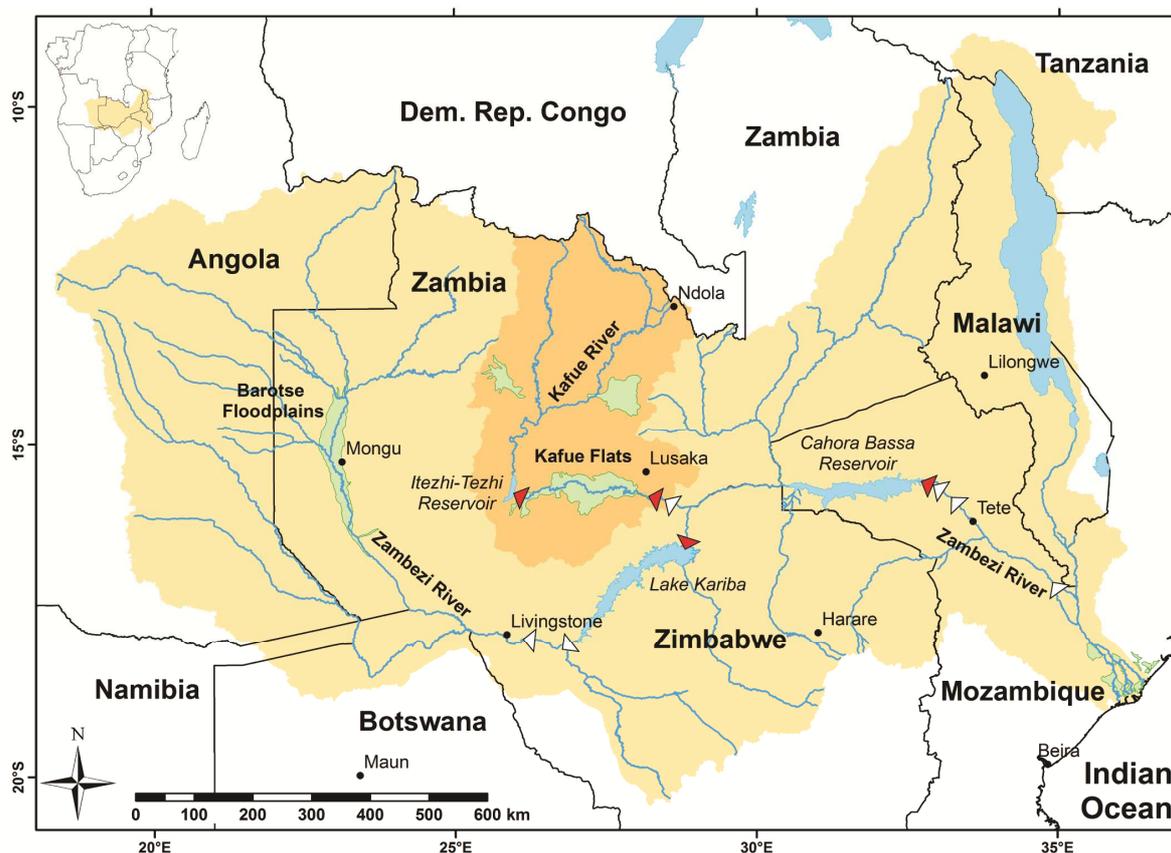


Figure 1. The Zambezi River basin in southern Africa. The Kafue River basin (Zambia) is marked as dark inlay. Existing dams are marked with red triangles, planned dams with white triangles, the green areas are the major wetlands (floodplains and swamps) in the basin.

Table1: Characteristics of large dams in the Zambezi River basin.

Dam	Country	Year commissioned	Reservoir surface area (km ²)	Installed hydropower (MW)
Kariba	Zambia/Zimbabwe	1958	5,364 ^a	1,320 ^a
Cahora Bassa	Mozambique	1974	2,739 ^b	2,075 ^b
Kafue Gorge	Zambia	1971	20 ^{c,d}	900 ^b
Itehi-Tezhi	Zambia	1978	364 ^c	- ^e

^a from Kunz et al. (2011a) and references therein

^b from SADC (2007)

^c from Kunz et al. (2011b) and references therein

^d 800-1,200 km² additional flooded area in the Kafue Flats (Obrdlik et al. 1989)

^e 120 MW currently being installed

The Kafue Flats

The Kafue Flats is a floodplain system along the Kafue River in the lower Kafue River basin (Figure 2). The floodplain is ~250 km long and up to 50 km wide and covers an area of 6,500 km² (Schelle & Pittock 2005). Flooding occurs after the rainy season (~800 mm; November-April) whereby direct precipitation, lateral tributaries and the Kafue River peak flows contribute to inundation (Figure 3). The inundated floodplain is a unique habitat for birds and large mammals, e.g., the endemic Kafue Lechwe, *Kobus leche kafuensis*. The Kafue Flats are listed in the Ramsar inventory of wetlands of international importance (Ramsar 2006) and include two national parks at Lochinvar and Blue Lagoon NP (Figure 2). The floodplain area contains a succession of typical vegetation zones (open water – littoral – termitaria – woodlands) providing an aboveground primary production of up to 2,000 g C m² yr⁻¹ (Ellenbroek 1987). The vegetation zone in the adjacent to the river is almost exclusively made of C₄-grasses (e.g. *Vossia cuspidata*).

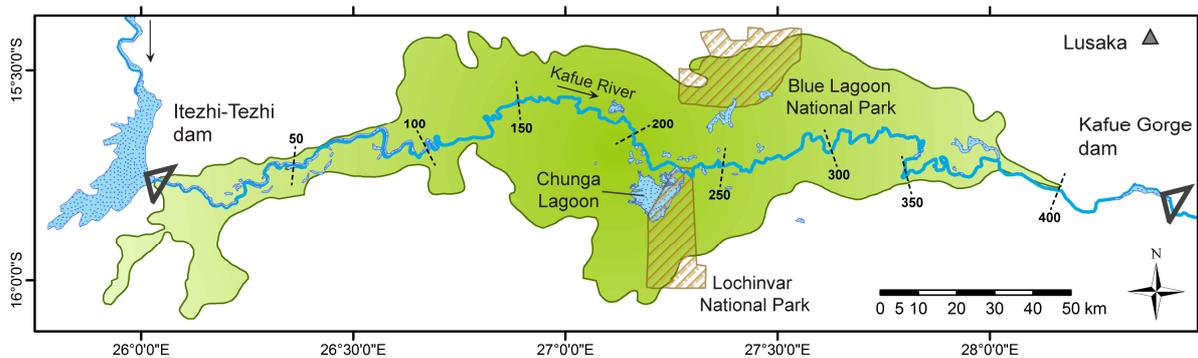


Figure 2. The Kafue Flats between Itezhi-Tezhi and Kafue Gorge dam. The dotted marks along the Kafue River indicate the river distance (km) from Itezhi-Tezhi dam, hatched areas are the national parks

The Kafue Flats experience a distinct wet-dry cycle, with changes in water level of up to 3 m (Figure 3) and large portions of the floodplain falling dry after flood recession (Figure 4). In some areas, the dry floodplain is used as cattle ground, after burning the collapsed floodplain vegetation. Otherwise the land use in the immediate catchment is traditional (subsistence farming, fisheries), and large areas are unused, making the Kafue Flats a relatively pristine floodplain. Sugar cane plantations and agriculture along the last 60 river-km of the Kafue River in the Kafue Flats may cause some anthropogenic nutrient inputs to the river (Sinkala et al. 2002).

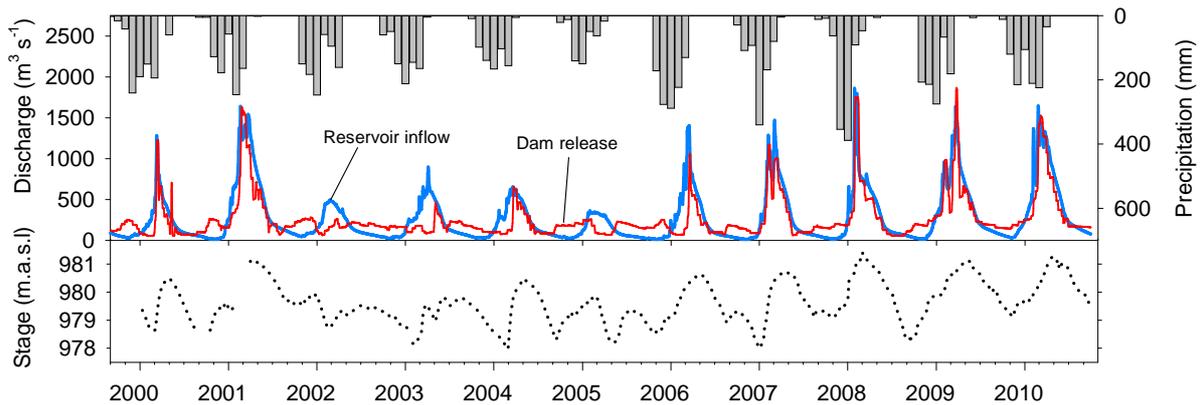


Figure 3. ITT reservoir inflow (blue) and dam release (red) between 2000 and 2010. Grey bars depict the monthly precipitation. The dotted line (lower panel) is the water level 230 km downstream of ITT dam (Data: ZESCO).



Figure 4. Floodplain grasses (mainly *Vossia cuspidata*) during flooding in May 2008 (a) and the dry season in October 2008 (b), 250 km downstream of ITT dam. During inundation, the water depth below the vegetation was >2 m, during the dry season, collapsed grasses cover the dry floodplain soil. (c) Changes in mean water level at Nyimba (230 km from ITT, Figure 6) under pre-dam conditions and after construction of Kafue Gorge and ITT dams, from Blaser et al. (in preparation).

The hydrology of the Kafue Flats has been influenced by an upstream and a downstream dam (Sardon 2009). The downstream dam at Kafue Gorge was built between 1964 and 1971 (closed in 1972) and includes a 900 MW hydropower plant (Figure 2). Upstream ITT dam was closed in 1978 and created a 370 km² storage reservoir to ensure year-round power production at Kafue Gorge. Turbine facilities of 120 MW are currently being installed at ITT. Under the current management scheme, water is released over the spillways at ITT dam (Figure 5), but the release pattern can differ considerably from the hydrology of the inflowing Kafue River (Figure 3). The hydrological modifications include smaller peak discharge and higher base flows, which have changed the flooding patterns in the Kafue Flats (Mumba & Thompson 2005). The construction of Kafue Gorge dam led to a rise in the water table of >2 m in the lower Kafue Flats (Figure 4c), creating a permanently flooded area of ~800 km² (McCartney & Houghton-Carr 1998). Management strategies aimed at restoring some degree of natural hydrology and flooding patterns in the Kafue Flats as timed “environmental flows” from ITT dam have been under development for more than a decade (Acreman 1996; Schelle & Pittock 2005). However, the efficiency of these releases remains unclear. Some studies suggest that

the hydrological changes have influenced habitats for the mammals (Chabwela & Ellenbroek 1990; Chansa & Kampamba 2010; Rees 1978a), and promoted the spread of the invasive shrub *Mimosa pigra* since the 1980s (Genet 2007; Mumba & Thompson 2005). Several studies have also documented effects of dams operation on water quality (Obrdlik et al. 1989; Salter 1985), and fish ecology (Dudley 1974; Dudley 1979; Dudley & Scully 1980).



Figure 5. Itzhi-Tezhi reservoir and dam in May 2010. Water is flowing over the spillways at a discharge of $\sim 380 \text{ m}^3 \text{ s}^{-1}$ and enters the Kafue Flats (courtesy of B. McMorrow).



Figure 6. The Kafue River flowing past the village of Nyimba, 230 km downstream of ITT dam into the Kafue Flats during the rainy season in April 2011 (courtesy of G. Shanungu).

Thesis objectives

Research questions

The goal of this study was to investigate the interaction between hydrological and biogeochemical processes in the Kafue Flats and how dams influence these processes. Specifically, we addressed the following research questions:

- How intense are the hydrological exchange processes between the Kafue River and the floodplain and how do they influence the chemistry of the Kafue River? How is hydrological exchange affected by dam operation?
- What are the sources and fate of the organic matter transported by the Kafue River and how does dam operation affect organic carbon and organic nitrogen dynamics?
- What are the sources and sinks of N and P in the Kafue Flats? How are OM mineralization and nutrient fluxes linked to river-floodplain exchange?

Approach and thesis overview

To address these questions, several field campaigns to the Kafue Flats were initiated between 2008 and 2010 using multiple approaches: We performed high resolution discharge and natural tracer measurements as integrators of physical and chemical processes along the Kafue River. Measuring concentrations of C, N and P species allowed calculating carbon and nutrient fluxes along the river and net exports from the system. The stable isotopic signatures of organic C and N species and spectroscopic properties of DOM were used to assess source and quality of the organic matter. On a system scale, the amount of OM mineralization was quantified with net consumption of dissolved oxygen and the production of inorganic C along the Kafue River. Nutrient fluxes and mineralization were also measured over an annual cycle, and related to the annual primary production and the flooded areas to obtain area-specific fluxes.

The main part of the thesis is divided into three chapters which are individual research articles, followed by a concluding chapter. An outlook over chapters 2-4 is given below:

▪ Chapter 2

River-floodplain exchange and its effects on the fluvial oxygen regime in a large tropical river system (Kafue Flats, Zambia)

In this study we quantified the river-floodplain exchange in the Kafue Flats during the flooding season in May based on discharge measurements and natural tracers ($\delta^{18}\text{O}\text{-H}_2\text{O}$ and specific conductivity). Detailed field measurements revealed that channel morphology is the main driver of river-floodplain exchange in the Kafue Flats. We examined the spatial and temporal variation of the exchange using field measurements, and historical flow data, which allowed comparing pre- and post-

dam exchange patterns. River-floodplain exchange was found to have profound effects on the river water quality, indicated by a steep decline in dissolved oxygen levels and hypoxia for 150 river-km. At the end of the floodplain, >80% of the water leaving the system had spent time in the floodplain. A combination of dissolved oxygen data and the extent of river-floodplain exchange constrained the contribution of in-stream mineralization and floodplain mineralization to the hypoxia in the Kafue River.

▪ Chapter 3

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

In chapter 3 we investigated the sources and quality of the organic matter in the Kafue River and the role of river-floodplain exchange for organic matter fluxes in the system. Based on the quantification of river-floodplain exchange in chapter 2, we expected a shift in OM quality in the river reach that is dominated by floodplain-derived water. Stable isotopic signatures of C and N were used as indicators of source and biogeochemical processes. Spectroscopic analyses and DOM source modeling completed the chemical analysis. We quantified C and N exports from the system and found that Kafue Flats are a large source of organic C and N. The distinct differences between DOM and particulate OM (POM) quality revealed that DOM was from terrestrial sources while POM was composed of phytoplankton. Despite a large injection of OM from the floodplain, the changes of OM quality along the river were small. This suggests that floodplain OM and OM from the upstream reservoir had similar origin and quality.

▪ Chapter 4

System-wide mineralization and C, N, and P export in a dam-impacted tropical floodplain (Kafue Flats, Zambia)

Chapter 4 is an integrated, system-scale analysis of biogeochemical processes in the Kafue Flats based on high resolution measurements along the river during several spatially intense field campaigns and sampling over an annual cycle. Considering results from chapters 2 and 3 we analyzed nutrient fluxes in the system and quantified annual N and P exports and the amount of mineralization and CO₂ emission on a system scale. Total mineralization showed a seasonal pattern, but was small relative to the floodplains' primary production. Over an annual cycle, the Kafue Flats were a net source of inorganic N and P, which was unexpected for a nutrient-poor tropical floodplain. However, only a small percentage of the N and P released during mineralization, was exported from the system, which suggests that most of the N and P was efficiently recycled within the floodplain, or in case of N lost via denitrification.

The African Dams Project

This thesis is part of the African Dams Project (ADAPT). ADAPT is an interdisciplinary project with the goal to provide scientific evidence for planning and operation of large dams in the Zambezi River basin towards social needs and environmental constraints. As a collaborative venture between EPF Lausanne, ETH Zürich, Eawag, and the University of Zambia, the project was funded by the Competence Center for Environment and Sustainability (CCES) of the ETH domain, ETH Zürich, and Eawag.

Within ADAPT, socio-economic effects of dam construction and operation, and aspects of water allocation were addressed at the scale of the entire Zambezi River Basin (Beck & Bernauer 2011; Tilmant et al. 2010; Tilmant et al. 2011). To study multidisciplinary effects of dam operation, a case study was initiated in the Itezhi-Tezhi/Kafue Flats system in Zambia. The goal of this sub-study was to assess combined hydrological, biogeochemical, ecological and socio-economic effects of dam operation in the Kafue Flats (Kunz et al. 2011b; Meier et al. 2010). This thesis addresses the biogeochemical processes in the Kafue River and the Kafue Flats, and how they are related to dam operation.

*River-floodplain exchange and its effects on the
fluvial oxygen regime in a large tropical river system
(Kafue Flats, Zambia)*

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Journal of Geophysical Research-Biogeosciences, 117: 1-12, G03008.
doi: 10.1029/2011JG001853

Abstract

Hydrological exchange between a river and its floodplain plays a critical role in maintaining key ecosystem services like habitat formation, nutrient transformation, and flood attenuation. We studied the spatial and temporal patterns of river-floodplain exchange in the Kafue Flats, a 6,500 km² dam-impacted floodplain ecosystem in Zambia. In addition, we characterized the effects of floodplain runoff on river biogeochemistry, and assessed dam-related changes in the hydrological regime. The basic flood pulse concept poorly describes conditions in the Kafue Flats. Instead, high resolution measurements of discharge and tracers (specific conductivity, $\delta^{18}\text{O}\text{-H}_2\text{O}$) along 410 km of river revealed substantial spatial variations in both the magnitude and direction of river-floodplain exchange. During peak discharge, a river channel constriction, 230 km into the floodplain, diverted as much as 80% of the river's $\sim 700 \text{ m}^3 \text{ s}^{-1}$ discharge into the floodplain. As a net result, >80% of the water exiting the Kafue Flats via the river, either passed through the floodplain or originated from precipitation on the floodplain. This floodplain-derived water had a strong impact on river water quality, resulting in a seasonally-recurring sharp decline in dissolved oxygen levels to $<50 \mu\text{M}$ that persisted for 150 km downstream. A comparison with historical flow data showed that concurrent bank overflow and floodplain inflows were a sustained pattern during the wet season. However, lateral exchange over an annual cycle has been reduced by as much as 50% due to dam operation.

Introduction

The high biodiversity and biological productivity of river floodplains place them among the most valuable ecosystems worldwide (Costanza et al. 1997; Mitsch & Gosselink 2000). Temporal and spatial variations in flooding shape floodplains vegetation patterns (Junk et al. 1989; Ward & Stanford 1995b) and govern their provision of key ecosystem services, such as wildlife habitat, fisheries, water supply, and natural flood attenuation (Tockner & Stanford 2002). The oscillations between wet and dry conditions also drive nutrient and carbon turnover (Baldwin & Mitchell 2000; Olde Venterink et al. 2002).

Hydrological exchange between a river and its floodplain acts as major driver of the spatial extent and duration of flooding by both filling and draining the floodplain (Hamilton 2009). Water leaves the river channel and spills into the floodplain by overbank flow when discharge exceeds the channel's carrying capacity. Direct precipitation and lateral inflows from the catchment can also contribute to floodplain inundation (Baker et al. 2009). While temperate river systems are often dominated by episodic flood pulses in response to heavy rainfall (Junk 1999), large tropical and subtropical floodplain systems are affected by prolonged flooding periods during and after rainy seasons (Hamilton 2009; Hamilton et al. 2002), which has been described as monomodal cycles of filling during the wet season and draining during flood recession (Junk et al. 1989). The prolonged flooding period and the gradually-moving flood edge create highly productive conditions. The extensive flooding of tropical and subtropical river corridors intensifies the turnover of nutrients and organic matter (Aalto et al. 2003; Mladenov et al. 2005).

Over the last century, floodplain ecosystems have decreased dramatically in their spatial coverage, falling victim to river channelization for flood control and land reclamation. This has resulted in large reductions in total wetland area in North America and Europe (60% and 53%, respectively), whereas only 2% of the African wetland area has been lost (Mitsch & Gosselink 2007). Compared to floodplains in temperate regions, many tropical floodplain ecosystems are in relatively intact catchments (Nilsson et al. 2005) with low fragmentation and other anthropogenic disturbance (Zedler & Kercher 2005), but are likely to face increasing pressure from hydrological alteration through water abstraction for hydropower or irrigation (Bratrich et al. 2004; Stevaux et al. 2009), changes in land use patterns (Downing et al. 1999), increased nutrient loading, or greater climatic variability (Hamilton 2010).

We explored river-floodplain exchange in the Kafue Flats, a 6,500 km² tropical floodplain along the Kafue River in Zambia (Figure 1). While the Kafue Flats' immediate subcatchment has experienced only minimal anthropogenic modifications and might otherwise be considered pristine, the system's hydrology has been altered since the 1970s by two large dams (Kunz et al. 2011b). The Kafue River upstream of both dams exhibits distinct seasonal hydrology (Figure 2b) leading to annual

flooding of the Kafue Flats. However, closure of the Itezhi-Tezhi dam diminished the extent of the seasonally flooded areas in the Flats (Mumba & Thompson 2005). Negotiations to restore some degree of natural hydrology and flooding patterns to the system via discharge from the upstream dam have been underway for more than a decade (Acreman 1996; Schelle & Pittock 2005), but no field-based studies have been undertaken to characterize the flooding regime under current conditions in order to establish appropriate environmental flows.

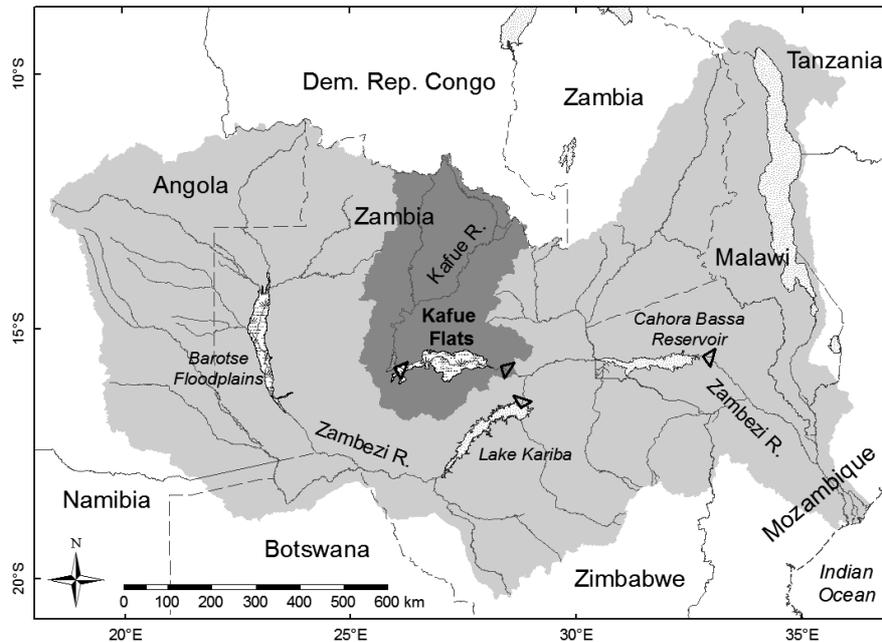


Figure 1. The Zambezi River basin with its eight riparian countries in southern Africa. The Kafue Flats are situated along the Kafue River in lower Kafue River basin (dark shaded) which is an economically important subbasin of the Zambezi River basin. Triangles mark large dams along the Kafue and Zambezi River.

The goals of this study were to (1) characterize temporal and spatial variation of river-floodplain exchange and its main drivers in the Kafue Flats; (2) explore the influence of that exchange on river chemistry; and (3) relate findings to historical data and assess dam-induced changes of the flooding regime. We determined discharge along the Kafue River at high spatial resolution (5-20 km) by acoustic Doppler current profiling (ADCP), and measured natural tracers to determine how flooding and drainage varied spatially along a 410 km stretch of river under current hydrologic forcings. Our results revealed significantly higher spatial variability in hydrological exchange processes compared to common concepts of flooding and recession, and a dramatic drop in oxygen concentration in the downstream reaches of the river that is associated with entry of water from the floodplain.

Methods

Study site - the Kafue River and the Kafue Flats

The Kafue Flats are a floodplain system along a meandering 425 km-reach of the Kafue River in Zambia (Figure 1; Hughes & Hughes 1992). The system is ~250 km long and up to 60 km wide but drops only 12 m from 980.0-968.3 m a.s.l. During the annual inundation, the floodplain turns into an extensive wetland area, evident as a complex mosaic of levees and depressions resulting in lagoons and vegetated areas that are partly disconnected from the Kafue River (Ellenbroek 1987). The rich wildlife habitats of the Kafue Flats are protected by the Ramsar convention (Ramsar 2006). The rainy season lasts from November to April with an average yearly precipitation of ~800 mm. The maximum annual flooding occurs between March and May with a typical flooded area of 2,500-4,500 km² (Meier et al. 2010). The Kafue River, which peak flows up to 1900 m³ s⁻¹, accounts for ~45% of the inundation, while lateral tributaries and direct precipitation contribute ~55% (Wamulume et al. 2011). With the onset of the rains, floodplain grasses fringing the river channel start growing and form dense stands, impeding water flow through the floodplain. The stage amplitude in the Kafue River is generally 2-3 m (Figure 2b). During the dry season from June-October, river discharge drops to <100 m³ s⁻¹ and the floodplain dries up almost completely.

The hydrology of the Kafue River has been altered by the downstream Kafue Gorge dam (closed in 1972) and the upstream Itezhi-Tezhi dam (1978). The impoundment at Kafue Gorge serves for hydropower production (900 MW) while the 370 km² Itezhi-Tezhi reservoir serves as an upstream storage to ensure water supply for Kafue Gorge reservoir (Figure 2a). At Itezhi-Tezhi dam, water is released to the floodplain over the spillways from the epilimnion of the reservoir. The construction of Kafue Gorge dam led to an average rise in water table of >2 m in the lower Kafue Flats and with measurable backwaters up to 180 km upstream of the dam, creating a permanently flooded area of >800 km² (McCartney & Houghton-Carr 1998). Even though there have been attempts to release artificial floods to mimic natural flooding in the Kafue Flats (Schelle & Pittock 2005), flows during the dry season have increased substantially and flood peaks have partly been delayed and attenuated, particularly during dry years, such as 1992, 1995 or 2005 (Figure 2b) which has changed the timing and extent of flooding in the Kafue Flats (Mumba & Thompson 2005). However, the exchange of water between the river and floodplain has not been quantified due to the lack of high resolution data. Understanding the exchange dynamics and its potential alteration by the hydropower scheme is essential to assess the effects of dam operation on water quality and floodplain ecology (Kambole 2003; Rees 1978a).

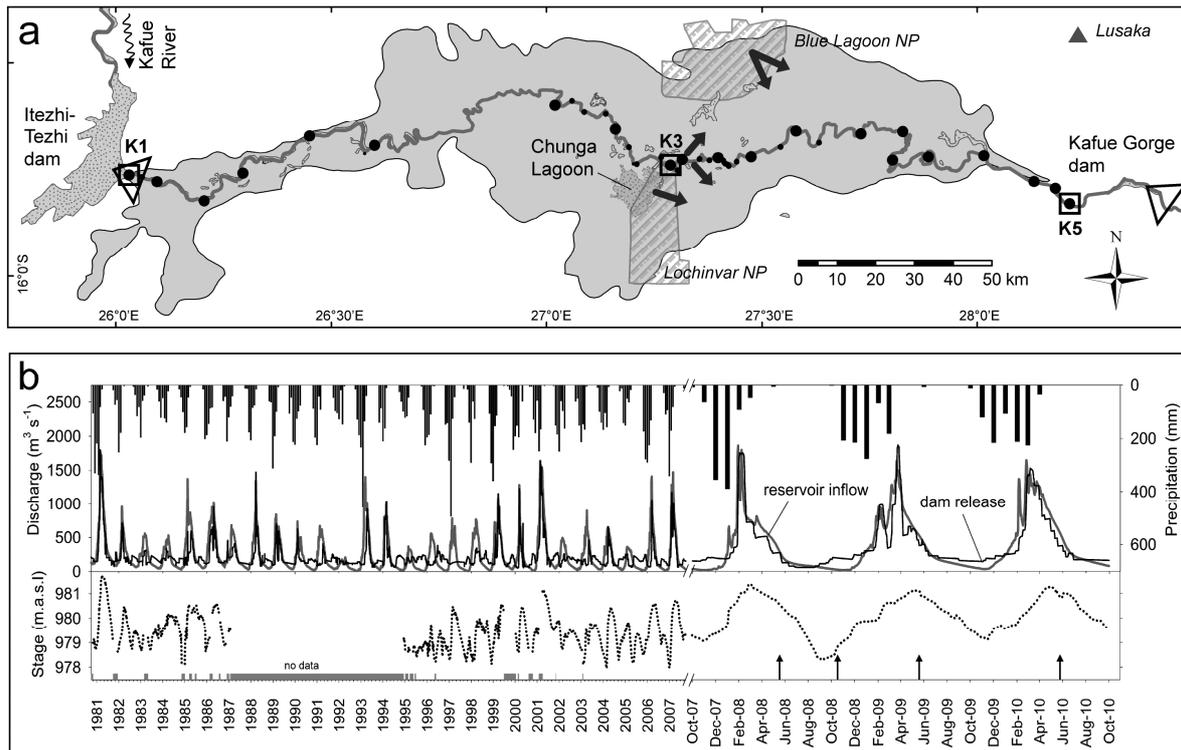


Figure 2. (a) The Kafue Flats are an expansive floodplain system along the Kafue River downstream of Itezhi-Tezhi reservoir. Dams at Itezhi-Tezhi and Kafue Gorge are marked with triangles. Large dots depict sampling stations sampled during all sampling campaigns, small dots are stations additionally sampled at higher spatial resolution in May 2010. Arrows mark transects into the floodplain sampled in May 2010. At stations K1, K3 and K5, framed by rectangles, historical flow data were available from 1962 to 2010. (b) Historical post-dam flow and stage data at from 1980 to 2010. The grey line shows daily flow data at the inflow to Itezhi-Tezhi reservoir, the black line shows the release at the dam spillways. The cascaded course of the dam release is due to spillway operation. Black bars depict monthly precipitation. The dotted line in the lower panel is the daily stage (m a.s.l.) at station K3 in the middle of the floodplain. The timing of the sampling campaigns is marked with black arrows.

Water sampling and field measurements

Initial data were collected during the receding floods in May 2008, followed by intensive sampling campaigns during the subsequent dry season (October 2008) and during flooding periods in May 2009 and May 2010. Sampling was conducted along 410 km of the main stem, starting downstream of Itezhi-Tezhi and ending at the end of the floodplain, 15 km upstream of Kafue Gorge. Sampling intervals were generally 20 km and approximately 6 km for river-km 175 to 280 (Figure 2a). In May 2010, we additionally sampled floodplain water along five 2-7 km-long transects, leading away from the Kafue River into the floodplain (arrows in Figure 2a). Two transects were sampled in Blue Lagoon National Park, which is at the edge of the floodplain (Figure 2a).

Discharge in the main channel of the Kafue River and its tributaries was measured using an ADCP (2008-2009: boat mounted RiverSurveyor, SonTek, USA; 2010: float-mounted RiverRay, RDI Teledyne, USA). Measurements, data analysis and quality control were done according to USGS guidelines (Mueller & Wagner 2009). Briefly, discharge measurements consisted of 3-7 single

transects with a relative standard deviation of 2-10% and 2-5% for the SonTek and RDI Teledyne instruments, respectively. During the flooding period the shore line was not visible, and the edge of the adjacent reed stands was defined as the end of the profile. Bottom-tracking was enabled to correct for boat movements and all profiles were corrected for vertical bank slope. Profiles were analyzed with the RiverSurveyor v4.60 and WinRiverII v2.07 software, respectively.

Water samples were collected in the middle of the main channel at mid-depth by pumping from specific depths through polyethylene tubing (previously rinsed with 2M HCl and deionized water) using a peristaltic pump (Ejikelkamp, The Netherlands). Specific conductivity and temperature profiles at selected stations demonstrated that the main channel was well mixed. Along floodplain transects, water samples were also collected at mid-depth using a similar approach as for the river channel. Dissolved oxygen (DO), pH, specific conductivity corrected to 25°C (κ_{25}) and temperature were measured immediately on-board by slowly pumping water through an overflow vessel and using a multiprobe (Multi 340i, WTW, Germany). Multiprobe measurements were confirmed by reference samples for dissolved oxygen, analyzed by Winkler titration. Unfiltered water samples for oxygen isotope analysis were stored cold and dark. Details on precipitation sampling are given as supplementary information.

Laboratory analyses

Samples for oxygen stable isotope measurements ($\delta^{18}\text{O}$) were filled in 3 mL Exetainer vials (Labco, UK) as 200 μL aliquots, the headspace replaced by 10 mol% CO_2 in helium and equilibrated for 4.5 h at 40°C. Analysis was done with a MultiFlow preparation module connected to a continuous flow IRMS (Isoprime, UK). Four in-house standards of 0‰, -8.8‰, -11.8‰, and -14.5‰ (Fette et al. 2005) were calibrated against IAEA-VSMOW2; data are hence indicated as ‰_{VSMOW2}. Precision was better than $\pm 0.1\text{‰}$.

Results

River discharge and channel morphology

The longitudinal variability in discharge is illustrated with data from field surveys during the flooding period in May 2009 (Figure 3a). After a small increase over the first 60 km downstream of the dam, discharge decreased by nearly a factor of 3 over the following 190 km. No outflows were observed in the field, nor detected on satellite images (NASA Landsat Program 2009) and maps, which suggests that flood water left the main channel and entered the floodplain in inconspicuous channels or as diffuse flow through riparian vegetation. Over the remaining 150 km, discrete channel inflows were visible and flow rates increased again by a factor of 2.5.

Flow measurements at higher spatial resolution in May 2010 indicated that this flow pattern of a losing and gaining river is a recurring phenomenon during the flooding period (Figure 3a). For simplicity the river was divided in five sections - I, II, IIIA, IIIB and IV - that represent the different hydrological reaches (e.g. losses or gains of river water; Figure 3). The measurements 180-225 km downstream of Itezhi-Tezhi dam (sections II), revealed a sharp six fold decline in discharge, reaching a minimum flow of $97 \text{ m}^3 \text{ s}^{-1}$ at 225 km. The subsequent flow increase resulted from readily discernible tributaries draining large floodplain areas entering at 220 km, 310 km, 340 km (Figure 3a), and from diffuse floodplain inflows (e.g. 380-410 km). In the dry season (October 2008), the dam-regulated discharge below Itezhi-Tezhi was $220 \text{ m}^3 \text{ s}^{-1}$. This flow was larger than the natural reservoir inflow (Figure 2b). In contrast to the May data, discharge was relatively constant over the first 225 km and the floodplain was completely dry for long stretches of river.

The large longitudinal variations in discharge during the flooding period were highly correlated with channel cross-sectional area ($R^2=0.96$, $P<0.001$). Transect area, measured in 2010, decreased by a factor of 2 along section II, and then increased by more than 5-fold until the end of the floodplain (Figure 4). The May 2009 transect areas exhibited the same pattern (not shown). Our findings of decreasing channel cross section along this stretch are consistent with older measurements from a river channel survey (DHV 1980). Flow velocity measured by ADCP also decreased from 0.78-0.25 m s^{-1} along section II in 2010, but returned to $\sim 0.5 \text{ m s}^{-1}$ after 225 km.

Natural tracers – specific conductivity and $\delta^{18}\text{O}$

The natural tracers specific conductivity (κ_{25}) and $\delta^{18}\text{O}$ of water helped to distinguish between river water and floodplain-derived water that experienced greater fractional losses to evaporation. Conductivity in the river channel in May 2009 and 2010 remained relatively constant until ~ 220 km, and increased sharply thereafter from ~ 150 to $190 \mu\text{S cm}^{-1}$ (Figure 3b). During both high-discharge sampling transects, $\delta^{18}\text{O}$ also increased substantially along the same stretch, from approximately -5.0

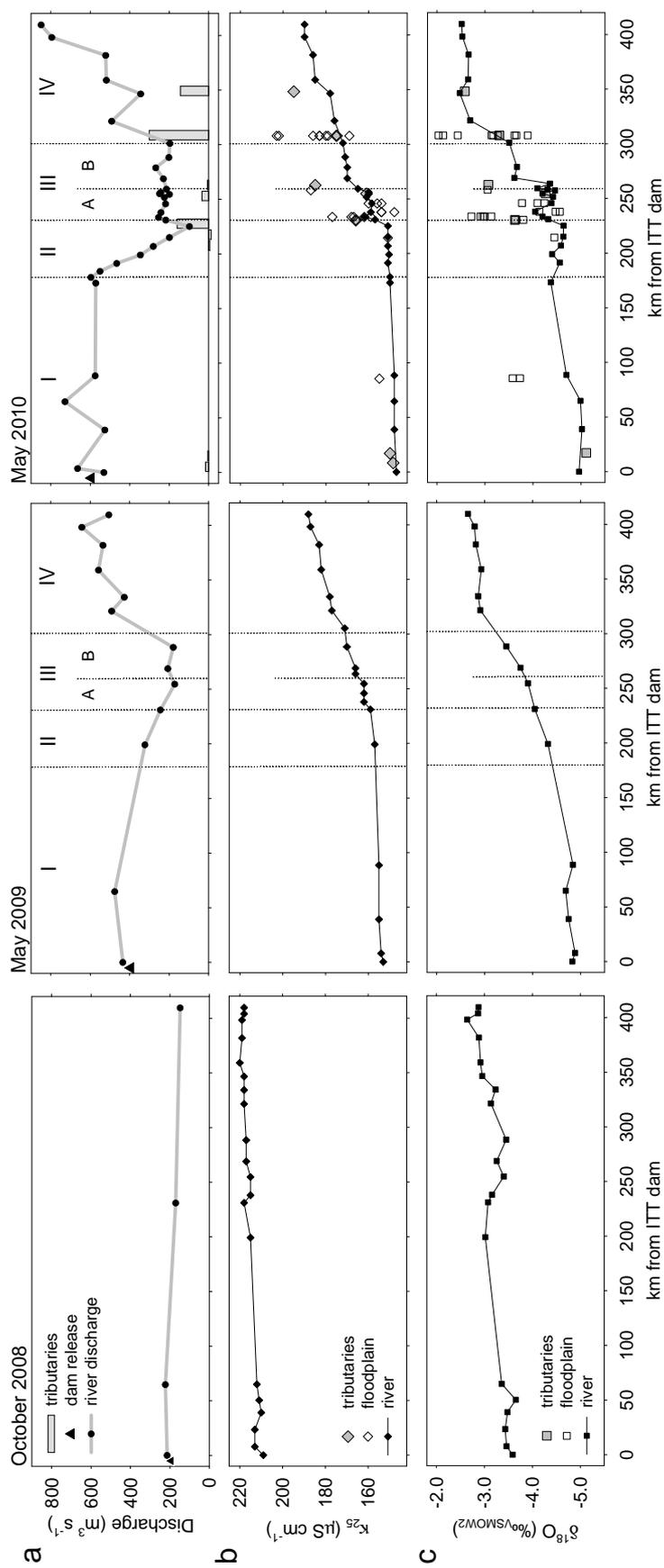


Figure 3. (a) Discharge, (b) specific conductivity (K_{25}) and (c) $\delta^{18}\text{O}$ of the sampling campaigns during the dry season in October 2008, and during flooding period in May 2009 and May 2010. May 2010 data include measurements from the river channel, tributaries and floodplain stations. Distances from river and floodplain stations and tributaries are in river-km along the main channel from downstream of Itezhi-Tezhi dam (0 km) to the end of the floodplain (410 km). Dotted lines indicate sections of different hydrological regimes (I-IV).

to -2.5‰ . The higher κ_{25} and $\delta^{18}\text{O}$ values observed downstream of ~ 225 km are consistent with the entry into the river of water masses that had experienced substantial evaporation during residence on the floodplain.

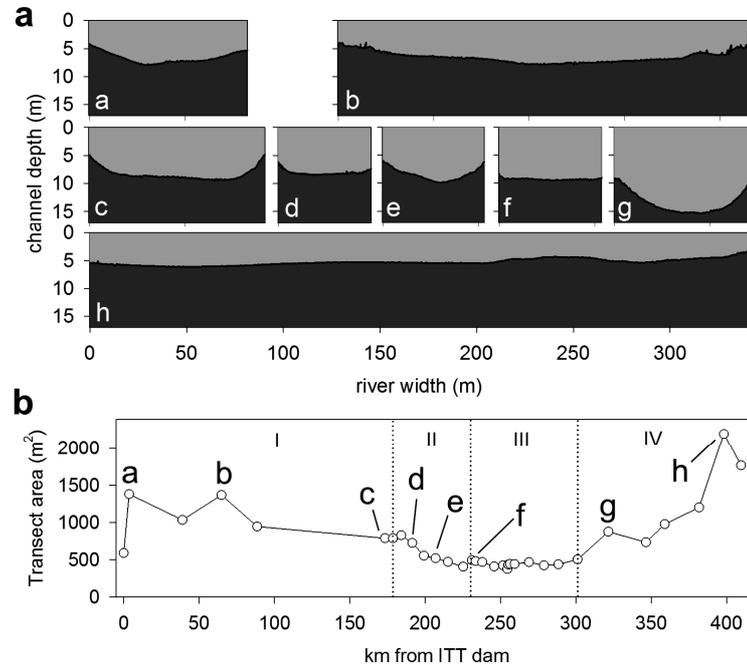


Figure 4. (a) River cross sections (river width vs. depth) from the left to the right bank along the Kafue River. The vertical banks at beginning and end of each cross section are defined by fringing floodplain vegetation. The flow velocities within the vegetated area were below detection limit of $\sim 0.5 \text{ cm s}^{-1}$. (b) River transect areas for May 2010, measured by ADCP. Sections I-IV as in Figure 3.

Tracer measurements confirmed that floodplain water had indeed experienced considerable evaporation. Floodplain $\delta^{18}\text{O}$ values in May 2010 (mean -3.4‰ , max -2.0‰) were substantially more ^{18}O -enriched than the isotopic signature of both the river water entering from Itezhi-Tezhi dam (-5‰ ; Figure 3c) and the annual weighted average $\delta^{18}\text{O}$ of precipitation collected during the rainy season 2008/2009 (-8.7‰ ; Figure S1, supplementary information). The floodplain $\delta^{18}\text{O}$ values were also generally higher than in the adjacent river channel, although river $\delta^{18}\text{O}$ values increased in the downstream direction and gradually approached those of the floodplain (Figure 3c). Conductivity displayed a similar pattern as $\delta^{18}\text{O}$, with values measured at the floodplain stations considerably elevated relative to Itezhi-Tezhi dam release, and κ_{25} in the floodplain was generally greater than in the adjacent river.

While the fairly constant increases in κ_{25} and $\delta^{18}\text{O}$ observed in May 2009 suggested that exchange with the floodplain was occurring at a steady rate along the river, higher resolution data from May 2010 revealed that inflow of water from the floodplain varied considerably along the river. Some locations had step increases in κ_{25} and $\delta^{18}\text{O}$ that were accompanied by increases in discharge. For example, between 225 km and 230 km, the inflow from the Chunga Lagoon (-3.6‰) approximately

doubled the river discharge (which was at its minimum at this location), and contributed relatively ^{18}O -enriched water resulting in a $\delta^{18}\text{O}$ maximum. Discharge and $\delta^{18}\text{O}$ also increased substantially between 300-320 km (Figures 3a and 3c) due to a visible inflow draining the floodplain. At other locations κ_{25} and $\delta^{18}\text{O}$ increased substantially while discharge remained relatively constant (section III, Figure 3b and 3c).

During the dry season, $\delta^{18}\text{O}$ and κ_{25} in the Kafue River differed markedly from measurements during the flooding period. Waters leaving Itezhi-Tezhi reservoir in October 2008 had higher κ_{25} ($210 \mu\text{S cm}^{-1}$) than during the flooding period (Figure 3b), and increased moderately compared to spatial variations observed in May 2009 and May 2010. In analogy to κ_{25} , high $\delta^{18}\text{O}$ values were observed below the dam and remained relatively constant over the 410 km. The observed change in $\delta^{18}\text{O}$ in October 2008 can be explained by $\sim 5\%$ evaporation occurring along the main channel (Table S1, supplementary information), which is also consistent with the $\sim 4\%$ increase in κ_{25} over the 410 km.

Dissolved oxygen concentrations

During the flooding period in May 2009, water exiting the upstream Itezhi-Tezhi reservoir entered the river via a surface spillway, and had super-saturated dissolved oxygen (DO) levels along with pH ~ 8 and T $\sim 24^\circ\text{C}$ (Figure 5). DO concentration decreased by 28% over the first 64 km, which could be explained by a combination of gas exchange of excess-DO out-gassing and some in-stream respiration. DO levels remained relatively constant until 190 km, and then dropped precipitously from ~ 190 to $\sim 30 \mu\text{M}$ between 230 and 260 km (depicted as section IIIA). A similar decreasing pattern in pH from 7.6 to 6.9 was observed over this stretch (Figure S2, supplementary information), consistent with the assumption that the low-oxygen regime which persisted over the subsequent ~ 150 km downstream was caused by respiration, and thus accompanied by elevated concentrations of dissolved carbon dioxide. DO levels exhibited a similar pattern in May 2010 (as well as during the preliminary field investigation in May 2008) in terms of the magnitude and location of the sharp DO decrease and in the downstream persistence of low oxygen, indicating that this is a seasonally recurring event (Figure 5). In May 2010, hypoxic conditions (with sometimes less than $15 \mu\text{M O}_2$) were observed at multiple locations in the floodplain, in particular along transects between 200-250 km. The sharp decline in DO was not observed in October 2008, however, an oxygen decrease was observed between 260 and 380 km, although the deficit was much less pronounced than during flooding.

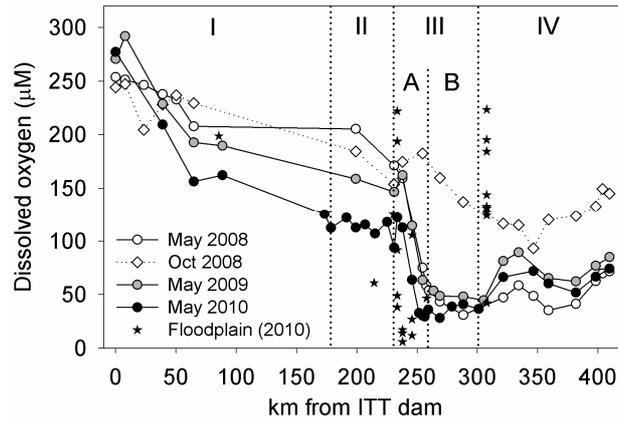


Figure 5. Dissolved oxygen concentrations along the Kafue River between 2008-2010. Floodplain measurements in 2010 are marked with stars. Sections I-IV depict stretches of different hydrological regimes. The distinct decline in dissolved oxygen occurred in section IIIA.

Discussion

Modes and magnitudes of river-floodplain exchange

In tropical systems, the phenomenon of river-floodplain exchange is generally thought of as a gradual filling of the floodplain during wet season followed by drainage during flood recession, (flood pulse concept (Junk 1999; Junk et al. 1989)). However, our observations along different sections of the Kafue River during the flooding period (I-IV, Figure 3) illustrate that lateral exchange can be more complicated and strongly depends on channel morphology, with filling and draining of the floodplain taking place concurrently at different locations along the river. Figure 6 provides an overview of the proposed exchange processes during the flooding period. Along section I (<180 km) discharge and tracer data suggested limited mixing with the narrow floodplain, but rather some branching of the channel and inflows of catchment tributaries that were lower in κ_{25} and relatively ^{18}O -depleted (Figure 3). In section II, the decrease in channel carrying capacity caused large-magnitude steady-state overbank flow in the absence of distinct channels, that is, water was forced into the floodplain through the dense stands of riparian vegetation. Downstream of 300 km (section IV) an expansion in the channel cross section was associated with the return of large volumes of water from the floodplain. Based on its evaporative signal, this water had spent ~ 2 months in the floodplain (see supplementary information for details). This large-scale exchange, evident as concurrent losses and gains of river water, cannot be explained by single flood pulse, where inflows and outflows would be out of phase.

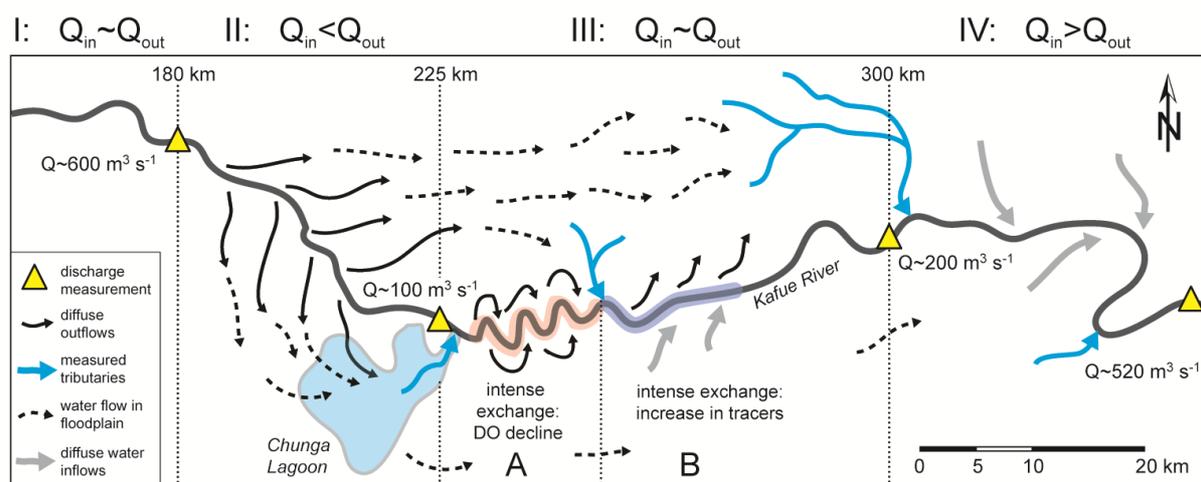


Figure 6. Conceptual illustration of river-floodplain exchange and its effects along the Kafue River in sections I, II, IIIA, IIIB and IV between ~ 160 km and 380 km downstream of Itezhi-Tezhi dam.

Along section III (225-300 km), a different exchange mechanism was observed since the tracer data suggest that lateral exchange must have occurred in the absence of a net change in discharge.

This is well-illustrated by detailed κ_{25} measurements between 257-259 km (Figure S3, supplementary information). Although discharge decreased by 10% along this stretch, >24% of the river water must have been exchanged by higher conductivity water ($\sim 180 \mu\text{S cm}^{-1}$) entering the main channel, to explain the increase in κ_{25} of $5 \mu\text{S cm}^{-1}$. Lateral exchange most probably occurred as crossflow, i.e. inflow from the south and loss at the northern bank (Figure 6). This exchange with the adjacent floodplain could have been caused by a lateral slope in terrain or by the momentum of the strongly meandering channel forcing water through dense fringing vegetation. This type of lateral exchange likely also occurs at other locations with constant discharge and changing tracer signatures in section IIIB.

At the scale of the entire Kafue Flats, we estimated the magnitude of river-floodplain exchange for May 2009 and May 2010 by combining discharge measurements and natural tracers in an end-member mixing model. Water leaving Itzhi-Tezhi reservoir and water from the floodplain served as end-members for κ_{25} and $\delta^{18}\text{O}$. For comparison, we also calculated what the floodplain contribution would have been in October 2008 if no evaporation occurred along the Kafue River. The lateral flows between river and floodplain, Q_{lat} , for each station was calculated as

$$Q_{\text{lat}} = Q_{\text{river}} \times \left(\frac{\delta^{18}\text{O}_{\text{river}} - \delta^{18}\text{O}_{\text{reservoir}}}{\delta^{18}\text{O}_{\text{reservoir}} - \delta^{18}\text{O}_{\text{floodplain}}} \right) \quad (1)$$

where $\delta^{18}\text{O}_{\text{river}}$ is measured at a given station, $\delta^{18}\text{O}_{\text{reservoir}}$ denotes the inflow from the reservoir (-5.0‰) and $\delta^{18}\text{O}_{\text{floodplain}}$ refers to the composition of floodplain inflows to the main channel. We used the heaviest signatures measured in the floodplain, that is, -2.0‰ and -2.2‰ for May 2009 and 2010, respectively, which minimized the calculated floodplain contribution Q_{lat} and should thus be considered as a lower limit of exchange. Based on a comparison of $\delta^{18}\text{O}_{\text{floodplain}}$ with annual weighted average $\delta^{18}\text{O}$ of precipitation, and using the relationships of Gonfiantini (1986), and Gibson & Reid (2010), floodplain waters had experienced 20-40% evaporation (Table S1, supplementary information). An analogous expression was developed for κ_{25} . Model results revealed an increasing proportion of floodplain-derived water along the river (Figures 7a and 7b). Downstream of 300 km, the minimum percentage of river water that had spent time on the floodplain is 83% in 2009 and 87% in 2010. For lower $\delta^{18}\text{O}_{\text{floodplain}}$ values, floodplain contribution would be as high as 95%. In comparison, the increase in $\delta^{18}\text{O}$ in October 2008 would correspond to a floodplain contribution of only 16% (Figure 7c).

Mechanisms of oxygen depletion

Dissolved oxygen concentrations along the Kafue River are a function of in-stream respiration (i.e. aerobic oxidation of organic carbon (OC) within the river channel), primary production, oxidation of reduced species, reaeration (gas exchange with the atmosphere), and the exchange with low-DO

floodplain water. Along the river stretch where DO decreased rapidly (section IIIA, Figures 5 and 6), an DO consumption rate of 8-20 $\mu\text{mol L}^{-1} \text{h}^{-1}$ would have been required for in-stream respiration to explain all of the DO decrease in the absence of lateral exchange. Such a rate is unrealistically high compared to rates typically observed in tropical river systems (0.1-3 $\mu\text{mol L}^{-1} \text{h}^{-1}$; Table S5, supplementary information), and 4-10 times faster than the apparent in-stream DO consumption rate of 1.9 $\mu\text{mol L}^{-1} \text{h}^{-1}$ derived for the first 88 km. In addition, a sharp increase in the respiration rate at 230 km would have required a large input of labile OC, and the respiration of $\sim 70 \mu\text{M}$ OC over this stretch, which is inconsistent with complementary OC data that suggests only a minor contribution of rather refractory OC entering from Chunga Lagoon [R. Zurbrugg, S. Suter, M.F. Lehmann, B. Wehrli, D. B. Senn, Organic carbon and nitrogen export from a tropical dam-impacted floodplain system, submitted to Biogeosciences, 2012]. Primary production in the river and the floodplain could mitigate hypoxic conditions. However, decreases in particulate OC concentrations along the river suggested that primary production in the channel might be rather small.

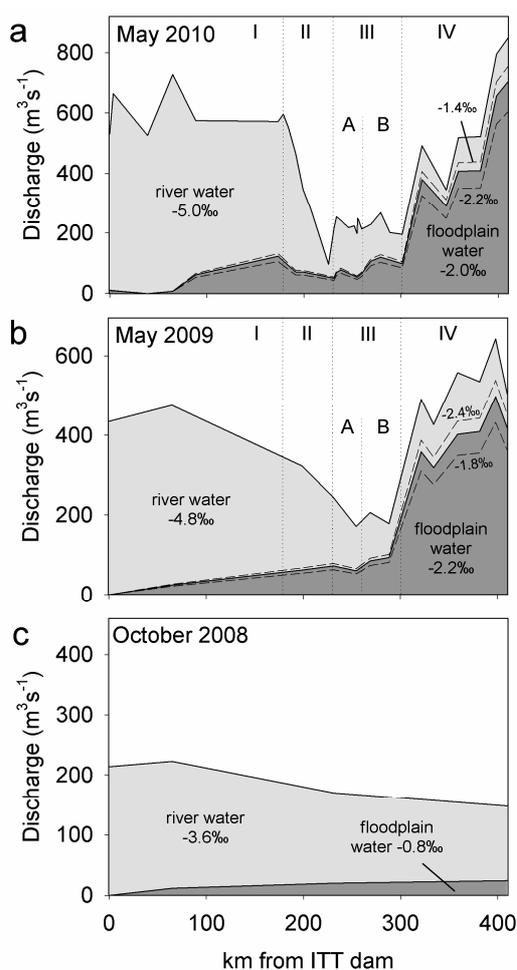


Figure 7. Floodplain contributions to river discharge calculated by a mixing model based on $\delta^{18}\text{O}$ data in May 2010 (a), May 2009 (b) and October 2008 (c). Dashed lines indicate floodplain contributions using alternative $\delta^{18}\text{O}$ end-member values. Analogous mixing models for κ_{25} gave floodplain contributions of 66-76% for the May campaigns and 18% for October 2008.

We therefore hypothesized that the seasonally-recurring sharp decline in DO concentrations in section IIIA and the low-DO persistence downstream resulted from a combination of low-DO floodplain water entering the river and in-stream respiration of OM supplied from the floodplain to the river (Devol et al. 1995; Hamilton et al. 1997). A box-model approach was developed to quantify these processes, and to assess whether in-stream respiration or lateral exchange of low-DO floodplain water exerted the greatest influence on DO levels in May 2010. Sections IIIA, IIIB and IV were assumed as well-mixed, steady-state boxes. Modeled parameters included in-stream respiration, reaeration, and lateral exchange of water with the floodplain. The in-stream respiration was kept constant for all three boxes at the same rate as deduced for section I ($1.9 \mu\text{mol L}^{-1} \text{h}^{-1}$) and we assumed that the inflowing floodplain water had $\text{DO} = 0 \mu\text{M}$ (the lowest floodplain DO was $6 \mu\text{M}$). A detailed description of the box-model is provided as supplementary information.

Table 1. Box-model results for sections IIIA-IV for May 2010.

Section	River-km	Contribution to DO consumption (%)	
		Lateral exchange	In-stream respiration
IIIA	225-260	90	10
IIIB	260-300	78	22
IV	300-410	49	51

Using this approach, lateral exchange was identified as the dominant factor for the DO consumption over the DO decline (IIIA) and in section IIIB (Table 1). For IIIA where lateral exchange was particularly important, the tracer mixing model predicted only moderate exchange with high κ_{25} and $\delta^{18}\text{O}$ water (Figure 7). Since any exchange along this section must have occurred with no net change in discharge, the floodplain water must have had similar κ_{25} and $\delta^{18}\text{O}$ as the river itself. Tracer data in floodplain samples from this area showed that this was in fact the case (Figure 3). Such an effect could result from a “near-field” exchange with the floodplain, where river water migrates into and through the dense grass stands, and spends sufficient time in the reducing environment to lose substantial quantities of oxygen but returns to the river before experiencing a level of evaporation that would significantly influence $\delta^{18}\text{O}$ and κ_{25} . The same effect also contributed 45-58% to the lateral exchange observed along section IIIB; the remaining 42-55% could be explained by the tracer mixing model (Figure 7). For the dry season, the observed decrease in DO concentrations could be explained by in-stream respiration at rates of $\leq 1.9 \mu\text{mol L}^{-1} \text{h}^{-1}$, in the absence of lateral exchange. This is consistent with the interpretation that the measured changes in tracers in October 2008 were a result of evaporation along the main channel and that very limited river-floodplain exchange was involved.

The low oxygen levels observed in the Kafue River likely resulted from largely natural phenomena, and were probably also a prominent feature of this system during pre-dam periods. Indeed, low DO levels have occasionally been documented in the Kafue Flats, before as well as after

closing of Kafue Gorge (1972) and Itezhi-Tezhi (1978) dam (Dudley 1979; Dudley & Scully 1980; Kambole 2003; Obrdlik et al. 1989), although the temporal and spatial occurrence had not been documented nor had the contributing processes been estimated. Such oxygen declines have so far been documented in only a few studies (Amazon: Devol et al. (1995); Paraguay River; Hamilton et al. (1997); Paraguay and Miranda Rivers, Oliveira et al. (2010)).

Long-term seasonality of river-floodplain exchange and dam impact

To characterize seasonal and interannual variations in river-floodplain exchange, findings from the 2008-2010 field measurements were compared with flow records from a longer post-dam period (1979-2010). Ten years of pre-dam discharge data (1962-1971) also allowed for comparison of exchange before and after dam construction. Discharge was derived from stage data and rating curves (supplementary information), available at three stations (K1, K3, and K5; Figure 2a) that divide the Kafue Flats into two control volumes (CV1 and CV2; Figure 8). As a measure of river-floodplain exchange, the fraction of water exchanged (FE) was calculated for each control volume. FE is defined as the fraction of water gained from (positive) or lost to (negative) the floodplain (Wamulume et al. 2011):

$$FE = \frac{Q_{out} - Q_{in}}{Q_{in}} \quad \text{for } Q_{out} < Q_{in} \quad (2)$$

$$FE = \frac{Q_{out} - Q_{in}}{Q_{out}} \quad \text{for } Q_{out} > Q_{in} \quad (3)$$

where Q_{in} and Q_{out} are the river inflows and outflows, of the control volume, respectively. Because travel times along the river through the control volumes were ~ 4 days (based on measured flow velocities), monthly average flows were used to calculate FEs so that short-term (daily) fluctuations in flow did not influence the estimate. This analysis focuses on flows in the river, and does not explicitly address water flows across CV boundaries within the floodplain, although such movement could have been occurring (Figure 6). Since FE is a discharge-normalized parameter, large positive or negative FE values indicate large relative differences between inflows and outflows.

Pronounced differences in both the relative magnitude and direction of lateral exchange were observed between the two CVs from October 2007-September 2010 (Figure 8a). Similar to the measurements from May 2009 and May 2010, CV1 was defined by large negative FE (i.e., outflows from the river to the floodplain) between November and June, with negative FE peaks in February at the onset of the annual flooding. During these periods of high flow, 40-60% of the water entering at K1 was diverted into the floodplain before reaching K3. Although substantial positive FEs (0.2-0.6) were also observed at other times of the year, it should be noted that flow in the river was low at those times ($\sim 150 \text{ m}^3 \text{ s}^{-1}$) and so the magnitudes of the gains from lateral exchange were small compared to

the losses during peak flow. In contrast to CV1, CV2 exhibited large positive FE (up to +0.7) over several months during and after the rainy season (Figure 8a), indicating that the large gains of floodplain-derived water observed in May 2009 and May 2010 are part of a sustained pattern in CV2. FE occasionally decreased to less than +0.1 at the end of the dry season, which is consistent with our flow measurements from October 2008.

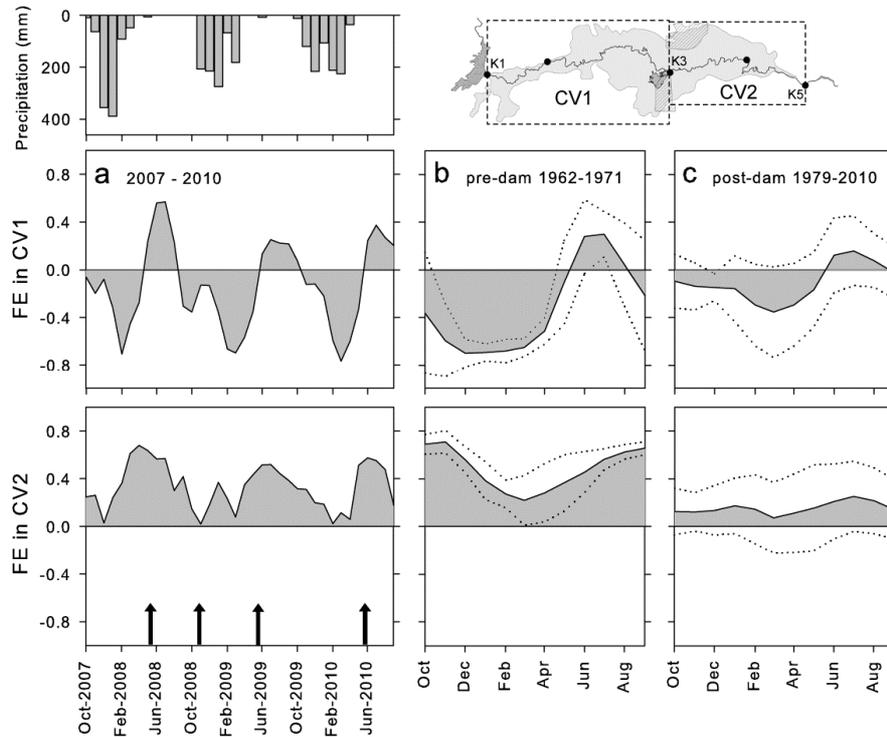


Figure 8. (a) Fraction of exchanged water (FE) calculated from monthly averaged flow data for Control Volumes (CV) 1 and 2 from October 2007 to September 2010, the time around the four field campaigns (indicated as arrows). For comparison, precipitation data from Figure 2b were redrawn. (b) Mean FEs over an annual cycle before and (c) after dam construction. Dotted lines indicate $\pm 1\sigma$ confidence intervals.

These longer-term flow records support the assertion that channel morphology plays an important role in dictating exchange between the Kafue River and the floodplain. The sharp reduction in channel cross-sectional area and bank-full capacity that occurred between 180 km and 225 km makes CV1 a losing river stretch over much of the year, diverting up to 80% of discharge into the floodplain during high-flow periods. Ellenbroek (1987) estimated the bank-full capacity of the river at K3 was $\sim 170 \text{ m}^3 \text{ s}^{-1}$, which approximately corresponds to the discharge at K3 when calculated FE shifts from positive to negative over the years studied. The large increase in cross-sectional area downstream of 300 km fosters drainage of the floodplain and explains the large positive FEs for CV2 over much of the year. Despite the 2008-2010 field study period being relatively wet years compared to the rest of the 30-year post-dam record, the FE values calculated for 1979-2006 for CV1 and CV2 are generally consistent with those calculated for 2007-2010. Over this time period a large fraction of the river

flow was lost to the floodplain in CV1, and large gains occurred downstream within CV2 (Figure S4, supplementary information). Monthly-mean FE plots for CV1 and CV2 (Figure 8b) over the post-dam period, therefore, show a similar pattern as identified for 2007-2010.

During the pre-dam period before 1972, the same dominant river-floodplain exchange features (as determined by FE) were observed as during the post-dam period, namely large losses (negative FE) from CV1 and large gains (positive FE) within CV2 (Figure 8c). However, the proportion of water lost from CV1 during peak discharge in February was substantially smaller during the post-dam period, which likely resulted from lower, managed flows released at Itezhi-Tezhi (i.e., during annual reservoir filling) compared to the pre-dam natural flows. In addition, discharge gains along CV2 from the floodplain were considerably lower during the post-dam period compared to the pre-dam period. These observations suggest that river-floodplain exchange after 1979 has been as much as 50-60% less than river-floodplain exchange pre-1972.

In the absence of chemical data from the pre-dam period we can only draw a tentative scenario of how the upstream dam might have altered biogeochemical processes in the floodplain. The construction of Kafue Gorge dam has resulted in a backwater effect, increasing the mean water levels at station K3 by >2 m and creating a permanently flooded area of 800-1,200 km² (Dudley 1979; McCartney & Houghton-Carr 1998). The slower post-dam rate of change in water level at K3 (Figure 2b) during flood recession (0.3 cm d⁻¹ compared to 1.3 cm d⁻¹ before dam construction) suggest that, to a first approximation, these areas may drain at a fourfold slower rate. These permanently flooded areas with reducing sediments would be poorly mixed and experiencing limited reaeration, and would thus have a tendency to be depleted in DO. As these areas drain to the river, they would be a steady source of low-DO water, which may contribute to the persistent oxygen depletion in the lower Kafue River, observed during our sampling campaigns (Figure 5). Kumm et al. (2006) also documented prolonged anoxia in the Tonle Sap and its floodplains due to slower drainage resulting from dam-induced reduction of the Mekong flood pulse. Low DO conditions in the permanently inundated areas would also influence OC cycling, with potentially lower mineralization rates (Baldwin & Mitchell 2000) and altered nitrogen cycling (e.g. disruption of coupled nitrification-denitrification; Kern et al. 1996; Olde Venterink et al. 2002).

Conclusions

Hydrological river-floodplain exchange is an important feature of tropical floodplain systems. It influences the timing and location of flooding, is responsible for habitat formation, and also strongly influences carbon and nutrient cycling and transport. Our study demonstrates that the coarse-grained picture of tropical floodplains as being gradually filled and drained during and after the wet season, respectively, needs to be completed by an analysis of meso-scale processes of lateral exchange driven by river morphology and local topography. In the Kafue Flats, filling and draining of the floodplain took place concurrently at different locations along the river during the flooding period. Channel morphology, namely changes in cross-sectional area and bank-full capacity, dictated the location, magnitude, and direction of river-floodplain exchange, with up to 80% of river flow being forced into the floodplain due to a channel constriction. Downstream expansions in channel capacity simultaneously induced lateral flows of comparable magnitude out of the floodplain and back into the river. Field investigations during the flooding period revealed that >80% of the river water in downstream stretches had travelled through or originated from the inundated floodplain and experienced up to 40% evaporation based on its $\delta^{18}\text{O}$. The lateral exchange with oxygen-depleted floodplain water was identified as the main driver for the very low oxygen concentrations (<50 μM) that persisted over 150 km of river reach.

Long-term discharge data showed that these large-scale exchange processes occurred during most years, and that the concurrent losses and gains along different river stretches extend over periods of months each year. Dam construction in 1972 and 1978 has reduced this river-floodplain exchange by as much as 50%. Management efforts to restore ecological flows and mimic natural flooding patterns in this and other systems need to take into account hydrological and morphological drivers of river-floodplain exchange processes. This will require more detailed hydrological models with spatially explicit river-floodplain exchange.

Acknowledgements

The authors thank E. Ngandu, B. Wishikoti and G. Shanungu (ZAWA), S. Mwale (ZRA), W. Sakala (ZESCO), A. Kabwe and N. Blank for assistance during field work. The study was supported by I. Nyambe (University of Zambia), W. Chansa and C. Simukonda (ZAWA), M. Mbuta (ZESCO), E. Siamakocha (ZRA), and A. Hussen and P. Chola (DWA). Funding was provided by the Competence Center for Environment and Sustainability (CCES) of the ETH domain, the Swiss National Science Foundation (Grant No. 128707) and Eawag.

Supplementary information

$\delta^{18}\text{O}$ measurements in precipitation

Precipitation samples were collected at the Zambia Electricity Supply Corporation (ZESCO) meteorological station close to Itezhi-Tezhi dam ($15^{\circ}44'43.16''\text{S}$, $26^{\circ}1'10.93''\text{E}$). Two acid rinsed LDPE rainwater collectors with 110 mm diameter opening and 10 mm layer of paraffin oil to prevent evaporation were exposed during the rainy season 2008-2009. >99% of the total precipitation of 975 mm between 21 May 2008 and 28 April 2009 was collected. Exposure times varied between 24 and 60 days and samples were split and analyzed in duplicates for $\delta^{18}\text{O}$ (see Methods). Precipitation was measured alongside in a separate rain gauge on a daily basis and provided by ZESCO. The results of $\delta^{18}\text{O}$ in precipitation are shown in Figure S1.

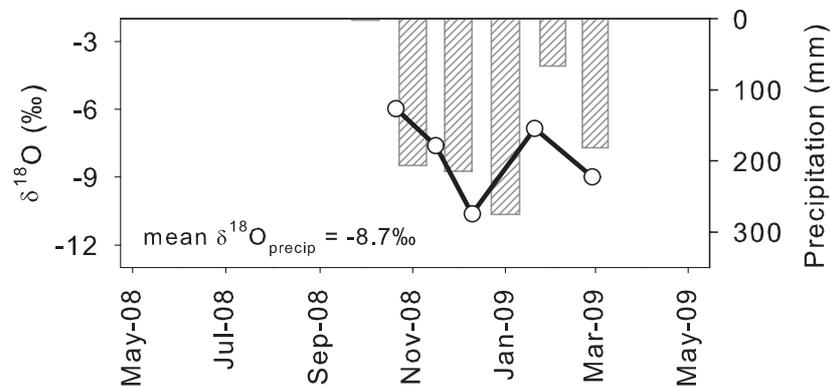


Figure S1. (a) $\delta^{18}\text{O}$ of precipitation (line) and monthly precipitation (bars) from May 2008 to April 2009. The precipitation-weighted mean $\delta^{18}\text{O}$ over the rainy season was -8.7‰ .

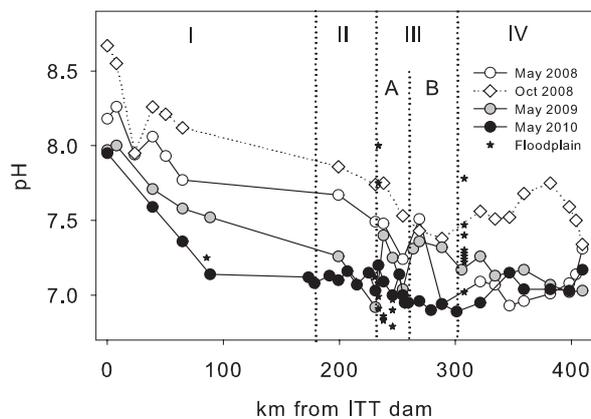


Figure S2. pH along the Kafue river during the sampling campaigns between 2008 and 2010. Dotted lines depict sections (I-IV) of different hydrological regimes.

CTD measurements between 257-259 km

In May 2010, a CTD (60M, Sea&Sun, Germany) was applied to explore small-scale changes in specific conductivity along some stretches of the Kafue River. Along a 1.8 km stretch of river (257-259 km), conductivity increased by $5 \mu\text{S cm}^{-1}$ while discharge decreased by $\sim 10\%$, and there were no visible tributaries or outflows. We investigated this area in more detail by moving downstream and across the channel in a zig-zag pattern recording CTD data at 6 Hz (Figure S3). We found that higher conductivity water of $\sim 180 \mu\text{S cm}^{-1}$ entered the river from the floodplain on the southern side and gradually mixed with river water, while some of the river water must have left the channel.

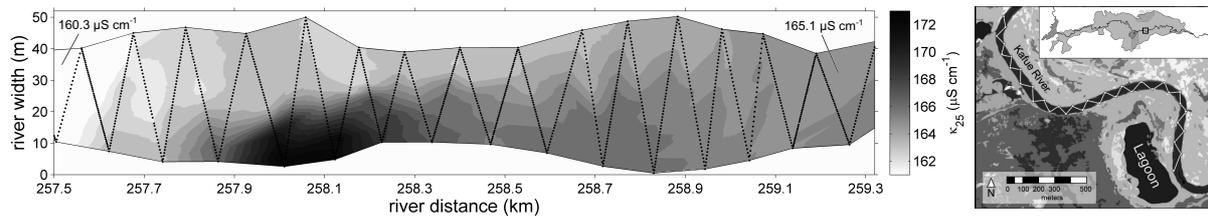


Figure S3. Lateral mixing of floodplain water detected by zig-zag shaped conductivity measurements averaged to 1 Hz (black dots) over a 1.8 km river stretch (257.5-259.3 km). Discharge along this stretch decreased from 243 to $214 \text{ m}^3 \text{ s}^{-1}$, while conductivity increased from 160.3 to $165.1 \mu\text{S cm}^{-1}$. For simplicity the course of the river channel was straightened.

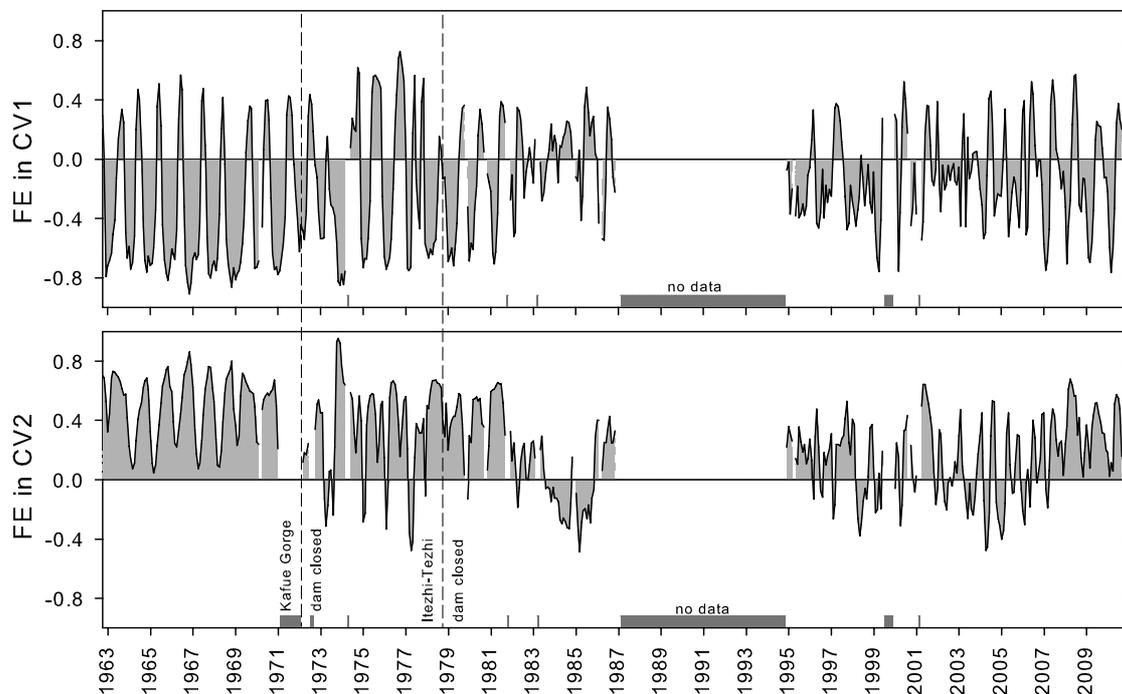


Figure S4. Fraction of exchanged water (FE) in CV1 and CV2 calculated from monthly averaged flow data. Data were available from October 1962 to September 2010, but are missing between 1987-1995 ('no data'). Vertical dashed lines mark the closing of the dams in 1972 and 1978, respectively.

Stage discharge relationships at K1, K3, and K5

Discharge at K1, K3 and K5 over longer time periods was derived from stage data and evaluated stage discharge relationships. Stage data from 1962 to 2010 were provided by ZESCO and the Department of Water Affairs (DWA). The existing stage discharge relationships at K1 and K3 were evaluated during several field campaigns between 2008 and 2010 (Wamulume et al. 2011). K1 was found to be accurate if compared to ADCP measurements and Itzhi-Tezhi dam release data provided by ZESCO (Figure S5a). The relationship at K3 had been revised since dam construction and also gave satisfactory results (Figure S5b). For reasons of consistency with the data from governmental agencies, the current equations were applied for our calculations and we did not establish a new relationship to improve accuracy.

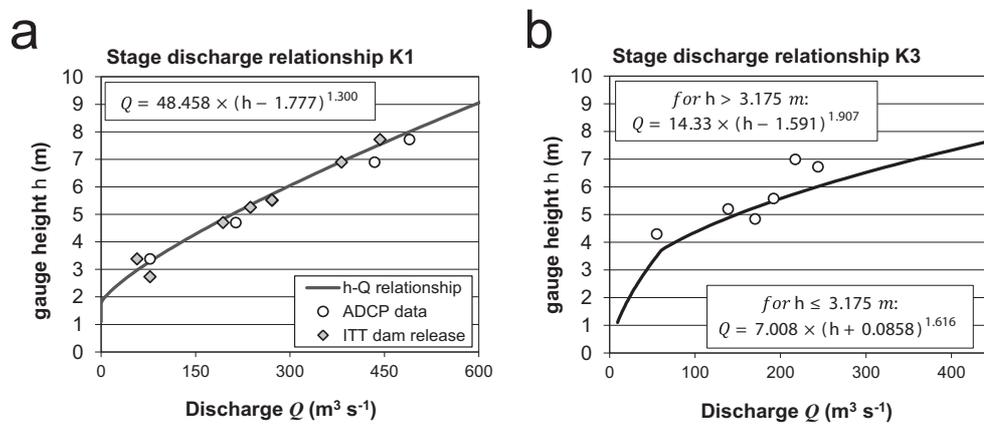


Figure S5. Stage discharge relationships for K1 (a) and K3 (b).

The stage discharge relationship at K5 had been established before construction of Kafue Gorge dam in 1972 (DWA, personal communication). We found that K5, situated only 15 km upstream of Kafue Gorge reservoir inflow, was strongly affected by the backwaters of the dam. Since changes in reservoir levels can result in a different stage discharge ratio (e.g. resulting in the same discharge for different gauge heights) we were unable to establish a definite revised relationship. For the calculations of the monthly fraction of exchanged water (FE) we approximated flows at K5 with the dam release at Kafue Gorge dam (sum of spillway and turbine discharge). On a monthly time scale, changes in reservoir levels had a minor influence on the calculated flows at K5 (data not shown). Dam release data therefore not corrected for reservoir storage to avoid possible bias from the water level/volume relationship of Kafue Gorge reservoir.

Evaporation based on $\delta^{18}\text{O}$ data

Cumulative evaporation in the Kafue Flats subcatchment

Evaporation in the Kafue Flats subcatchment based on $\delta^{18}\text{O}$ was calculated as described by Kendall and Caldwell (1998) with the ratio of evaporation to precipitation according to Gibson et al. (1993). Calculated evaporation rates are given in Table S1, equations and parameters used are shown in Table S2.

Evaporation in standing water bodies (floodplain)

Floodplain evaporation was calculated with the approach described in Gibson and Reid (2010) with the equations and parameters given in Table S3. Table S1 shows the results for calculated parameters and evaporation rates. Based on its evaporative signal, the mean residence time of water in the floodplain was ~2 months for May 2009 and May 2010.

Table S1. Evaporation in the Kafue Flats based on $\delta^{18}\text{O}$.

Cumulative evaporation in the Kafue Flats subcatchment during flood recession ^a						
Year	h^b	δ_L (‰)	δ_E (‰)	P (mm)	δ_P (‰)	E (% of P)
2009	0.67	-2.2	-42.2	975	-8.7	16
2010	0.72	-2.0	-47.2	924	-8.7 ^c	15
Floodplain evaporation based on river and floodplain $\delta^{18}\text{O}^d$						
Sampling campaign	h	δ_{in} (‰)	δ_{FP} (‰)	f (mm/mm %)		
October 2008	0.39	-3.6	-2.6	5 ^e		
May 2009	0.67	-4.8	-2.2	24		
May 2010	0.72	-5.0	-2.0	44		

^a Evaporation occurring on the scale of the entire subcatchment from the rainy season (November-February) until the sampling campaigns in May 2009 and May 2010, respectively.

^b Relative humidity data were averaged from February to June.

^c Assumed the same mean $\delta^{18}\text{O}$ in precipitation as for the rainy season 2008-2009.

^d Evaporation occurring in the floodplain based on river inflow $\delta^{18}\text{O}$ data after ITT dam

^e In October the floodplain was dry for most of the sampled 410 km. The f value therefore depicts evaporation occurring solely in the main channel of the Kafue River.

Table S2. Equations and parameters used to calculate evaporation in the subcatchment.

	$\frac{E}{P} = \frac{\delta_P - \delta_L}{\delta_E - \delta_L}$
E	Evaporation [mm]
P	Precipitation [mm]
δ_P	Mean $\delta^{18}\text{O}$ of precipitation:
δ_L	$\delta^{18}\text{O}$ of the evaporating water body
δ_E	$\delta^{18}\text{O}$ of the evaporating moisture calculated according to the Craig-Gordon model (Craig & Gordon 1965; Gonfiantini 1986):
	$\delta_E = \frac{\left(\frac{\delta_L - \varepsilon^*}{\alpha} - h\delta_A - \varepsilon_K \right)}{1 - h + \varepsilon_K}$
ε^*	equilibrium isotopic separation between liquid and vapor: $\varepsilon^* = \alpha - 1$
α	Liquid-vapor equilibrium fractionation calculated with the regression from Horita and Wesolowski (1994).
h	relative humidity. Daily relative humidity data for Lusaka were obtained from the National Climatic Data Center of NOAA (www.ncdc.noaa.gov/oa/ncdc.html).
δ_A	$\delta^{18}\text{O}$ of the atmosphere approximated according to Jacob and Sonntag (1991).
ε_K	Kinetic isotope effect, which is $\varepsilon_K = 0.0142 \times (1 - h)$ for ^{18}O (Gibson & Reid 2010; Gonfiantini 1986).

Diurnal fluctuations in dissolved oxygen concentrations

Dissolved oxygen concentrations and pH are subject to diurnal fluctuations particularly in tropical wetlands with high photosynthesis rates and high abundance of organic matter (Mitsch & Gosselink 2007; Ramberg et al. 2010; Reddy & Delaune 2008). For comparison, duplicate samples at 9.30 am and 3 pm that were taken at a river and a floodplain station in May 2010. We found that oxygen concentrations varied less than 15%, which does not exclude that samples that were taken in the early morning could have been biased by the effects of enhanced respiration during night time. However, no significant correlation was found between sampling time and oxygen concentration for any of the sampling campaigns ($P=0.57-0.82$) and neither the steep oxygen decline, nor the downstream persistency of low oxygen levels could be explained by diurnal fluctuations.

Table S3. Equations and parameters used to calculate floodplain evaporation.

	$f = 1 - \left(\frac{\delta^* - \delta_{FP}}{\delta^* - \delta_{in}} \right)^{\left(\frac{1}{m} \right)}$
f	evaporated fraction (mm evaporation/mm initial water column)
δ_{FP}	$\delta^{18}\text{O}$ in the floodplain of the Kafue Flats
δ_{in}	$\delta^{18}\text{O}$ in the inflow to the Kafue Flats
δ^*	$\delta^* = \frac{h\delta_A + \varepsilon}{h - \varepsilon}$
m	$m = \frac{h - \varepsilon}{1 - h + \varepsilon_K}$
ε	Total isotope fractionation $\varepsilon = \varepsilon^* + \varepsilon_K$

DO consumption box-model for sections IIIA, IIIB, and IV

Model setup

In order to constrain the relative contributions of lateral exchange and in-stream mineralization, we set up a box-model for the sections IIIA, IIIB and IV. For discharge, depth, DO concentrations, specific conductivity, $\delta^{18}\text{O}$ of the Kafue River and the tributaries in section IV we applied measured values. The boxes were assumed well-mixed and the setup and equations in Table S4 were applied.

Reaeration

Exchange with the atmosphere (reaeration) was modeled as a first order process ($k_{O_2, aer}$). For reaeration, a gas transfer velocity of 1.5 m d^{-1} chosen, which corresponds to a first order rate of 0.2 d^{-1} using average depth of 7.5 m. The mean depth of the Kafue River is $7.5 \pm 0.9 \text{ m}$ with the exception of a deepening of the channel at $\sim 360 \text{ km}$ (12.5 m). Similar gas transfer velocities were used in Amazon studies $0.6\text{-}4.5 \text{ m d}^{-1}$ (Devol et al. 1987; Hamilton et al. 1997), and in temperate river systems (Raymond & Cole 2001). Comparable values were obtained from relevant empirical equations for reaeration rates (Cox 2003). Residence time in the boxes was calculated as travel time along the river sections.

Atmospheric reaeration is a crucial process in low oxygen water, strongly dependent on river morphology and wind speed (Raymond & Cole 2001). We found that changes in reaeration rates affected the calculated contribution of lateral exchange, particularly in section IIIB and IV, but very marginally in section IIIA. A 20% deviation in reaeration rate would change lateral exchange in section by 20%, in section IV by 30%.

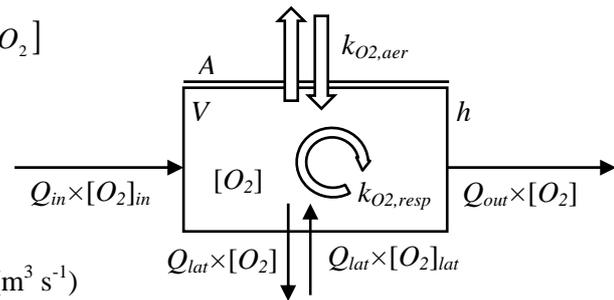
In-stream mineralization

In-stream mineralization was modeled as a first order ($k_{O_2,min}$) process. Mineralization rate was derived from a calculated zero-order DO consumption rate, observed along section I (0-88 km) which was $1.9 \mu\text{mol L}^{-1} \text{h}^{-1}$ after correcting for oversaturation and reaeration. A corresponding $k_{O_2,min} = 0.01 \text{d}^{-1}$ was chosen as in-stream mineralization rate. A comparison with zero-order mineralization rates $K_{O_2,aer}$, derived for tropical rivers (see Table S5), shows that the chosen rate is a rather high value and the contribution of in-stream mineralization to the overall DO consumption an upper limit. For the dry season (October 2008), a similar box-model approach showed that in-stream mineralization rates of $0.86 \mu\text{mol L}^{-1} \text{h}^{-1}$ for 0-254 km, $1.89 \mu\text{mol L}^{-1} \text{h}^{-1}$ for 255-346 km, and $0.13 \mu\text{mol L}^{-1} \text{h}^{-1}$ for 347-410 km would be required to explain the dissolved oxygen levels, if the reaeration rate was kept constant at 0.2d^{-1} (Table S5). These rates are equal or lower than for flood recession and suggest that in-stream mineralization has the potential to explain DO consumption in the Kafue River during the dry season.

Table S4. Equations and parameters used in the DO box-model.

$$V \times \frac{dM}{dt} = K_{O_2,aer} \times A \times ([O_2]_{sat} - [O_2]) - k_{O_2,resp} \times [O_2]$$

$$k_{O_2,aer} = K_{O_2,aer} \times \left(\frac{A}{V} \right) = \frac{K_{O_2,aer}}{h}$$



Q_{in} Inflow to the box (river section) ($\text{m}^3 \text{s}^{-1}$)

Q_{out} Outflow from the box (river section) ($\text{m}^3 \text{s}^{-1}$)

Q_{lat} Flow of exchanging water ($\text{m}^3 \text{s}^{-1}$)

$K_{O_2,aer}$: Gas transfer velocity (m d^{-1})

$k_{O_2,aer}$: Reaeration rate (d^{-1})

$k_{O_2,resp}$: Respiration rate (d^{-1})

A : Area over which surface flux occurs (m^2)

V : Volume of the section (m^3)

h : Mean depth (m)

$[O_2]$: Oxygen concentration in the section (μM)

$[O_2]_{in}$: Oxygen concentration entering the section (μM)

$[O_2]_{lat}$: Oxygen concentration in the inflow = $0 \mu\text{M O}_2$

Table S5. Zero-order respiration rates in large river systems and in-stream oxygen consumption rates that would be required to account for the steep oxygen decline in the Kafue River during flood recession in May 2008-2010 and the oxygen concentrations in October 2008.

River system	Zero-order respiration rate ($\mu\text{mol L}^{-1} \text{h}^{-1}$)	Reference
Amazon	<0.1-3.4 ^a	Richey et al. (1980)
Amazon	0.61-1.79	Devol et al. (1987)
Amazon	0.9-1.6	Richey et al. (1990)
Amazon	0.15-1.89 mean 0.61	Benner et al. (1995)
Amazon	0.1-1.6 ^b	Devol et al. (1995)
Paraguay River/ Pantanal	max 7.2 ^a mean 1.6 ^c	Hamilton et al. (1997)
Tana River, Kenya	0.3-1.0	Bouillon et al. (2007)
Yangtze River, China	0.18-0.71	Zhai et al. (2007)
Zero-order oxygen consumption rates in this study ($\mu\text{mol L}^{-1} \text{h}^{-1}$)		
Sampling campaign	Required rate without lateral exchange	
May 2008	12.1	
May 2009	8.2	
May 2010	19.6	
October 2008	0.13-1.89 ^d	

^a Single measurement.

^b Over an annual cycle.

^c Measured during a 24h incubation.

^d Dissolved oxygen concentrations in October 2008 can be explained with the specified rates.

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

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Biogeosciences Discussions 9(6): 7943-7981
under review for publication in Biogeosciences

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) in the Kafue River flowing through the Kafue Flats (Zambia). The Kafue Flats are a tropical dam-impacted 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 75 kg OC km⁻² d⁻¹ and 2.9 kg ON km⁻² d⁻¹, 80% of which was in the dissolved form. Mass budget estimates showed that ON export, denitrification, and burial caused an annual deficit of ~21,000 t N yr⁻¹ in the Kafue Flats. A N isotope balance and the $\delta^{15}\text{N}$ of DON and PON suggest that N-fixation must level out the large N losses. The elemental C:N ratio of ~20, the $\delta^{13}\text{C}$ values of higher than -24‰, and 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 river DOM characteristics remained relatively constant along the sampled 400 km river reach. This suggested that floodplain DOM had similar properties than DOM from the upstream reservoir. In contrast, based on its low $\delta^{13}\text{C}$ of -29‰ and the C:N ratio of ~8, POM originated from phytoplankton production in the upstream reservoir and in the floodplain. While the reservoir had little impact on DOM properties, terrestrial POM was efficiently trapped and, instead, phytoplankton-derived POM was discharged to the downstream Kafue Flats.

Introduction

Tropical floodplains are among the most productive and valuable ecosystems worldwide. They can act as major sources or sinks for riverine carbon (C) and nitrogen (N), regulating organic matter (OM) export to downstream systems such as lakes and oceans (Ludwig et al. 1996). Despite the importance of wetlands in the global C cycle, the role floodplains play for riverine C storage, transformation and export has not been well constrained (Battin et al. 2009b). This is particularly true for the large wetland areas in the tropics (Bastviken et al. 2010).

A number of 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 has frequently been associated with plant debris, the source allocation of DOC is more complex and often inconclusive (Tremblay & Benner 2009). The N bound in organic matter (dissolved organic N; DON), however, has seldom been used as a means of DOM characterization in tropical systems (Mladenov et al. 2005), despite DON accounting for 50-90% of total dissolved N (TDN) and generally high DON exports from tropical catchments (Berman & Bronk 2003; Wiegner et al. 2009).

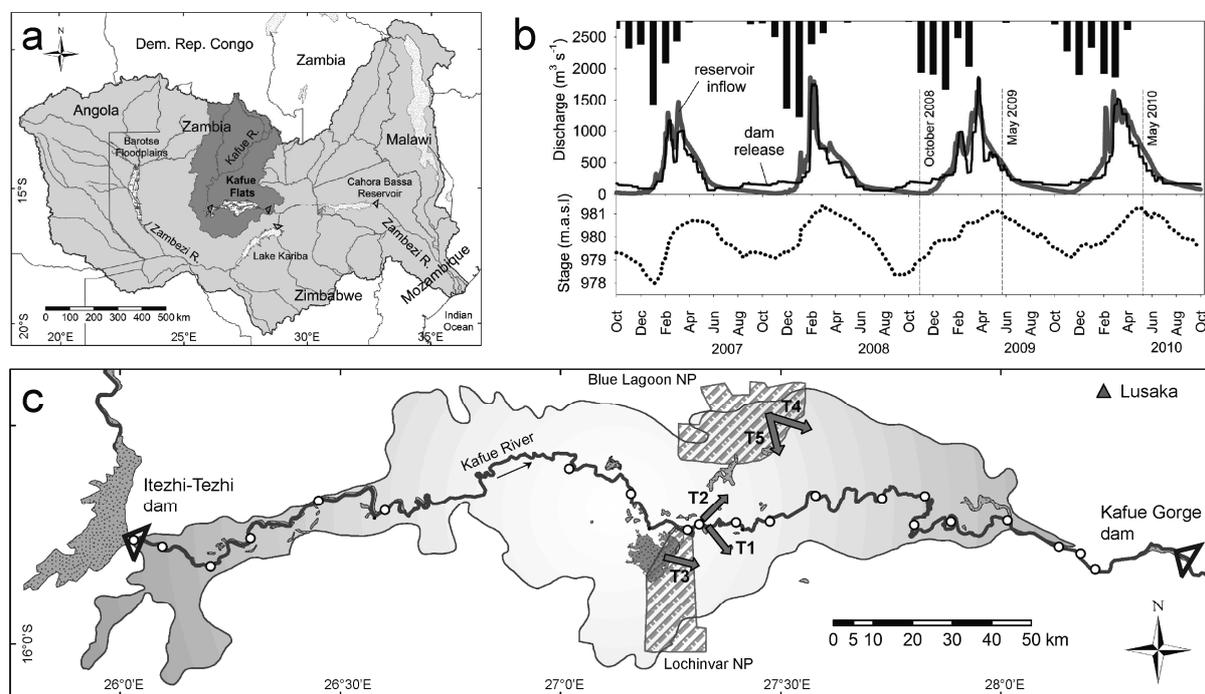


Figure 1. (a) Kafue Flats in the Kafue River basin (dark shaded), a subbasin of the Zambezi River basin (light gray). (b) The hydrograph from 2007-2010 shows the reservoir inflow (gray line), dam release (black line), rainfall (bars), and to the water level in the middle of the floodplain (dotted line, lower panel). The three sampling campaigns are marked by vertical lines. (c) Map of the Kafue Flats. Large dams are marked with triangles, white dots indicate sampling stations along the main channel, arrows T1-T5 depict transects into the floodplain.

The exchange between floodplains and rivers 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 floodplain-derived OM to rivers (Richey et al. 1990), and foster in-stream mineralization of OM (Mayorga et al. 2005). The emerging number of dams in tropical catchments have the potential to change downstream flooding and thus the hydrological connectivity between rivers and floodplains (Gergel et al. 2005). Dams also efficiently trap particles (Vörösmarty et al. 2003), and both hydrological alteration and particle trapping may affect riverine OM loads and quality in tropical systems (e.g., Bouillon et al. 2009).

To gain better insight into OM dynamics in tropical floodplains and to assess potential dam-impacts OM cycling, we examined the source, quality, and export of OM in the Kafue Flats (Figure 1a), a floodplain system along the Kafue River, the largest tributary of the Zambezi River. In the Kafue Flats, more than 80% of the river discharge during the wet season ($\sim 600\text{-}800\text{ m}^3\text{ s}^{-1}$) passes through the highly productive floodplain (Zurbrügg et al. 2012b). For comparison, only $\sim 30\%$ of the river water of the Amazon travels through floodplains (Richey et al. 1989). Intense river-floodplain exchange exerts a strong influence on river biogeochemistry of the Kafue River, as evidenced by pronounced hypoxia over a 150 km long stretch (Zurbrügg et al. 2012b). We hypothesized that the backflow from the floodplain carries large OM loads with terrestrial characteristics to the river and would thus affect the riverine OM pool. Additionally, the Kafue Flats system has been impacted by two large dams that have altered the hydrological regime (Zurbrügg et al. 2012b), and the flooding patterns in the Kafue Flats (Meier et al. 2010; Mumba & Thompson 2005). We hypothesized, that dam operation has changed the characteristics of the OM entering the Kafue Flats and also influenced OM mobilization, transport and quality in the floodplain. The goals of this study were (1) to quantify net export of OC and ON from the floodplain to the river, (2) to determine source, quality and fate of the exported OM, and (3) to explore potential dam impacts on OM characteristics. The stable isotopic composition ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$) and C:N ratios of DOM and POM were measured to characterize its sources and fate. We also examined spectroscopic properties to identify microbial and terrestrial contributions to DOM (Coble 1996).

Methods

Study site - Kafue Flats

The Kafue Flats are a 6,500 km² floodplain system along the Kafue River in Zambia (Figure 1a). The annual flooding occurs from January to August and is caused by direct precipitation during the rainy season (November-April; mean 800 mm), peak flows of the Kafue River (up to 1900 m³ s⁻¹; Figure 1b), and seasonal tributaries, creating an extensive wetland area and rich wildlife habitat. The floodplain vegetation fringing the river channel is composed of highly productive C₄-grasses, providing a net primary production of 800-2,000 g C m⁻² yr⁻¹ (Ellenbroek 1987). During the dry season from June-October, river discharge drops to <100 m³ s⁻¹ (Figure 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. Large sugar cane plantations are located along the last 60 river-km, leaving the Kafue Flats a relatively pristine floodplain.

The hydrology of the Kafue River ($Q_{\text{avg}} \sim 300 \text{ m}^3 \text{ s}^{-1}$) 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 (Figure 1c). At ITT dam, water is released to the floodplain via spillways, draining the reservoir's epilimnion. A recent study by Kunz et al. (2011b) 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.

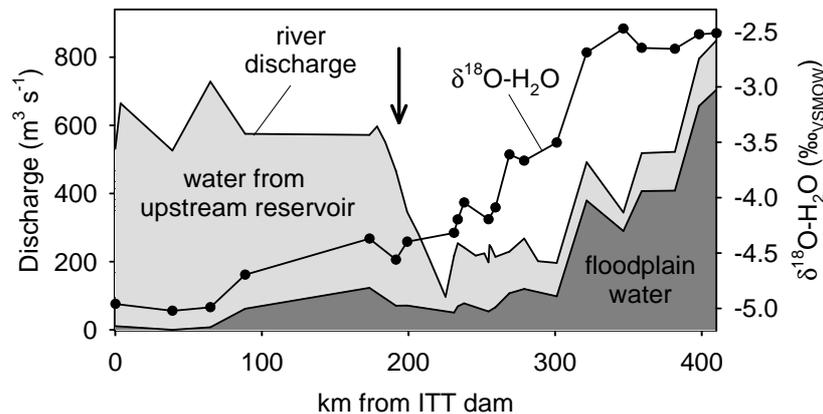


Figure 2. Evidence of river-floodplain exchange in May 2010, indicated by an increasing proportion of floodplain-derived water (dark gray shading) relative to water discharged from the reservoir (light gray shading). The contribution of floodplain water was calculated by a mixing model based on $\delta^{18}\text{O-H}_2\text{O}$ along the river (full circles). For details see Zurbrügg et al. (2012b). The arrow marks the steep decline in discharge (180-225 km) caused by a constriction in the river channel.

Intense hydrological exchange between river and floodplain has been identified as a major feature in the Kafue Flats (Zurbrügg et al. 2012b). Lateral exchange with the inundated floodplain emerged 220 km downstream of ITT dam, where a channel constriction diverted $\sim 70\%$ of the stream flow into

the floodplain (Figure 2). The backflow from the floodplain caused a seasonally-recurring steep decline in dissolved oxygen (DO) concentration to $<1 \text{ mg L}^{-1}$ and low DO levels ($<2 \text{ mg L}^{-1}$) along a 150 km reach of the river. Based on natural tracer calculations (specific conductivity and $\delta^{18}\text{O-H}_2\text{O}$), more than 80% of the water leaving the system passed through the floodplain (Figure 2). Changes of timing and extent of ITT dam release have altered the flooded areas in the Kafue Flats and reduced water exchange between river and floodplain by up to 50% (Zurbrügg et al. 2012b).

Sampling campaigns

After a pilot campaign in May 2008, three spatially intensive sampling campaigns were carried out during the dry season (October 2008), and flooding season in May 2009 and May 2010 (Figure 1b). Sampling was conducted along the Kafue River at $\sim 20 \text{ km}$ resolution from downstream of the spillways at ITT dam (0 km) until the end of the floodplain (410 km; Figure 1c). To characterize floodplain waters, additional 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; Figure 1c) in May 2010. Water samples were pumped from mid depth in the middle of the well-mixed river channel through polyethylene tubing, using a peristaltic pump (Ejikelkamp, 12 VDC Standard). Samples for DOC and DON, and spectroscopic analyses were filtered in the field through $0.7 \mu\text{m}$ 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 3-4 weeks after sampling. Water samples for elemental and isotope analyses were acidified to pH 2.5 and frozen until further analysis. For POC and particulate ON (PON) characterization, particles from $\sim 2 \text{ L}$ of water were collected on GF filters ($0.7 \mu\text{m}$ /Whatman) and frozen until analysis. All sampling equipment was 2M HCl/MilliQ-washed, glassware and filters were, in addition, pre-combusted (6h at 450°C). For comparative analyses, we also sampled floodplain vegetation and soil, river sediment, and dry deposition (see supplementary information for details).

Laboratory analyses

Concentrations and stable isotopic composition of DOC, POC and PON

DOC concentration was measured on a Shimadzu 5050 TOC analyzer. POC and PON concentrations and its C and N isotopic composition ($\delta^{13}\text{C-POC}$ and $\delta^{15}\text{N-PON}$, respectively), were measured on dried (3h at 40°C) GF filters. The sediments of ITT reservoir contained only negligible amounts of inorganic carbon (Kunz et al. 2011b) and the epilimnion was undersaturated with respect to CaCO_3 (data not shown), which made acidification of POM samples redundant. Filter sections were enclosed in tin capsules and measured on a FlashEA 1112 coupled to a DeltaV Advantage Continuous-Flow Isotope Ratio Mass Spectrometer (FlashEA-CF-IRMS; ThermoFinnigan). In-house EDTA

($\delta^{13}\text{C} = -30.25\text{‰}_{\text{VPDB}}$; $\delta^{15}\text{N} = -1.1\text{‰}_{\text{air}}$) and ammonium oxalate ($\delta^{13}\text{C} = -17.02\text{‰}_{\text{VPDB}}$; $\delta^{15}\text{N} = +32.7\text{‰}_{\text{air}}$) were used as standards, with a precision of $\pm 0.1\text{‰}_{\text{VPDB}}$ for $\delta^{13}\text{C}$ and $\pm 0.2\text{‰}_{\text{air}}$ for $\delta^{15}\text{N}$. The isotopic ratios are reported using the delta notation, that is, $\delta^{13}\text{C}$ or $\delta^{15}\text{N} = (R_{\text{sample}} - 1) \times R_{\text{standard}} \times 1000\text{‰}$, where R is the isotopic ratio ($^{13}\text{C}:^{12}\text{C}$ or $^{15}\text{N}:^{14}\text{N}$) of the sample (R_{sample}) and the standards (R_{standard}), which are Vienna Pee Dee Belemnite (VPDB) for C and atmospheric N_2 for N.

For the C-isotope analysis of DOC ($\delta^{13}\text{C}$ -DOC), 1 mL of 5 g L⁻¹ high-purity, precombusted K_2SO_4 was added to 40 mL of sample and the acidic samples were purged for 2 min with Ar to remove inorganic C (HCl had been added after sampling in the field), refrozen and freeze-dried (Schwendenmann & Veldkamp 2005). The precipitate was measured on the same FlashEA-CF-IRMS using IAEA-CH6 sucrose ($\delta^{13}\text{C} = -10.45\text{‰}_{\text{VPDB}}$), EDTA and ammonium oxalate as standards at an analytical precision of $\pm 0.1\text{‰}_{\text{VPDB}}$. The analytical precision is based on replicate measurements of untreated standards of sucrose (n=7) and ammonium oxalate (n=7) of and standards that were processed as samples (n=6 and n=8), respectively.

Concentrations of DIN and DON, and $\delta^{15}\text{N}$ -TDN

For dissolved inorganic N (DIN), NH_4^+ and NO_2^- were measured using standard colorimetric techniques. The sum of NO_3^- and NO_2^- was determined by reduction to NO_x (Braman & 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 Solorzano 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 peroxodisulfate ($\text{K}_2\text{S}_2\text{O}_8$) and 6 g NaOH (both ACS-grade) per 100 mL MilliQ water (Knapp et al. 2005). In order to reduce the nitrogen blank of POR, the peroxodisulfate salt was recrystallized 3-5 times according to Grasshoff et al. (1999) and stored under Ar atmosphere. Samples with POR were autoclaved in 30 mL Pyrex vials (acid washed, precombusted, PTFE-lined lids) for 55 min and NO_3^- concentration was measured as described above. IAEA-N2 ($+20.3\text{‰}_{\text{air}}$), USGS-41 ($+47.6\text{‰}_{\text{air}}$), urea ($+0.24\text{‰}_{\text{air}}$), and EDTA were used as processing and isotopic standards, and were oxidized with the samples over the expected concentration range (Figure S1, supplementary information). 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 $0.5 \pm 0.3\text{ }\mu\text{M}$ per sample which is equal to $\sim 3\%$ of the sample TDN. DON concentrations were calculated as $\text{DON} = \text{TDN} - \text{NO}_3^- - \text{NO}_2^- - \text{NH}_4^+$.

The $\delta^{15}\text{N}$ ratio of TDN-derived NO_3^- ($\delta^{15}\text{N}$ -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 ($+4.7\text{‰}_{\text{air}}$) and in-

house UBN1 (+14.2‰_{air}) were used as $\delta^{15}\text{N-NO}_3^-$ standards. DON dominated TDN in all samples (generally >94%), therefore, $\delta^{15}\text{N-TDN}$ can be considered a reasonable approximation to $\delta^{15}\text{N-DON}$.

Spectroscopic analyses

The spectroscopic analyses consisted of UV absorbance spectroscopy and fluorescence spectroscopy. 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

$$\text{SUVA}_{254} = \frac{\text{Abs}_{254}}{[\text{DOC}]} \quad [\text{L mg}^{-1} \text{ m}^{-1}] \quad (1)$$

whereby Abs_{254} is the absorption measured at 254 nm and $[\text{DOC}]$ is the DOC concentration.

Excitation-emission matrixes (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 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 for the Raman area. Parallel factor analysis (PARAFAC) was used to identify underlying fluorescence components following the procedures of Stedmon et al. (2003) and Stedmon & 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. Details on PARAFAC modeling are given in the supplementary information section. In order to distinguish between terrestrial and microbial (i.e., algal/bacterial) origin of DOM, the fluorescence index (FI; Cory et al. 2010) was calculated as

$$\text{FI} = \frac{\text{Em}_{470}}{\text{Em}_{520}} \quad (2)$$

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. FI values of >1.4 indicate microbial and <1.4 primarily terrestrial origin (Cory et al. 2010).

Statistical analyses

Correlations between normally-distributed parameters were determined by linear regression, and by Spearman's correlations for not normally-distributed data. To evaluate differences between pooled data, we used ANOVA, if normally-distributed, otherwise non-parametric Kruskal-Wallis tests, both at a critical level of 0.05. Averaged data are given as mean \pm SD. Statistical analyses were done with SigmaPlot 11.

Results

Organic carbon and nitrogen concentrations along the Kafue River

During both flooding season campaigns in May 2009 and May 2010, DOC concentrations increased from ~250 μM immediately downstream of ITT dam (0 km) to ~400 μM at end of the floodplain (410 km; Figure 3a). Most of the DOC increase occurred after 230 km, where we have documented that a large influx of floodplain-derived water begins entering the river (Figure 2). In the dry season (October 2008), DOC concentrations remained relatively constant at 280 ± 50 μM along the entire river reach. DON concentrations showed a similar 2-fold increase, from ~10 μM at the dam site to maximum concentrations of ~20 μM at 410 km in May 2009 and May 2010. In October 2008, 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). DOC concentrations in the inundated floodplain (May 2010) tended to be higher than in the adjacent river station, reaching up to 600 μM (Figure 3a). Floodplain DON concentrations were comparable to those measured in the Kafue River.

During the flooding season, concentrations of POC and PON were ~40 μM and ~6 μM , respectively, after ITT dam (Figure 3b) and decreased by a factor of 2-3 between 200 km and the end of the Kafue Flats. POC and PON concentrations measured in May 2009 increased slightly over the first 70 km. In October 2008, the concentrations of both parameters were comparable to values observed during flooding, but pronounced peaks in POC and PON were detected between 200 and 300 km, which are consistent with higher particle concentrations along this stretch (Figure S2a, supplementary information).

The molar ratio of DOC:DON remained relatively constant along the river during flooding season sampling campaigns, with values of 19.7 ± 2.4 in May 2010 and 23.2 ± 2.3 in May 2009, respectively (Figure 3a). In general, DOC:DON was similar (mean 19.3) in October 2008, with the exception of some lower values between 200-300 km. Across all three sampling campaigns, POC:PON (7.9 ± 0.9 in May 2010; 8.6 ± 0.7 in May 2009; 10.7 ± 1.9 in October 2008) was 2-3 fold lower than DOC:DON (Figure 3b).

Carbon and nitrogen stable isotopes

Values for $\delta^{13}\text{C}$ -DOC in the river were confined to a fairly narrow range (-21.0‰ to -24.7‰) for all three sampling campaigns (Figure 4). Nonetheless, some systematic variations were evident. During the May 2010 campaign, $\delta^{13}\text{C}$ -DOC exhibited a distinct increase from -23.9‰ to -21.7‰ over the first 90 km, and during both flooding season campaigns $\delta^{13}\text{C}$ -DOC decreased by 2.5‰ after 250 km. Along the floodplain transects, high $\delta^{13}\text{C}$ -DOC tended to co-occur with high DOC

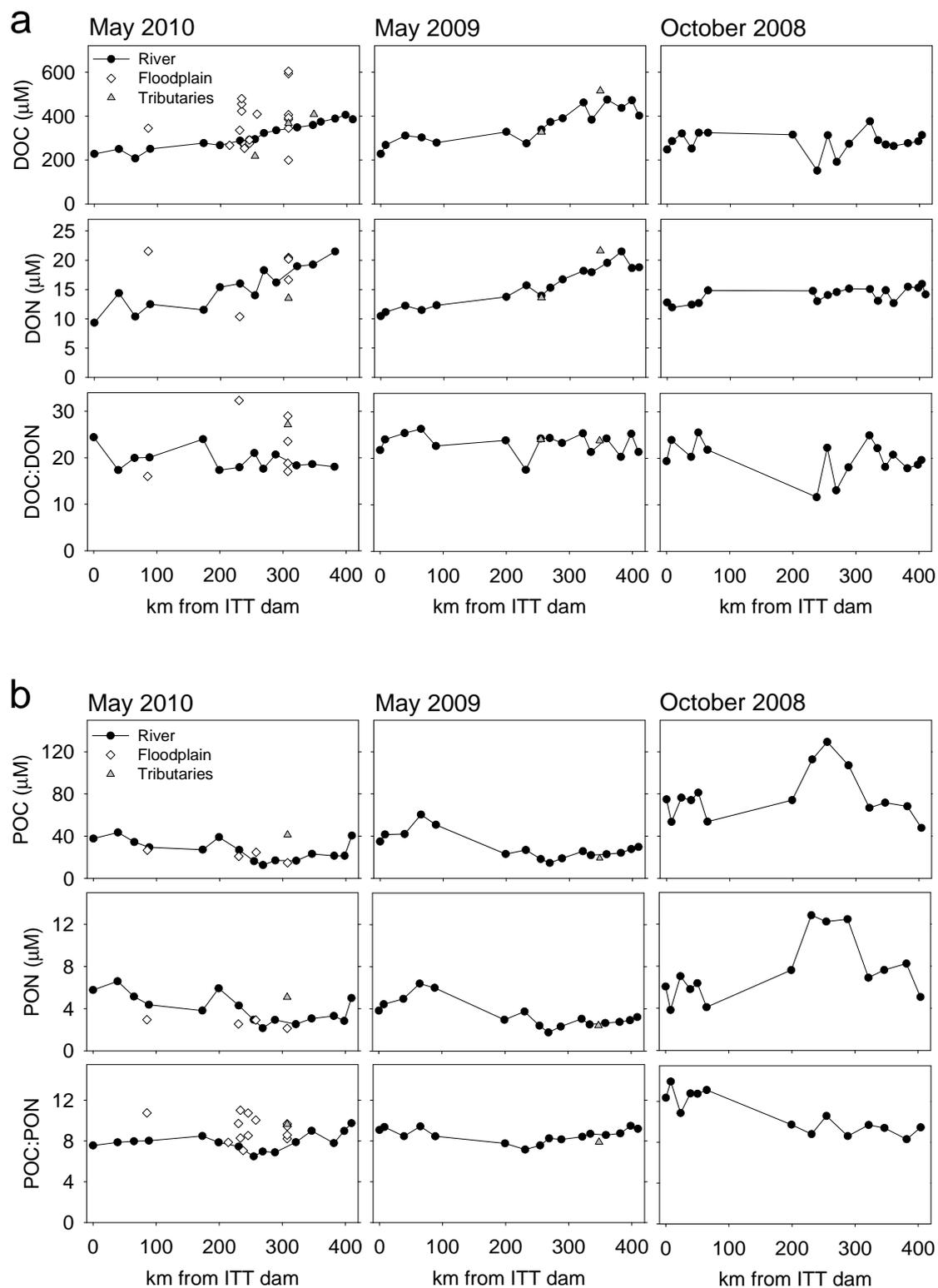


Figure 3. (a) Concentrations of DOC and DON, and molar DOC:DON ratio, (b) concentrations of POC and PON, and molar POC:PON ratio for May 2010, May 2009, and October 2008 along the Kafue River channel (black dots and lines), at floodplain stations (empty diamonds) and tributaries (gray triangles).

concentrations, mostly in the more distant sections from the river channel. During the dry season, $\delta^{13}\text{C}$ -DOC did not show systematic variation along the river channel. Across all sampling campaigns, POC at river stations was systematically depleted in ^{13}C relative to the corresponding DOC (mean difference = $5.1 \pm 1.7\text{‰}$; Figure 4). During the flooding season, $\delta^{13}\text{C}$ -POC increased by 2.5‰ over the first 100 km downstream of ITT dam. The $\delta^{13}\text{C}$ -POC of floodplain samples varied substantially, covering a range of -33.7‰ to -23.4‰ . During the dry season, $\delta^{13}\text{C}$ -POC along the river was again relatively constant at -26‰ .

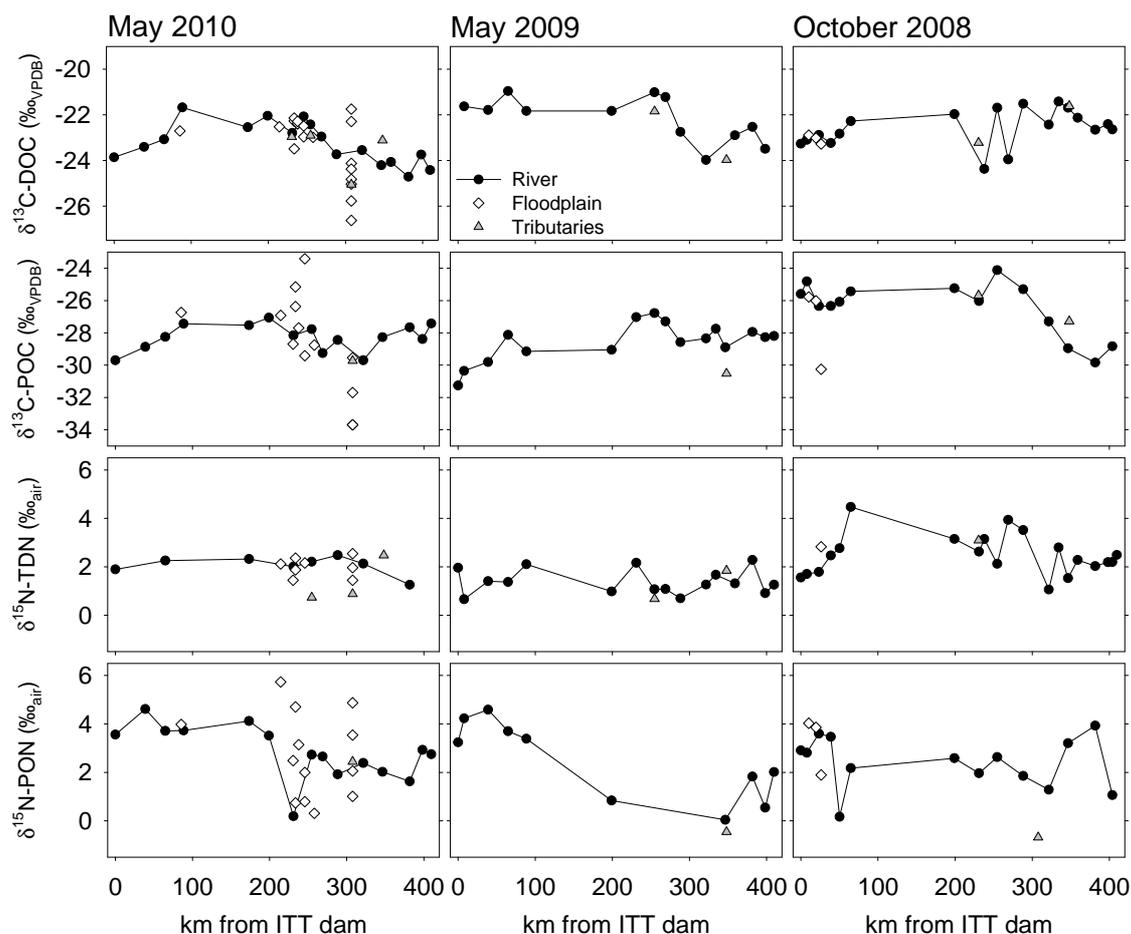


Figure 4. Stable isotope signatures of dissolved and particulate organic carbon and nitrogen for the three sampling campaigns (symbols as indicated in Figure 3).

$\delta^{15}\text{N}$ -TDN values during the May 2010 and May 2009 campaigns exhibited limited variability along the river ($2.1 \pm 0.4\text{‰}$ and $1.4 \pm 0.5\text{‰}$, respectively; Figure 4). On average, $\delta^{15}\text{N}$ -TDN was similar in October 2008, but had somewhat greater variability ($2.5 \pm 0.9\text{‰}$). During the flooding season campaigns, $\delta^{15}\text{N}$ -PON immediately downstream of the ITT dam was $\sim 2\text{‰}$ higher than $\delta^{15}\text{N}$ -TDN, and gradually decreased to values comparable to $\delta^{15}\text{N}$ -TDN further downstream (Figure 4). Floodplain $\delta^{15}\text{N}$ -PON in May 2010 covered a considerably wider range than observed in river samples (0.3‰ to 5.7‰).

Spectroscopic analyses of DOM

SUVA₂₅₄ did not change significantly along the river ($P=0.077$) but remained at 3.5 ± 0.3 L mg⁻¹ m⁻¹ (Figure 5a) and was not affected by intensified river-floodplain exchange after 230 km. Floodplain and tributary samples showed smaller but more variable values than the adjacent river reach. Similar to SUVA₂₅₄, FI values along the main channel fell in a very narrow range between 1.42 and 1.47 and exhibited only minor, non-significant ($P=0.117$) variation along the river (Figure 5b). The EEMs showed a high degree of similarity among the stations along the river (Figure 6a) and floodplain transects (Figure 6b). Two main fluorescence peaks were detected at an excitation/emission wavelength of 345/440 nm, and 240/430 nm (Figure 6). These peaks are common features in natural DOM and have been named Peak A and Peak C (Coble 1996), respectively.

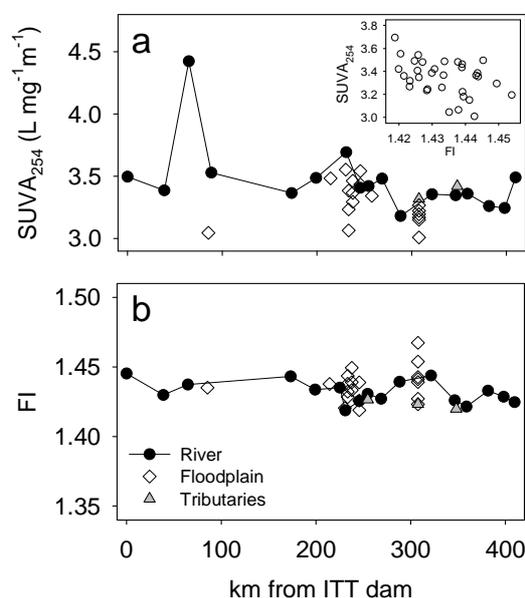


Figure 5. (a) Specific UV absorption at 254 nm (SUVA₂₅₄), and (b) fluorescence index (FI) along the river (black circles) and the in floodplain (empty diamonds) and in tributaries (gray triangles) in May 2010. The inlaid in (a) shows the negative correlation of the pooled SUVA₂₅₄ and FI data ($P<0.001$). Samples with SUVA₂₅₄ > 4.0 L mg⁻¹ m⁻¹ were removed for clarity.

Discussion

Net export of organic carbon and nitrogen 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 (Figure 2). Between 180 and 225 km, a large fraction of the stream flow was forced into the floodplain, while downstream of the 300 km mark, water returned from the floodplain into the river, resulting in a ~4-fold increase in discharge (Figure 2). Thus, most of the discharge of the lower Kafue River in May 2010 and May 2009, as well as its chemical loads, originated in, or passed through, the floodplain. Comparable levels of exchange occurred when flow rates substantially exceeded $\sim 200\text{-}300\text{ m}^3\text{ s}^{-1}$ (December-July; Zurbrügg et al. 2012b). During low-flow periods (August-November), the exchange with the floodplain was substantially reduced.

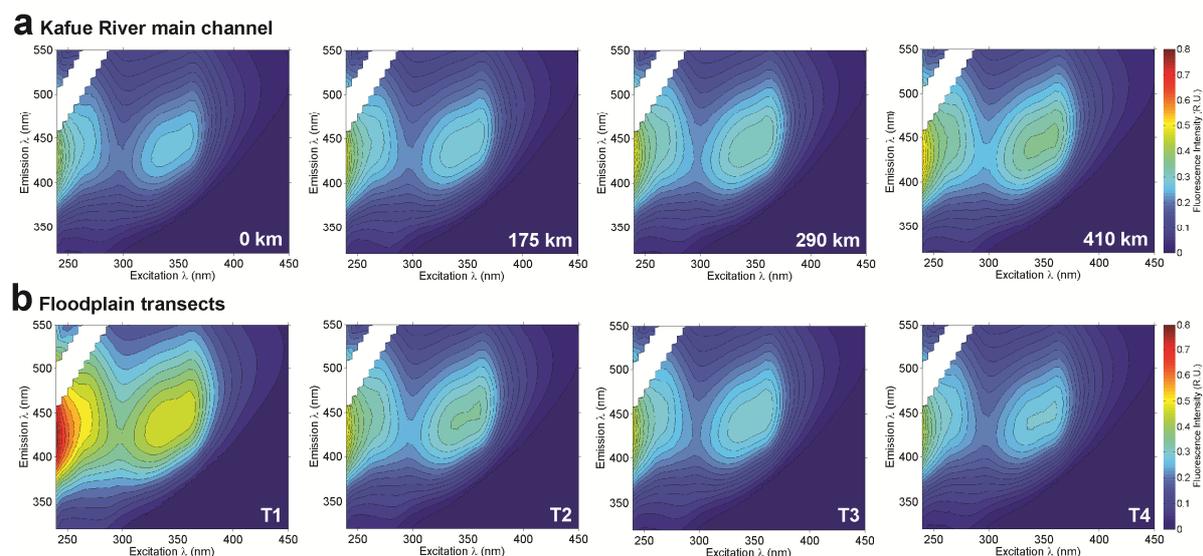


Figure 6. Excitation-emission matrices (EEMs) for (a) four river samples indicated with distance from ITT dam, and (b) four floodplain samples on different floodplain transects. The two main fluorescence peaks are at excitation/emission wavelengths of 240/430 nm and 345/440 nm, and have been named by Coble (1996) as Peak A and Peak C, respectively.

We combined discharge measurements with concentration data to quantify mass loads of OC and ON along the river (Figure 7; Table 1). In May 2010, the minimum discharge and minimum DOC and DON loads were observed at ~ 230 km (Figure 2) after $\sim 85\%$ of the flow and loads had been diverted to the floodplain (Figure 7). Downstream of 230 km, discharge and concentrations of both DOC and DON 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 DOC and DON entering the floodplain may have been metabolized before reentering the river, a minimum of 63% of DOC and

56% of DON in the river originated from the floodplain. Load patterns in May 2009 for DOC and DON 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 (Figure 7). In contrast, during the dry season (October 2008), loads were reduced and remained relatively constant along the river. Loads for POC and PON increased by ~70% and ~40% in May 2010 but decreased by 1-2% in May 2009 and by >40% during the dry season.

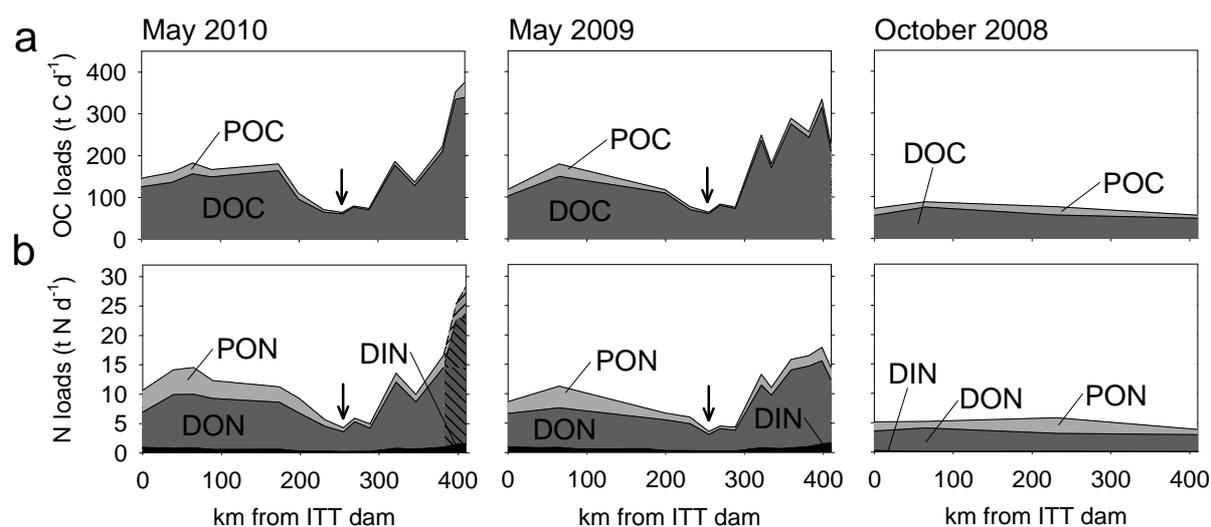


Figure 7. (a) Organic carbon loads ($t C d^{-1}$) and (b) organic nitrogen loads ($t N d^{-1}$) calculated as discharge \times concentration for the three sampling campaigns. The hatched areas in May 2010 N loads are calculated with concentrations extrapolated from the regression line between DOC and 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. (2012b).

The short travel times of 1.5 weeks along the river (average velocity of $\sim 0.5 m s^{-1}$) and relatively constant flows for several weeks around the sampling time period (Zurbrügg et al. 2012b) allowed for a comparison of upstream and downstream loads. Strictly speaking, our results represent “snapshots” in time, which may not represent the conditions between the annual sampling campaigns, i.e., the bulk of the year. However, results from a bi-monthly sampling campaign that was carried out over one year at several stations along the river indicate, that the net export of OM predominates for several months each year. Over an annual cycle, the net export from the Kafue Flats was $\sim 60,000 t OC yr^{-1}$ and $\sim 1,800 t ON yr^{-1}$, respectively (Wamulume et al. 2011).

The maximum flooded area during the 2009/2010 rainy season was estimated $3,060 km^2$ in March 2010 (F. Köck, personal communication, based on an inundation model described in Meier et al. (2010)). The least inundation was recorded in October 2009 ($234 km^2$). Based on the export estimates for the 2010 and 2009 flooding seasons and the maximum flooded area, the area specific OC (=DOC+POC) yields were $75 kg C km^{-2} d^{-1}$ for May 2010, and $35 kg C km^{-2} d^{-1}$ for May 2009 (Table 1). The yields correspond to 1-3% of the floodplain’s annual estimated primary production of $1,200 g C m^{-2} yr^{-1}$ (Ellenbroek 1987), suggesting that OM burial, mineralization, burning and grazing

are more important C-turnover processes in the floodplain. The use of the maximum flooded area may substantially overestimate the flooded area that is in connection with the river, e.g. due to high evaporation in the floodplain (up to 40%; Zurbrügg et al. 2012b) and disconnected water bodies. However, even with a 10 times smaller area, the OC yields would be <30% of the estimated primary production, which shows that other fates of OM are more important.

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 ~230 km ^b (×)	Floodplain contribution to export ^c (%)	Net export ^d (t C or N d ⁻¹)	Yields (kg C or N km ⁻² d ⁻¹) ^e
May 2010 – flooding season					
DOC	339	3.3	82	214	69.8
POC	35.7	3.0	92	14.9	4.9
DON	13.6	4.6	75	7.6	2.5
PON	5.1	11	88	1.4	0.5
DIN	1.6	7.6	85	0.6	0.2
May 2009 – flooding season					
DOC	210	2.5	72	108	35.2
POC	15.6	4.0	80	-0.2	-0.1
DON	11.5	3.0	75	6.0	2.0
PON	2.0	3.5	78	0.0	0.0
DIN	0.9	4.1	80	-0.2	-0.1
October 2008 – dry season					
DOC	48.1	n.a.	n.a.	-6.9	n.a.
POC	7.4	n.a.	n.a.	-9.3	n.a.
DON	2.9	n.a.	n.a.	-0.5	n.a.
PON	0.9	n.a.	n.a.	-0.7	n.a.
DIN	0.1	n.a.	n.a.	-0.2	n.a.

^a Calculated as discharge × concentration at the outflow (410 km).

^b Flooding season C and N loads had a minimum at ~230 km, caused by a channel constriction and reduced river discharge (marked with arrow in Figure 7). The increase in C and N loads thereafter were assumed to originate from the floodplain.

^c The floodplain contribution to the exported OM was calculated under the assumption of negligible in-stream production of DOM or POM.

^d Calculated as the difference of discharge × concentration between 0 km and 410 km.

^e The export per area was calculated using the maximum flooded area for the rainy season 2009/2010 of 3,060 km² (Meier et al. 2010).

The ON (=DON+PON) exports from the Kafue Flats were on the order of 6-9 t N d⁻¹, which corresponds to area normalized yields of 2.9 kg N km⁻² d⁻¹ for May 2010 and 1.9 kg N km⁻² d⁻¹ for May 2009 (Table 1). Compared to model predictions on the scale of the entire Zambezi River basin of 0.14-0.27 kg N km⁻² d⁻¹ for DON (Harrison et al. 2005a) and 0.30-0.49 kg N km⁻² d⁻¹ for total ON (Mayorga et al. 2010), the Kafue Flats represent a substantial local source of riverine ON to the Kafue and the Zambezi Rivers, in particular given that these areal rates are likely underestimates based on

the use of maximum area. South American tropical catchment DON export rates (0.5-1.0 kg N km⁻² d⁻¹) are also substantially less than those from the Kafue Flats (Mayorga et al. 2010).

Source of organic matter

Floodplain-derived DOM can in principle originate from three main sources which can have distinct chemical signatures and bioavailability: (1) mobilization from floodplain soils during drainage (aged OM; Mladenov et al. 2005), (2) decaying floodplain vegetation (young OM; Maie et al. 2006), or (3) exudates from phytoplankton, periphyton or microbial biomass (Ziegler & Brisco 2004). POM could be 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). Significant differences between the C:N ratios of DOM and POM ($P < 0.05$) and between $\delta^{13}\text{C}$ of DOC and POC across all campaigns indicate that DOM and POM derived from distinctly different sources (Figure 8). POM had a substantially lower C:N elemental ratio (~8) than DOM and floodplain soils and sediments (Table S1, supplementary information). The relative elemental N-enrichment (i.e., lower C:N) and ¹³C-depletion suggest of POM mainly consisted of phytoplankton (Hamilton & Lewis 1992). This is consistent with the high C content of the suspended particulate material leaving the ITT reservoir (30-40 wt% C), which supports the notion that POM immediately downstream of the dam consisted of the primary production of the reservoir (Figure S2b, supplementary information). The consistently high DOC:DON (19-23; Figure 3a) observed during all sampling campaigns and across all sites indicates an N-poor DOM pool, one that had likely undergone considerable reworking and was probably fairly refractory. 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 contrast to other systems like the Tana River in Kenya (Bouillon et al. 2007) or the Amazon (Raymond & Bauer 2001), where $\delta^{13}\text{C}$ -POC was higher than $\delta^{13}\text{C}$ -DOC and DOC could originate from POC degradation, this is unlikely in the Kafue Flats, because of the consistently higher $\delta^{13}\text{C}$ -DOC (Figure 4).

Spectroscopic results generally support the chemical data that DOM was primarily of terrestrial origin, but also revealed a microbially-derived contribution. The SUVA₂₅₄ values for the Kafue River of ~3.5 L mg⁻¹ 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). The FI of ~1.43, however, indicates both terrestrial (FI < 1.4) and microbial (FI > 1.4) contributions to DOM (Cory et al. 2010). Because of the relative stability of terrestrial DOM, the FI is often negatively correlated with DOC concentration (Johnson et al. 2011; Petrone et al. 2011), but no significant correlation of FI or SUVA₂₅₄ with DOC was found in the Kafue River ($P < 0.05$). FI in other

tropical systems ranged from 1.21-1.41 on the Guayana Shield, 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 & Zheng 2012). The microbial signal in the FI of the Kafue River DOM could be associated with the onset of microbial degradation of mobilized of terrestrial OM after the peak flow (Johnson et al. 2011; Mladenov et al. 2005).

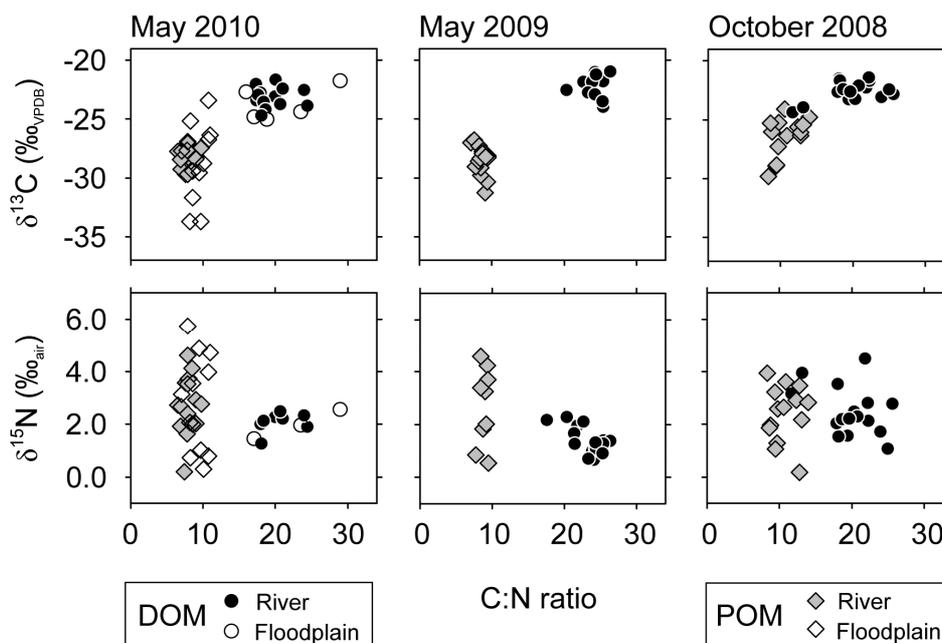


Figure 8. $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values of dissolved and particulate organic matter, relative to their C:N ratio. Significant differences ($P < 0.05$) were found between C:N ratios and $\delta^{13}\text{C}$ of DOM and POM, throughout all sampling campaigns, but not for $\delta^{15}\text{N}$.

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 (Figure S3 and Table S2, supplementary information) and were found characteristic for humic-like substances (Stedmon & Markager 2005). The components C1 and C3 are exclusively from terrestrial origin while C2 and C4 can also have microbial origin. A detailed evaluation of components C2-C4 is given in Ishii and Boyer (2012). In summary, DOM in the Kafue River was mainly of terrestrial origin with some microbial contribution while POM had a distinct phytoplankton signature. During the flooding period, the chemical characteristics ($\delta^{13}\text{C}$, $\delta^{15}\text{N}$, C:N) showed only small variation along the river which is discussed in the next section.

Dam effects and changes in POM characteristics along the river

In the Kafue River basin, terrestrial POM is efficiently retained in the ITT reservoir upstream of the Kafue Flats, as indicated by intense sediment accumulation (Figure 9a; Kunz et al. 2011b) and the

elevated $\delta^{13}\text{C}$ and C:N relative to epilimnetic POM (Table S1, supplementary information). The POM that was released from the reservoir had lower $\delta^{13}\text{C}$ and C:N, and likely consisted of phytoplankton from the reservoir's primary production. This injection of authigenic, ^{13}C -depleted POM has also been documented in other systems (Bouillon et al. 2009; Chen & Jia 2009). In these studies, $\delta^{13}\text{C}$ -POC rebounded after the dam, similar to our observation from 0-90 km during the flooding season (Figure 4). However, C:N ratios remained relatively constant along the river, despite the 3 to 10-fold increase in POC and PON loads after 300 km (Figure 7) that requires POM from the floodplain entering the river. The increasing loads and decreasing concentrations suggest that some POM settled out, or was degraded during the floodplain transit, but was replaced by floodplain-derived POM. This additional POM dominated particle loads in the river after 230 km but caused only modest changes in the C:N ratio and the isotopic signatures of riverine POM. We therefore conclude that floodplain-derived POM and reservoir POM have similar characteristics. The floodplain-derived POM could originate from phytoplankton and periphyton from the floodplain, which would explain the low $\delta^{13}\text{C}$ -POC along some floodplain transects (Figure 4). Periphyton was found ubiquitous on inundated floodplain vegetation, and open lagoons on the floodplain can be sites of high primary production, even under low nutrient conditions (Cotner et al. 2006).

Dam effects and changes in DOM characteristics along the river

Given the fresh, reservoir-derived POM entering the Kafue Flats, one would also expect strong evidence for recently-fixed C in the DOM pool, e.g. as DOM released from algae or bacteria or produced during their decomposition. We found that, based on spectroscopic data (SUVA_{254} , EEMs and FI), DOM sampled even directly after the dam wall showed a strong terrestrial signal with only minor microbial contribution. In addition, DOM characteristics (C:N, $\delta^{13}\text{C}$, $\delta^{15}\text{N}$) only moderately shifted with the addition of a large proportion of floodplain-derived DOM. The relatively constant DOM composition suggests that a large fraction of the DOM that exited the reservoir was of terrestrial origin and transited the reservoir basically unchanged (Figure 9a). Any more bioavailable DOC produced within the reservoir was probably metabolized under the fairly warm in situ conditions ($T \sim 20\text{-}27^\circ\text{C}$). Upstream wetlands that are hydrologically connected to the Kafue River (Lukanga and Busanga Swamps; total area = 4,600 km²) are a potential source of this floodplain-like DOM that had entered the ITT reservoir (Figure 9a).

Results from fluorescence spectroscopy and stable isotope measurements revealed subtle changes in DOM composition along the river transect beginning at ~250 km. The decrease in $\delta^{13}\text{C}$ -DOC after ~250 km during flood season (Figure 4), for example, indicates an inflow of DOC with an average $\delta^{13}\text{C}$ of -30.2‰, based on a two end-member mixing calculation. This, in turn, suggests, a relative increase in the abundance isotopically-light DOM, produced from bacteria or algae. Kafue River $\delta^{13}\text{C}$ -DOC values (-25‰ to -21‰) were intermediate between $\delta^{13}\text{C}$ -values for floodplain soil/sediment, and

C₃-plant signatures (Table S1, supplementary information), and do not indicate any significant contribution from vegetation fringing the Kafue River, which is heavily dominated by C₄-plants (Ellenbroek 1987), with a distinct C isotopic signature of -13‰. Grazing, fire or rapid microbial turnover of C₄-derived DOM could explain the absence of a distinct isotopic C₄ signal in δ¹³C-DOC.

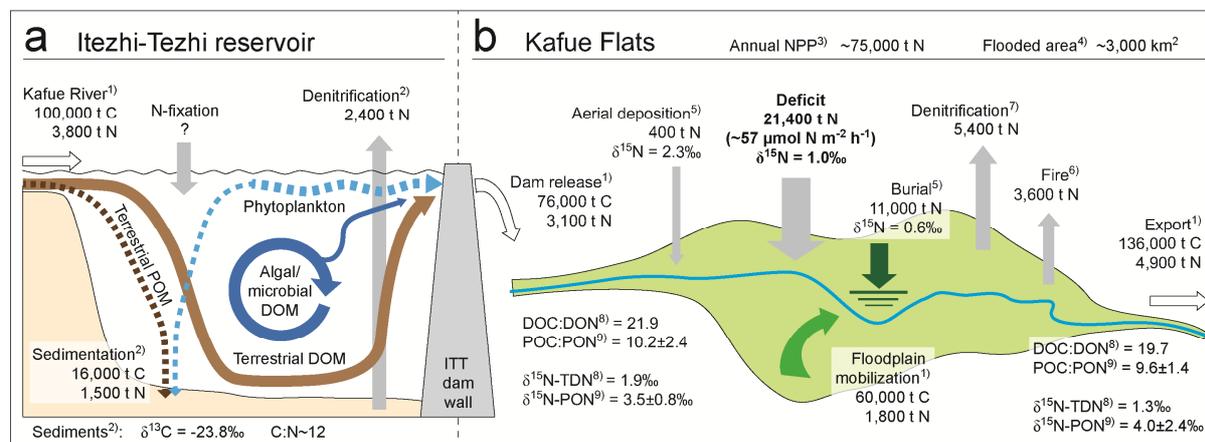


Figure 9. (a) Schematic illustration of the annual C and N fluxes in ITT reservoir. (b) System-scale N balance of the Kafue Flats based on own data and literature estimations. ¹) data from Wamulume et al. (2011); ²) data from Kunz et al. (2011b); ³) estimated based on Ellenbroek (1987); ⁴) from the model of Meier et al. (2010); ⁵) Deposition based on trap data, burial from on sediment cores (R. Zurbrügg, unpublished data); ⁶) burnt areas from Munyati (2000); ⁷) Estimated based on studies from the Amazon floodplains (Kern et al. 1996); ⁸) data from October 2008, May 2009, and May 2010; ⁹) data from annual sampling campaign (Figure S3, supplementary information).

The PARAFAC components showed additional variation in DOM composition along the river. The component's peak fluorescence intensity (F_{\max}) sharply increased ($P < 0.001$) between 230 and 280 km for all four components (Figure S4, supplementary information). 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 (Cory & McKnight 2005; Stedmon et al. 2003), we present the F_{\max} ratios of C1, C2 and C4 relative to C3 (Figure 10). The decrease in terrestrial-humic C1 and the sharp decrease of C2 after 230 km indicate that the chromophoric DOM shifted towards more terrestrial origin as floodplain waters entered the river. Along the floodplain transects, C1 and C4 increased with increasing distance from the river to the floodplain and from the shore to floodplain (Figure S6, supplementary information), indicating higher abundance or production, of DOM with C1 and C4-like fluorophores in the floodplain. On the other hand, abundance of C2-like DOM decreased along the river and along the floodplain transects, which suggests that C2 could be related to upstream OM sources and is being diluted by floodplain waters.

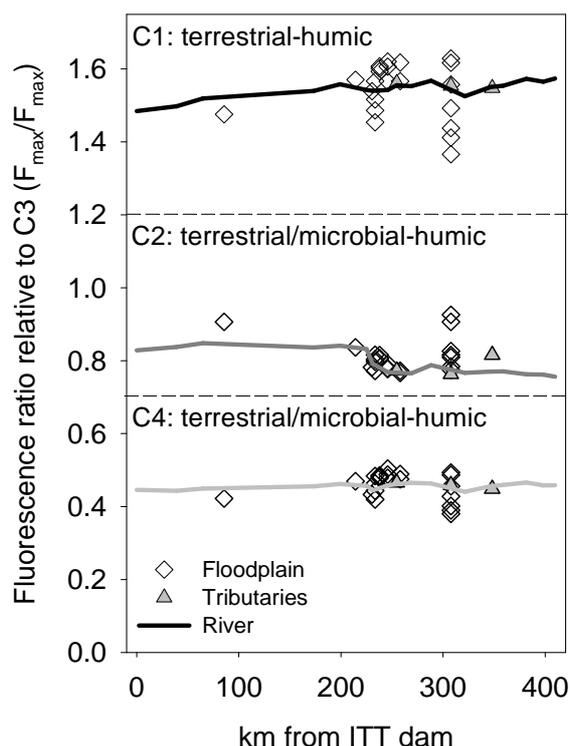


Figure 10. Ratios of components, identified by PARAFAC analysis. Components C1, C2, and C4 are shown relative to C3 along the river, in floodplain and tributaries, measured in May 2010.

Nitrogen balance, DON bioavailability and N-fixation

We combined N loads and stable isotopic signatures to obtain a N balance for the Kafue Flats flooded area over an annual cycle (Figure 9b). The N fluxes were calculated using own data, literature values from the Kafue Flats, except for denitrification which was approximated using conservative rates from the Amazon floodplains (Kern et al. 1996; Villar et al. 1998). Budget calculations revealed an N deficit of $\sim 21,000 \text{ t N yr}^{-1}$ in the Kafue Flats, which is six times higher as the N input from the reservoir and equal to $\sim 57 \mu\text{mol N m}^{-2} \text{ h}^{-1}$. The availability under natural hydrological conditions is unknown, but the construction of the ITT dam in 1978 may have increased the N-deficit. Burial and denitrification in the reservoir remove up to $3,900 \text{ t N yr}^{-1}$ from the river, which is equivalent to $\sim 50\%$ of the N inflows in ITT reservoir (Kunz et al. 2011b). The annual measured N inflows reservoir from Wamulume et al. (2011) which are indicated in Figure 9a underestimated the actual loads because of the insufficient sampling resolution during the "first flush" of N at the onset of the rainy season. The revised loads are $7,900 \text{ t N yr}^{-1}$ based on the model fluxes of Kunz et al. (2011b). Nevertheless, dam removal is substantial compared to the N that enters the Kafue Flats through the reservoir (Figure 9b), a large part of which we identified as refractory DON.

The narrow range of $\delta^{15}\text{N-TDN}$ (Figure 4) did not allow to discriminate between floodplain DON and reservoir DON ($1.9 \pm 0.4\%$; Table S1, supplementary information), but supports the paradigm that riverine DON in general originates from terrestrial sources (Berman & Bronk 2003). Intense cycling

of DON would affect the $\delta^{15}\text{N}$ -TDN, as shown by 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, e.g. from concomitant release, uptake, and degradation along the main channel resulting in a constant $\delta^{15}\text{N}$ -TDN cannot be excluded completely, but is considered unlikely (Knapp et al. 2005). Bioavailable DON produced in the reservoir might rapidly be degraded or taken up by bacteria or phytoplankton before reaching the Kafue Flats (Bronk et al. 1994).

While $\delta^{15}\text{N}$ -TDN remained fairly constant along the Kafue River, $\delta^{15}\text{N}$ -PON decreased by >2‰ in the flooding season (Figure 4), most likely due to the lateral input or in-situ production of PON with lower $\delta^{15}\text{N}$. The fixation of atmospheric N leads to a $\delta^{15}\text{N}$ close to 0‰ in the fixed product (Martinelli et al. 1992) and the observed ^{15}N -depleted PON could thus be dominated by N-fixing organisms. Previous studies in tropical floodplains have found N-fixation rates of several $\text{g N m}^{-2} \text{yr}^{-1}$ (Cleveland et al. 1999), through symbiotic (Martinelli et al. 1992) or through asymbiotic fixation by free-floating or attached cyanobacteria (Kern & Darwich 2003). To balance the overall N budget N-fixation rates that high but comparable with measured rates in other systems would be needed. This is consistent with the isotope mass balance which requires a mean $\delta^{15}\text{N}$ of 1.0‰ and supports the hypothesis that N-fixation is the main N source to the Kafue Flats (Figure 9b). The high abundance of periphyton on inundated vegetation and the high diversity and spreading of N-fixing plants in the floodplain (Ellenbroek 1987) support this idea. The complementary measurements of N pools across the Kafue Flats fell in a relatively narrow range (-1 to 4‰; Table S1, supplementary information), which is within the data range reported for the Amazon floodplains (Aufdenkampe et al. 2007; Bernardes et al. 2004; Hedges et al. 2000) and may be characteristic for such systems.

Conclusions

During the flooding season, up to 80% of the discharge in the Kafue River passed through the floodplain. This intense river-floodplain exchange caused net exports of 35-75 kg C km⁻² d⁻¹ in the form of DOC, 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. 2005a; Mayorga et al. 2010). Stable isotope and spectroscopic analyses showed that DOM was mainly of terrestrial origin, but devoid of any distinct plant-derived signal. Export of autochthonous DOM from the upstream reservoir thus seems to be of minor importance. The exported POM was clearly distinguishable from DOM by its overall lower C:N ratio and lower $\delta^{13}\text{C}$. Both indicators underline the phytoplankton origin of POM. In the upper parts of the Kafue Flats, the POM pool was dominated by algal OM from the reservoir, and, further downstream, by phytoplankton or periphyton production in the floodplain based on an OC and ON mass balance.

The Kafue Flats are a net source of N to downstream ecosystems, despite a 50% removal of riverine N by the upstream dam. A N mass and isotopic balance suggests that high N-fixation rates are needed to compensate the annual deficit of 21,000 t N. Our study underlines how intense river-floodplain exchange leads to very high OM export to a tropical river basin. In contrast to a forested system like the Amazon, the flooded grassland ecosystem of the Kafue Flats exports more phytoplankton POM than plant debris. Finally, the upstream reservoir had little effect on overall DOM quality, which indicates that aquatic DOM production in the reservoir was negligible compared to the large wetland sources.

Acknowledgements

The authors thank Jason Wamulume, Griffin Shanungu, Manuel Kunz, Wilma Blaser, and Event Ngandu and the ZAWA wildlife officers for assistance during field work; Mark Rollog (University of Basel), Ruth Stierli (Eawag), Kate Ashe, the ETHZ Soil Chemistry and Environmental Chemistry groups for laboratory support, Britt Peterson (ETHZ) for assistance with excitation-emission spectroscopy analyses, Linda Jørgensen (University of Copenhagen) and Dolly Kothawala (University of Uppsala) for support with PARAFAC modeling and interpretation. This study was supported by the following Zambian partners and agencies: Imasiku Nyambe (University of Zambia), Zambia Wildlife Authority, Zambia Electricity Supply Corporation (ZESCO), Zambezi River Authority, and the Department of Water Affairs. Funding was provided by the Competence Center for Environment and Sustainability (CCES) of the ETH domain, the Swiss National Science Foundation (Grant No. 128707) and Eawag.

Supplementary information

Sampling of additional C and N pools in the Kafue Flats

Sampling, sample preparation, and analyses

In order to constrain the sources of dissolved organic matter (DOM) and particulate organic matter (POM), the stable isotopic composition of dry deposition, plants, periphyton, soils, and sediments from the Kafue Flats was analyzed. We also measured $\delta^{15}\text{N}$ -TDN from the water column of ITT reservoir (Station IT1 in Kunz et al. 2011b). To measure N dry deposition, three acid-washed HDPE deposition traps, 600 cm² each, were installed at two locations in the dry floodplain in Lochinvar National Park (Figure 1c) and one trap on a float in the middle of the large adjacent lagoon (Figure 1). The land-based traps were installed at 2 m above ground and exposed for 5 to 11 days in May 2010. Deposited matter was dissolved in 2M HCl, and its $\delta^{15}\text{N}$ was measured as described in the main article. Plant samples were taken from the first fully expanded leaves of C₃-grass *Phragmites australis* and C₄-grass *Vossia cuspidata*, two dominant species in the floodplain areas adjacent to the river channel (Ellenbroek 1987). Plant, periphyton, soil, and sediment samples were collected along the main channel in October 2008. Plant material and soil was dried at 40°C, periphyton from submerged floodplain grasses and surface sediment samples were freeze-dried. All solid samples were homogenized and analyzed for C and N isotopic signature as described for POM in the main article.

Stable isotopes of floodplain and reservoir C and N pools

$\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of the measured floodplain and reservoir pools are presented in Table S1. The plant samples showed the typical C₃ and C₄ isotopic signatures for ^{13}C of -26‰ and -13‰, respectively (Martinelli et al. 1991; Smith & Epstein 1971). The other floodplain pools were found to cluster around -20‰, sediment trap and sediments at ITT displayed a somewhat lower $\delta^{13}\text{C}$. For $\delta^{15}\text{N}$, dry deposition, periphyton, river sediments, reservoir sediments and sediment traps averaged around 2‰. C₃-grass *Phragmites australis* had a $\delta^{15}\text{N}$ of ~4‰, and soils and the C₄-grass *Vossia cuspidata*, were close to 0‰.

Table S1. Stable isotopic signatures and C:N ratios of Kafue Flats and ITT reservoir C and N pools.

	$\delta^{13}\text{C}$ (‰ _{VPDB})	$\delta^{15}\text{N}$ (‰ _{air})	C:N
	mean±SD	mean±SD	mean±SD
Kafue Flats floodplain			
Dry deposition	n.a.	2.3±0.2	n.a.
<i>Vossia cuspidata</i> (C ₄)	-13.3±0.3	0.5±0.8	n.a.
<i>Phragmites australis</i> (C ₃)	-25.5±0.4	3.9±0.6	n.a.
Periphyton ^a	-20.5±3.1	1.4±0.9	n.a.
Floodplain soil	-20.3±2.5	0.6±1.2	15.9±2.1
River sediment	-19.6±1.8	2.2±1.2	15.0±2.5
Itezhi-Tezhi reservoir			
Sediment traps ^b	-25.8±0.5 ^c	2.5±1.5	9.7±0.5 ^c
Sediments ^d	-23.8±3.5 ^c	n.a.	12.1±0.6 ^c
TDN ^e	n.a.	1.9±0.4	n.a.

^a sampled from inundated stems of floodplain grasses.

^b sampled from October 2008 to May 2009 at depths of 13 to 40 m behind the dam wall.

^c data from Kunz et al. (2011b)

^d sampled in May 2008

^e sampled in June 2009 behind ITT dam wall.

Calibration of $\delta^{15}\text{N}$ -TDN

The calibration of $\delta^{15}\text{N}$ -TDN was done using four different organic N isotopic standards. An isotope calibration curve is shown in Figure S1.

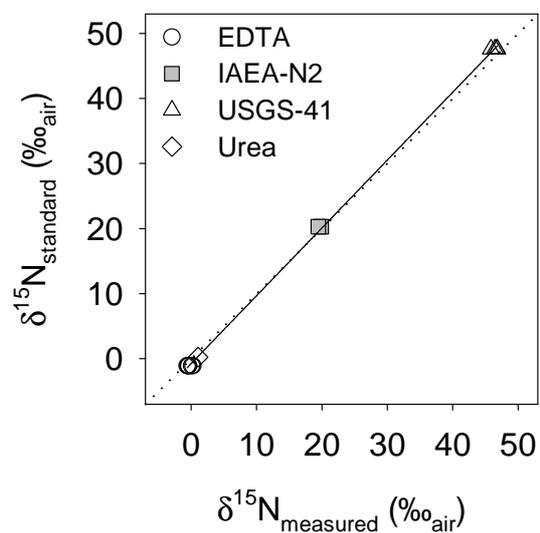


Figure S1. Calibration curve of a $\delta^{15}\text{N}$ -TDN analysis run. EDTA, USGS-41 and urea are organic N isotope standards, IAEA-N2 is a $(\text{NH}_4)_2\text{SO}_4$ isotope standard. The dotted line is the 1:1 line, the solid line represents the linear regression of $\delta^{15}\text{N}_{\text{standard}} = 1.043 \times \delta^{15}\text{N}_{\text{measured}} - 0.756$ ($R^2 = 0.9997$).

Total suspended solids (TSS) in October 2008 and May 2009

The quantification of TSS in October 2008 and May 2009 allowed calculating wt% C and N in the particles along the river. TSS was measured by weighing 47 mm pre-combusted 0.7 μM GF filter (Whatman) before and after filtration of ~ 2 L of water sample and subsequent drying (3h at 40°C). TSS showed a different pattern for flooding and dry season, evidenced as decrease (May) and peak (October) of TSS after ~ 200 km (Figure S2). The high C content of 35-45% suggests that the particles leaving ITT reservoir were comprised of plankton from the epilimnion.

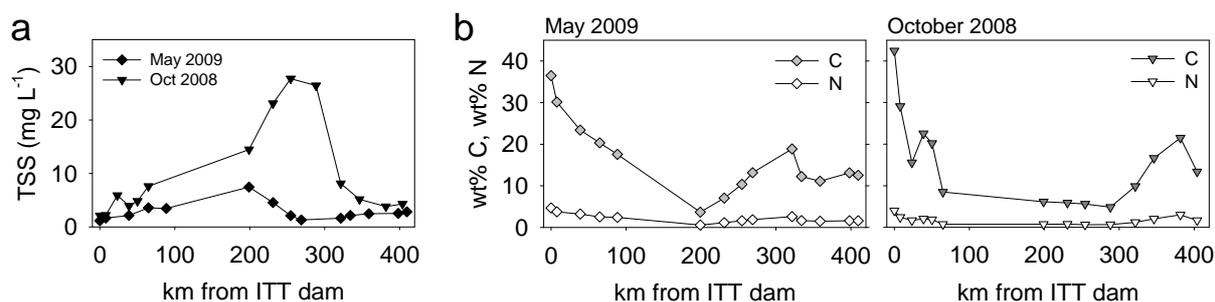


Figure S2: (a) TSS and (b) C and N content of the particles in the Kafue River for May 2009 and October 2008.

POC and PON monitoring over an annual cycle

During a monitoring campaign from June 2008 to May 2009, the concentrations and stable isotopic signatures of POC and PON were measured at five selected stations (0, 88, 231, 334, and 410 km) on a bimonthly basis (Wamulume et al. 2011). Concentrations of POC and PON and POC:PON showed an overall similar course like for the higher resolution October 2008 and May 2009 campaigns. $\delta^{13}\text{C}$ -POC showed higher temporal variation after the dam than along the river, but was fairly constant at $-28.5 \pm 1.2\text{‰}$ at the end of the floodplain (Figure S3d). Higher $\delta^{13}\text{C}$ -POC was associated with higher POC concentrations which might be indicative of a higher contribution of plant derived POM (Figure S3e). $\delta^{15}\text{N}$ -PON was in the range of other sampled N pools (Table S1) and did not vary systematically along the river.

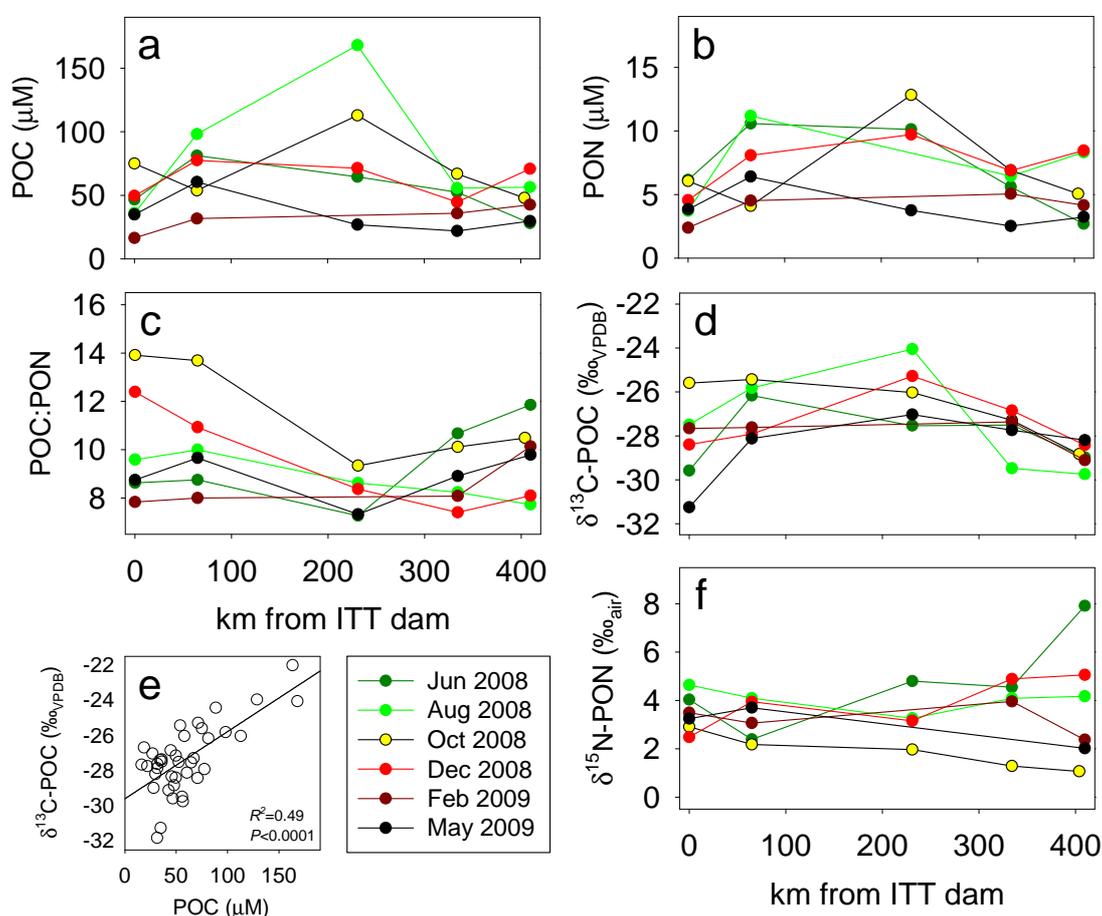


Figure S3. (a) POC and (b) PON concentrations, (c) POC:PON molar ratio, (d) $\delta^{13}\text{C}$ -POC, (e) correlation between concentration and $\delta^{13}\text{C}$ of POC, (f) $\delta^{15}\text{N}$ -PON at five stations along the Kafue River over an annual cycle, from June 2008 to May 2009. Data from October 2008 and May 2009 are reprinted for consistency.

PARAFAC modeling of excitation-emission matrices

PARAFAC model results

The comparison of different PARAFAC models with an increasing number of components resulted in a four-component model minimizing the sum of squared errors, relative to a three and five-component model (Figure S4). Higher component models were found inappropriate since they caused in discontinuities in the resulting components, indicated as sharp peaks in the 5-component line in Figure S2.

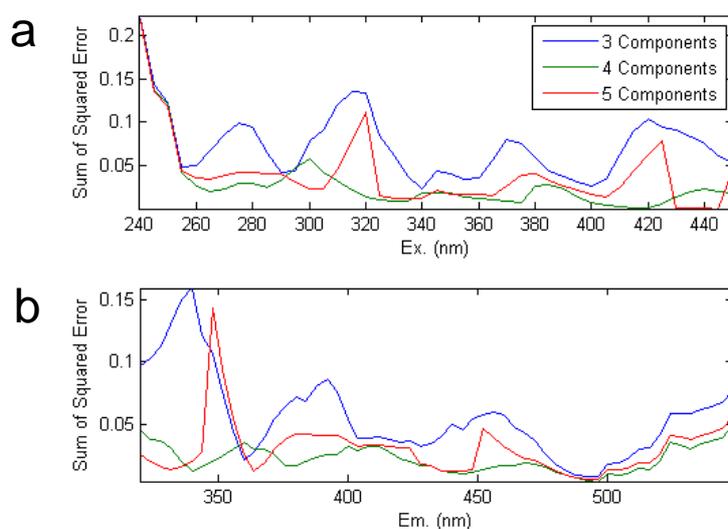


Figure S4. Sum of squared errors of 3-, 4-, and 5-component PARAFAC models for (a) excitation, and (b) emission wavelengths. Sharp peaks in the 5-component errors are caused by discontinuities in the components.

Identification of PARAFAC components

All four components resulting from the PARAFAC analysis (Figure S3) of 45 samples had been found previously in other systems (Table S2 and references therein).

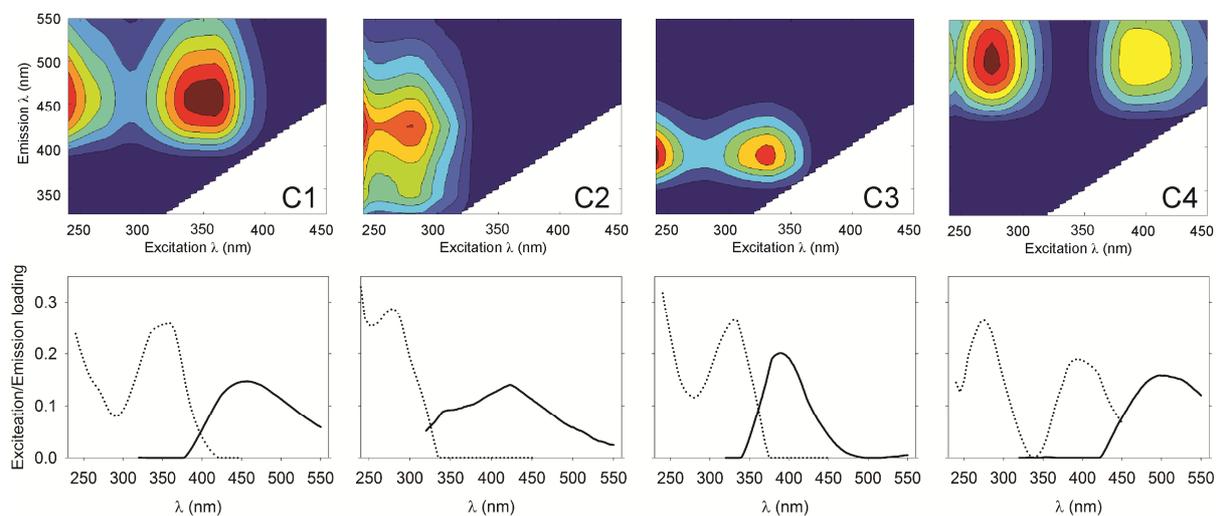


Figure S5. Components C1-C4 resulting from PARAFAC analysis. The upper panel shows the excitation-emission matrices (EEMs), the lower panel shows the excitation (dotted line) and emission (solid line) loadings of the components.

Table S2. Characteristics of the four components identified by PARAFAC analysis.

Component	C1	C2	C3	C4
Ex λ (nm)	360	280	330	275, 390
Em λ (nm)	450	420	390	500
Description	Visible humic like	UV humic like	Humic like	Humic like
Origin	Terrestrial	Terrestrial/microbial forested regions, wetlands	Terrestrial, degradation of terrestrial OM	Terrestrial/microbial degradation of terrestrial OM
Reference ^a : component name in reference	1: Peak C 3: Component 3 6: C1	1: Peak A 4: Comp. 6 / 2 (Q2) 5: Component 1 7: Component 1	1: Peak M 2: C4 3: Component 6 4: Component 3 5: Component 6 6: C4 7: Component 3	2: C3 4: Component 7 7: Component 2

^a References: 1. Coble (1996) and Coble et al. (1998); 2. Stedmon and Markager (2003); 3. Stedmon and Markager (2005); 4. Cory and McKnight (2005); 5. Yamashita et al. (2008); 6. Jørgensen et al. (2011); 7. Ishii & Boyer (2012).

Fluorescence intensities (F_{max}) of PARAFAC components C1-C4

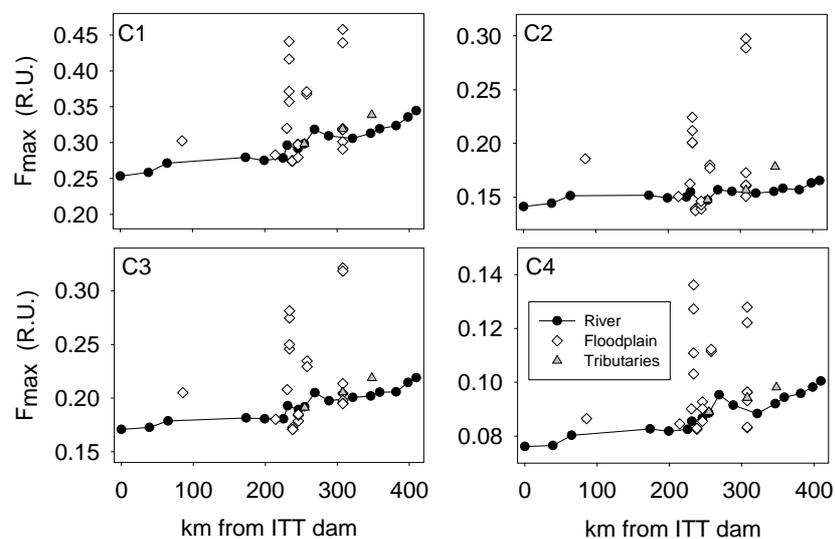


Figure S6. Fluorescence maxima (F_{max} in Raman units) for components C1-C4 along the river channel (black dots, solid line), for floodplain stations (empty diamonds) and tributaries (grey triangles).

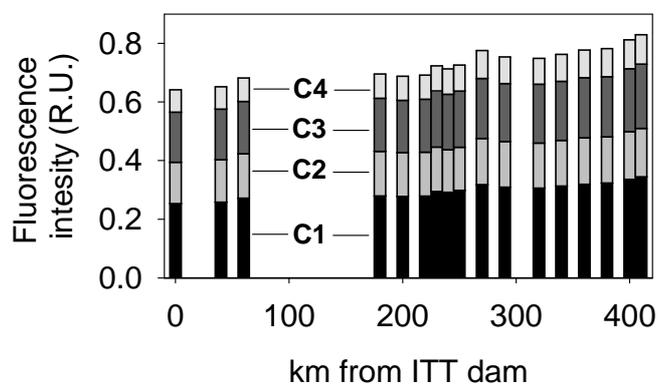


Figure S7. Contributions of components C1-C4 to the overall fluorescence (F_{max} in Raman units). C1 accounted for $40.7 \pm 0.6\%$, C2 for $20.9 \pm 0.8\%$, C3 for $26.4 \pm 0.2\%$, and C4 for $12.0 \pm 0.2\%$ of the total fluorescence.

Ratios of component fluorescence relative to C3 along floodplain transects

Even though the component ratios for floodplain stations were overall statistically indifferent the river ($\rho=0.097-0.872$), some deviations from river stations were evident (Figure 9 in the main text). Floodplain transects T1-T5 (Figure 1) generally showed higher ratios for C1 and C4 when moving from river or shore towards the floodplain, while C2 ratio to C3 decreased.

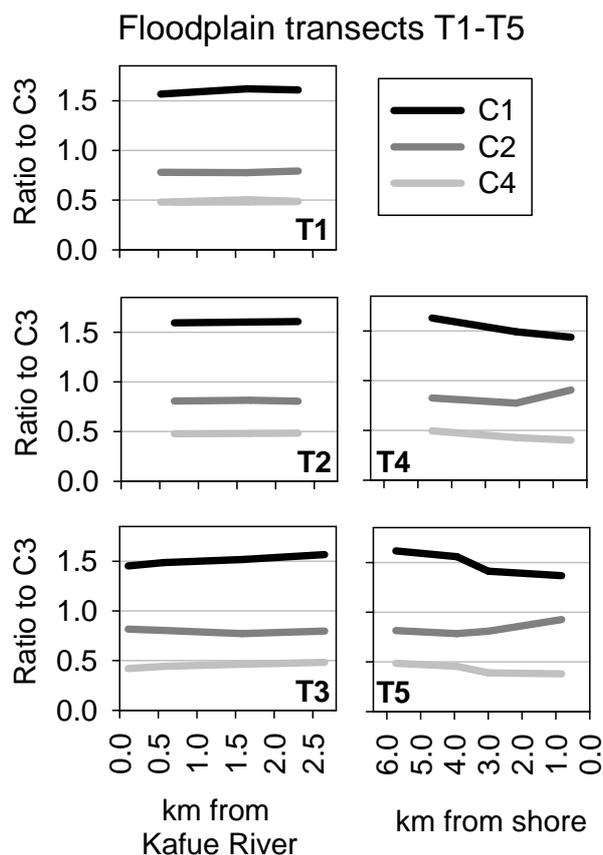


Figure S8. Ratios of the peak fluorescence F_{\max} of C1, C2 and C4 relative to C3 ratios along floodplain transects T1-T5 (Figure 1c). Component C3 showed the highest correlation with DOC concentration ($R^2=0.87$). Note the reversed distance axis for different transects.

*System-wide mineralization and C, N, and P export in a
dam-impacted tropical floodplain
(Kafue Flats, Zambia)*

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David B. Senn

In preparation for submission to Biogeochemistry

Abstract

Tropical floodplains are important biogeochemical reactors that strongly influence riverine carbon (C) and nutrient transport between headwaters and downstream systems. We quantified the rates of organic C mineralization and the mass loads and fate of inorganic nitrogen (N) and phosphorus (P) in the dam-impacted Kafue Flats in Zambia. During the flooding season, intense hydrological exchange between the Kafue River and its floodplain allowed to evaluate biogeochemical processes in the productive wetlands by measurements of dissolved oxygen, inorganic C and nutrients in the draining river. Over an annual cycle, 58,000-97,000 t C were respired whereof the outgassing of CO₂ from the Kafue River accounted for 48,000±19,000 t C yr⁻¹. Only 2% of N and 7% of P that had been released during mineralization was exported from the system, which suggests considerable retention and losses in the floodplain. During detailed measurements along the Kafue River, a substantial increase in CO₂ concentration, and N:P ratios of <4 were evident along reaches of intense river-floodplain exchange, indicating high losses of N in the floodplain. Despite substantial nutrient retention due to upstream dam operation and high N and P losses in the floodplain, the Kafue Flats are a net source of 130 t N yr⁻¹ (~43 kg N km⁻² yr⁻¹) and 76 t P yr⁻¹ (~25 kg P km⁻² yr⁻¹) to downstream systems and a hotspot for nutrient turnover in the Zambezi River basin.

Introduction

Floodplains are important biogeochemical reactors along large rivers that can act as sources or sinks for riverine carbon (C), nitrogen (N) and phosphorus (P) (Aufdenkampe et al. 2011; Baldwin & Mitchell 2000). As sites of fixation and respiration of organic C (OC) and release of nutrients and greenhouse gases, floodplains play a crucial role in the ecosystem metabolism (Battin et al. 2009a). However, global C budgets have not considered OC burial and CO₂ fluxes from mineralization in floodplains, because of the variability in space and time of these processes (Battin et al. 2009b; Cole et al. 2007).

Tropical wetlands contribute one third of the total CO₂-outgassing from aquatic systems (1.12 Pg C yr⁻¹), compared to 0.47 Pg C yr⁻¹ from temperate wetlands (Aufdenkampe et al. 2011). Floodplains account for large fraction of tropical wetlands, with areas of e.g. >10⁶ km² in South America and >1.5×10⁵ km² in Africa (Tockner & Stanford 2002). Because of the large area, the periodic flooding and changing redox conditions, the high temperatures, and intense rates of primary production (>2,000 g C m⁻² yr⁻¹; Junk & Piedade 1993), the fate of organic matter (OM) and the associated nutrients is of particular significance. But detailed studies of the fate of OM and nutrients have been conducted in only few systems, such as the Amazon (Alin et al. 2011; Ellis et al. 2012).

The Amazon floodplains are characterized by particularly intense CO₂ emissions of 500-800 Tg C yr⁻¹ (Alin et al. 2011; Richey et al. 2002). However, only a relatively small and young fraction (<5 years) of the OM transported by the Amazon fuels in-stream mineralization (Mayorga et al. 2005). For the Amazon main stem, Devol et al. (1995) found that respiration and reaeration (gas exchange with the atmosphere) were almost balanced. The high dissolved oxygen (DO) consumption and dissolved inorganic C (DIC) production during high flows were attributed to (1) changes in river depth (and thus smaller area/volume ratio) and (2) substantial contribution of floodplain respiration and which became evident in the main stem due to intense river-floodplain exchange. The actual contribution of floodplain respiration to the respiration signal in the river was not quantified and remains unknown for river-floodplain systems in general (Battin et al. 2009a).

Floodplain ecosystems are susceptible to changes in nutrient inflows (Tockner et al. 2010), and their highly valued ecosystem services, like habitat provision, water purification and food supply, strongly depend on the nutrient regime (Junk 2002). Floodplains provide favorable conditions (high T, periodic flooding) for the removal of dissolved inorganic N (DIN) and dissolved inorganic P (DIP). To constrain DIN and DIP budgets in tropical catchments, models have been developed on the global (Harrison et al. 2010; Mayorga et al. 2010) and catchment scale (e.g. Yan et al. 2010; Yasin et al. 2010). While models may provide appropriate nutrient export loads, they are unable to resolve relevant sub-system scale processes. For example, the N removal models by Harrison et al. (2009) and Wollheim et al. (2008) do not resolve river-floodplain interactions.

River-floodplain exchange, (i.e. the water transfer between a river and its floodplain) has been identified as a key process for the ecological and biogeochemical functioning in temperate (e.g. Hunsinger et al. 2010; Tockner et al. 2010) and tropical systems: For example, lateral exchange was shown to affect sediment erosion and transport (Dunne et al. 1998), and OM mineralization (Devol et al. 1995) and carbon fluxes (Pettit et al. 2011) and nutrient supply (Villar et al. 1998).

We examined OM mineralization and nutrient fluxes at the ecosystem-scale in the Kafue Flats, a highly productive tropical floodplain system in the Zambezi River basin (Figure 1). The Kafue River and its floodplain undergo intense river-floodplain exchange, with up to 80% of the river flow migrating through the floodplain (Zurbrügg et al. 2012b). Two dams constructed in the 1970s have substantially reduced this exchange and altered timing and extent of flooding (Mumba & Thompson 2005). Here we quantify the changes in the concentration, speciation, and loads of C, N and P along the Kafue River and use this information to quantify nutrient uptake, OM, N- and P-turnover and atmospheric emissions of CO₂. We discuss the seasonality of these processes by comparing three spatially intensive campaigns and a one-year monitoring effort. Finally, we explore the implications of river damming and the altered hydrological regime on floodplain biogeochemistry, and the role of the Kafue Flats' nutrient turnover for Zambezi River basin.

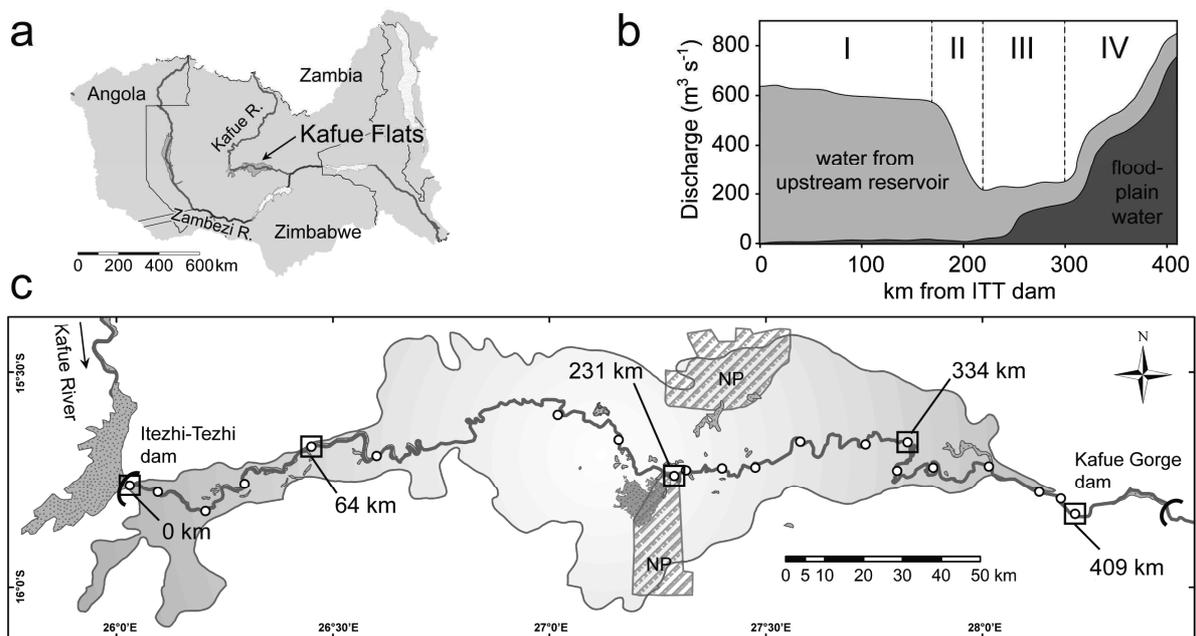


Figure 1. (a) The Kafue Flats along the Kafue River in the Zambezi River basin. (b) Schematic contribution of reservoir and floodplain water to river discharge (Q) during the flooding season (Zurbrügg et al. 2012b). Four regimes can be distinguished along the river: (I) constant Q , and little river-floodplain exchange, (II) Q losses to the floodplain, (III) constant Q , high exchange with the floodplain, (IV) increase in Q from receding floodplain waters and tributaries. (c) Sampling stations along the Kafue River in the Kafue Flats. White circles depict sampling stations of the spatially intensive campaigns, framed circles with distances from the upstream dam are stations sampled during the annual campaign 2008-2009.

Methods

Study site

The Kafue Flats is a 6,500 km² floodplain system along the Kafue River in Zambia. After the rainy season from November to April the floodplain turns into an extensive wetland area which is an important wildlife habitat and listed in the Ramsar Convention inventory (Ramsar 2006). Flooding lasts from January to August and results from direct precipitation (975 mm in 2008/09), seasonal tributaries, and the peak flows of the Kafue River of up to 1,900 m³ s⁻¹. For the remaining time the floodplain falls dry and river discharge drops below 100 m³ s⁻¹. The floodplain vegetation adjacent to the Kafue River is mainly composed of C₄-plants, including large floating species like *Vossia cuspidata*, *Echinochloa scabra* or *Cyperus papyrus*, while C₃-grasses prevail in the more distant areas (Ellenbroek 1987). The land use in the immediate catchment is traditional, that is, subsistence farming and animal husbandry, preserving the Kafue Flats as a pristine system.

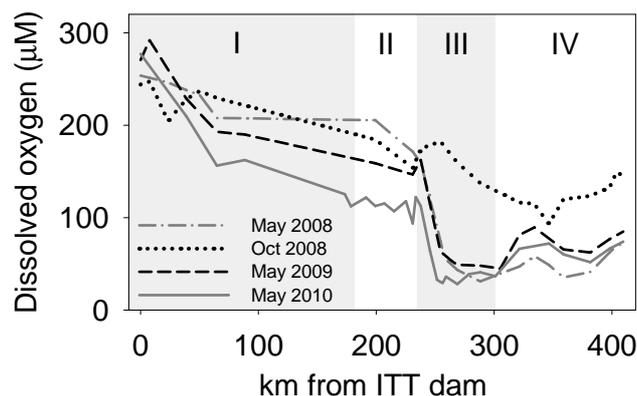


Figure 2. Dissolved oxygen concentrations along the Kafue River in May 2008, October 2008, May 2009 and May 2010. Reprinted from Zurbrügg et al. (2012b). Sections I-IV mark the different river-floodplain exchange regimes from Figure 1b.

The hydrology of the Kafue Flats has been modified by two large dams along the Kafue River. The downstream Kafue Gorge dam and upstream Itezhi-Tezhi dam were closed in 1972 and 1978, respectively. Itezhi-Tezhi reservoir (370 km²) with a hydraulic residence time of 0.7 years is an efficient particle trap and removes 50% of N and 60% of P inputs from the Kafue River (Kunz et al. 2011b). Itezhi-Tezhi is currently used as a storage reservoir and water from the epilimnion is released over regulated spillways. Despite their large size, the Kafue Flats are hydrologically and spatially well-constrained system by one main in- and outflow. The clear separation of a sections where the river is losing water to the floodplain and downstream reaches where floodplain waters return to the river is a special feature of this wetland system. During the flooding period, the hydrological regime of the Kafue River can be divided into four sections (I-IV, Figure 1b). In section I (0-180 km from

Itezhi-Tezhi dam), river discharge shows no systematic variation and the exchange with the floodplain is small. Between 180 and 225 km (section II), a constriction of the river channel diverted 64% and >70% of the river discharge in May 2009 and May 2010, respectively, into the floodplain (Zurbrügg et al. 2012b). Between 225 and 300 km (section III) the river discharge is $\sim 200 \text{ m}^3 \text{ s}^{-1}$ but high river-floodplain exchange caused a steep decline in DO concentration (Figure 2). After 300 km (section IV), receding floodplain waters that are depleted in DO raised the river discharge by a factor of four and suppressed DO levels for 150 km. Waters leaving the system have thus experienced strong river-floodplain interaction and export integrated chemical signals, which facilitates the analysis floodplain processes.

Sampling and approach

After a pilot campaign in May 2008 (data presented as supplementary information) we pursued a dual approach: (1) Spatially intensive sampling at ~ 20 km resolution for two campaigns during the flooding period in May 2009 and May 2010, and one during the dry season in October 2008. (2) Bimonthly sampling of five selected stations over an annual cycle between May 2008 and May 2009. The five stations included the dam site after spillways (0 km), 64, 231 and 334 km downstream of the dam and at the end of the floodplain system (409 km; Figure 1c). Water samples were taken along the Kafue River, in tributaries and at floodplain stations.

Chemical data

Dissolved oxygen (DO), T, and pH were measured with a multiprobe (WTW Multi 430i). DIC concentration and dissolved CO_2 (H_2CO_3^*) was calculated from alkalinity, T and pH (Stumm & Morgan 1996). Alkalinity was measured by end-point titration to pH 4.3 (Metrohm Titrino 716). Excess CO_2 (ΔCO_2) was calculated as the difference between measured (H_2CO_3^*) and equilibrium dissolved CO_2 ($\text{H}_2\text{CO}_3\text{eq}$) from Weiss (1974):

$$\Delta\text{CO}_2 = \text{H}_2\text{CO}_3^* - \text{H}_2\text{CO}_3\text{eq} \quad (1)$$

The sum of NO_2^- and NO_3^- was determined by reduction to NO_x (Antek 754) followed by chemoluminescence detection (Antek 9000) (Braman & Hendrix 1989). NO_2^- , NH_4^+ , o-PO_4^{3-} were measured by spectrophotometry on a Hitachi U-2000, and NO_3^- calculated by difference. For simplicity, o-PO_4^{3-} will be called dissolved inorganic P (DIP) hereafter. Ion concentrations (Ca^{2+} , Mg^{2+} , SO_4^{2-} , Cl^-) were measured by ion chromatography (Metrohm 882 Compact IC plus) and are presented as supplementary information.

Samples for the C stable isotopes DIC ($\delta^{13}\text{C}_{\text{DIC}}$) were preserved with CuCl and closed air-free and kept at 4°C in the dark until analysis. For analysis, 2 mL aliquots were filled in Exetainer vials (Labco), the headspace replaced by Helium, 85% H_3PO_4 was added and equilibrated for 4.5 h at 40°C .

Analysis was done with a MultiFlow preparation module connected to a continuous flow IRMS (Isoprime). NBS-19 (+1.95‰_{VPDB}), IAEA-CO8 (-5.76‰_{VPDB}), and IAEA-CO9 (-47.32‰_{VPDB}) were used as standards. Precision was ±0.2‰_{VPDB}.

The headwaters of the Kafue River are influenced by its carbonate-rich bedrock (Pettersson & Ingri 2001; Pettersson et al. 2000) resulting in alkalinity of 1-2 mM C_{eq}. Alkalinity contributed 83±2% (May 2009) and 75±5% (October 2008) to specific conductivity, based on the ion pairing model from Pawlowicz (2008). To account for DIC from carbonate dissolution, we calculated DIC from mineralization of organic matter (DIC_{min}) by subtracting DIC from dolomite dissolution:

$$\text{DIC}_{\text{min}} = \text{DIC} - (\text{Ca}^{2+} + \text{Mg}^{2+}) \quad (2)$$

Results

Dissolved inorganic carbon along the Kafue River

DIC concentration varied between 1.1 and 1.9 mM for the sampled campaigns in October 2008 and May 2009. For both campaigns, DIC increased along the Kafue River, with a steeper increase for the flooding campaigns than for the dry season (Figure 3). DIC_{min} accounted for approximately half of total DIC (October 2008: $52 \pm 8\%$, May 2009: $49 \pm 6\%$) and DIC_{min} and total DIC exhibited similar patterns along the main channel (Figure 3). The Kafue River was 1.7-30-fold supersaturated with respect to CO_2 for both October 2008 and May 2009, with the exception of the stations 0-15 km after the dam in October 2008. The maximum ΔCO_2 concentrations were $330 \mu M$ at 231 km in May 2009, which coincided spatially with the onset low DO levels (Figure 2). In October, ΔCO_2 reached $140 \mu M$ at 290 km at a similar (but less pronounced) decline in DO levels. May 2008 data were consistent with May 2009, but exhibited a more distinct increase in ΔCO_2 (supplementary information). $\delta^{13}C_{DIC}$ varied between -1.5 and -7.9‰ and decrease consistently after 231 km, by 2.7‰ in October and by 3.0‰ in May, which suggests inflow or production of lighter DIC towards the end of the floodplain system.

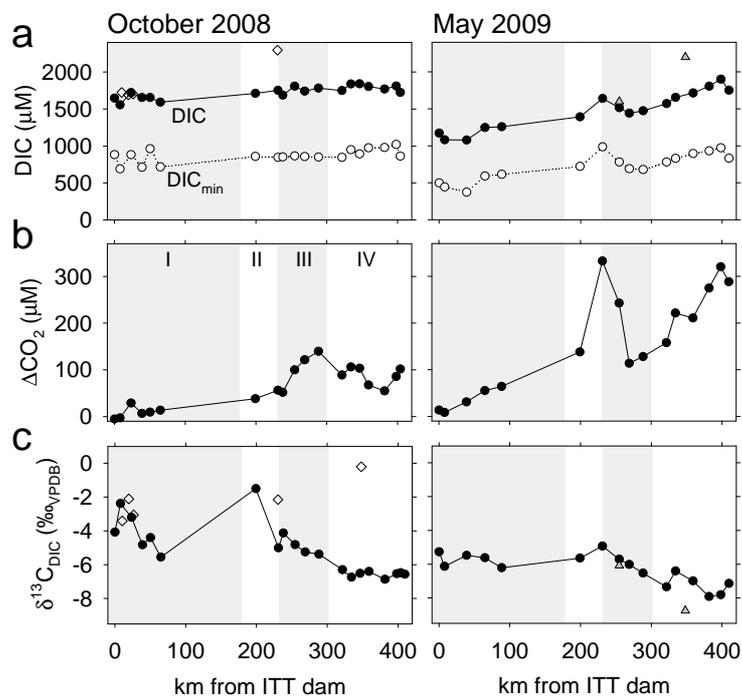


Figure 3. (a) DIC and DIC_{min} concentrations, (b) ΔCO_2 , and (c) $\delta^{13}C_{DIC}$ along the Kafue River in October 2008 and May 2009. Sampled floodplain stations are marked with empty diamonds, tributaries with gray triangles. The shading refers to sections I-IV.

Dissolved inorganic N and P concentrations along the Kafue River

Dissolved inorganic N (DIN) was $\leq 2 \mu\text{M}$ and consisted mainly of NH_4^+ and NO_3^- (Figure 4). NO_2^- accounted for only small percentage of DIN ($1\pm 2\%$ in October 2008, $10\pm 6\%$ in May 2009, and $4\pm 2\%$ in May 2010; supplementary information). For all campaigns, NH_4^+ concentrations were generally between 0.2 and $0.7 \mu\text{M}$ with the exception of peaks at ~ 360 km caused by a tributary (Figure 4a). For the flooding periods, NH_4^+ consistently increased in sections III and IV. In contrast, NO_3^- concentrations tended to be highest at the dam outflow (0.8 - $1.7 \mu\text{M}$; Figure 4b). DIP concentrations along the Kafue River were consistently $< 1 \mu\text{M}$ and increased along river with distance from the upstream dam for all sampling campaigns (Figure 4c).

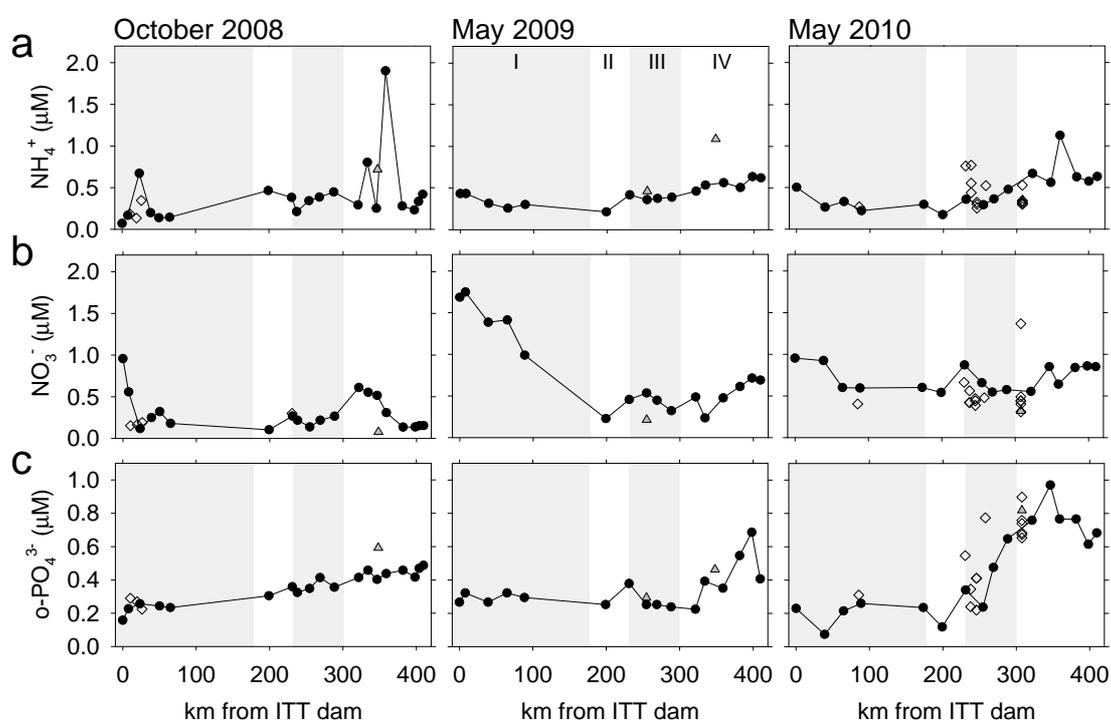


Figure 4. Concentrations of (a) NH_4^+ , (b) NO_3^- , and (c) o-PO_4^{3-} along the Kafue River in October 2008, May 2009 and May 2010. Symbols and shading as depicted in Figure 3.

Elemental ratios 2008-2010

The ratio of DIC_{\min} to DIN ($\text{DIC}_{\min}:\text{DIN}$) ranged between 200 and 2,800 and was > 500 for 89% of the sampled stations (Figure 5a). For May 2009, the ratio was consistently higher in the reaches dominated by floodplain water (sections III, IV) than upstream. In the dry season, $\text{DIC}_{\min}:\text{DIN}$ featured two sharp increases, over the first 75 km downstream of Itezhi-Tezhi dam and at the end of the floodplain. $\text{DIN}:\text{DIP}$ was 6-8 at the dam site and consistently decreased along section I (Figure 5b) as a result of NO_3^- -loss. Overall, $\text{DIN}:\text{DIP}$ was < 4 for 90% of the sampled stations.

DIC_{min}, DIN and DIP loads in the Kafue Flats

Nutrient and inorganic carbon loads along the Kafue River varied considerably between the dry and the flooding season (Figure 6a-c), as expected based on the different discharge regime (Figure 6c). Due to the small variation in concentration and discharge, October loads remained relatively constant and the floodplain was a net sink for DIC_{min} (-32%) and DIN (-62%) but a net source of DIP (+34%; Table 1). The loads during the flooding period showed minima in section III due to the discharge minimum at this point (Figure 6c). Along the downstream section IV, all loads but specifically DIP strongly increased as a result of the inflowing water from the floodplain. During the flooding period, 0.9-1.6 t DIN d⁻¹ and 0.6-1.6 t DIP d⁻¹ were exported from the Kafue Flats, whereof, 80% or more must have originated from the floodplain, based on the difference between the load minimum at 250 km and the load at the end of the Kafue Flats (409 km; Figure 6). Overall, the Kafue Flats were a net source of DIC_{min} and DIP to downstream systems during the inundation period. For DIN, inputs and exports (loads at 0 and 409 km, respectively) were roughly balanced in May 2009 and May 2010, although the pronounced mid-reach minima during both campaigns indicate that a large fraction of DIN was replaced over the sampled reach. The export rates from the Kafue Flats during the wet season were ~3 times higher for DIC_{min}, 9-16 times higher for DIN and 3-8 times higher for DIP than during the dry season (Table 1).

Table 1. Inorganic C, N, and P exports, net exports and yields from the Kafue Flats.

	Export from Kafue Flats ^a (t C, N, P d ⁻¹)	Load increase after 250 km ^b (×)	Floodplain contribution to export (%)	Net export ^c (t C, N, P d ⁻¹)	Yields (mg C, N, P m ⁻² d ⁻¹) ^d
May 2010 – flooding season					
DIC _{min}	n.a.	n.a.	n.a.	n.a.	n.a.
DIN	1.57	5.8	85	0.62	0.21
DIP	1.55	11	92	1.22	0.41
May 2009 – flooding season					
DIC _{min}	436	2.1	68	211	130
DIN	0.94	3.6	78	-0.22	-0.07
DIP	0.55	3.8	79	0.24	0.08
October 2008 – dry season					
DIC _{min}	132	n.a.	n.a.	-63.7	n.a.
DIN	0.10	n.a.	n.a.	-0.16	n.a.
DIP	0.19	n.a.	n.a.	0.10	n.a.

^a Calculated as loads (discharge × concentration) at the end of the floodplain (409 km): $Q_{out} \times C_{out}$.

^b Flooding season DIC_{min} and N loads had a minimum at ~250 km, caused by a channel constriction and reduced river discharge. The increase in C, N, and P loads thereafter must originate from the floodplain.

^c Calculated as exports – inputs, that is discharge × concentration after the dam wall: $Q_{out} \times C_{out} - Q_{in} \times C_{in}$

^d Yields were calculated using a maximum flooded area of 3,000 km².

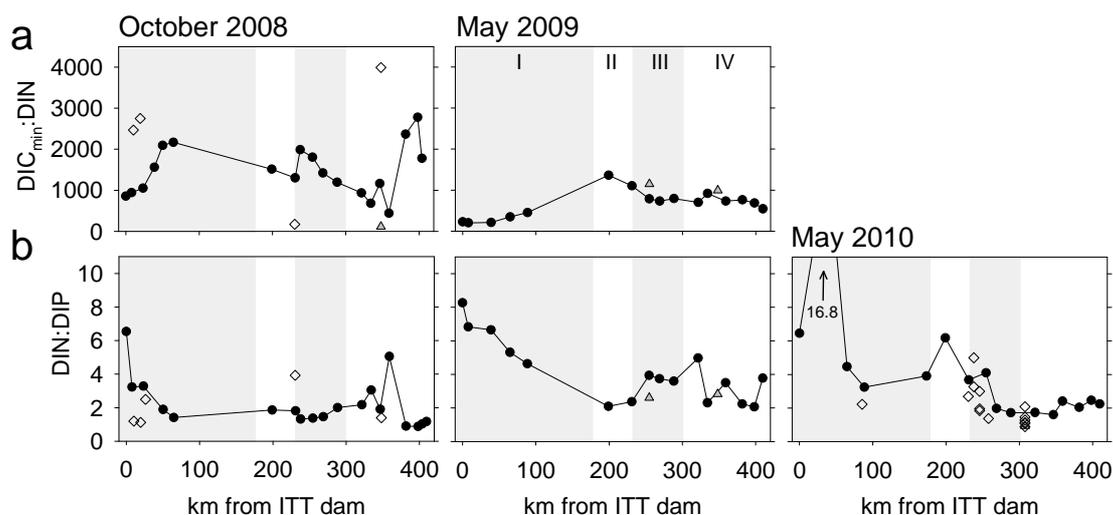


Figure 5. (a) Elemental DIC_{min}:DIN ratio for October 2008 and May 2009. (b) Elemental DIN:DIP ratio for October 2008, May 2009 and May 2010. Symbols and shading as depicted in Figure 3.

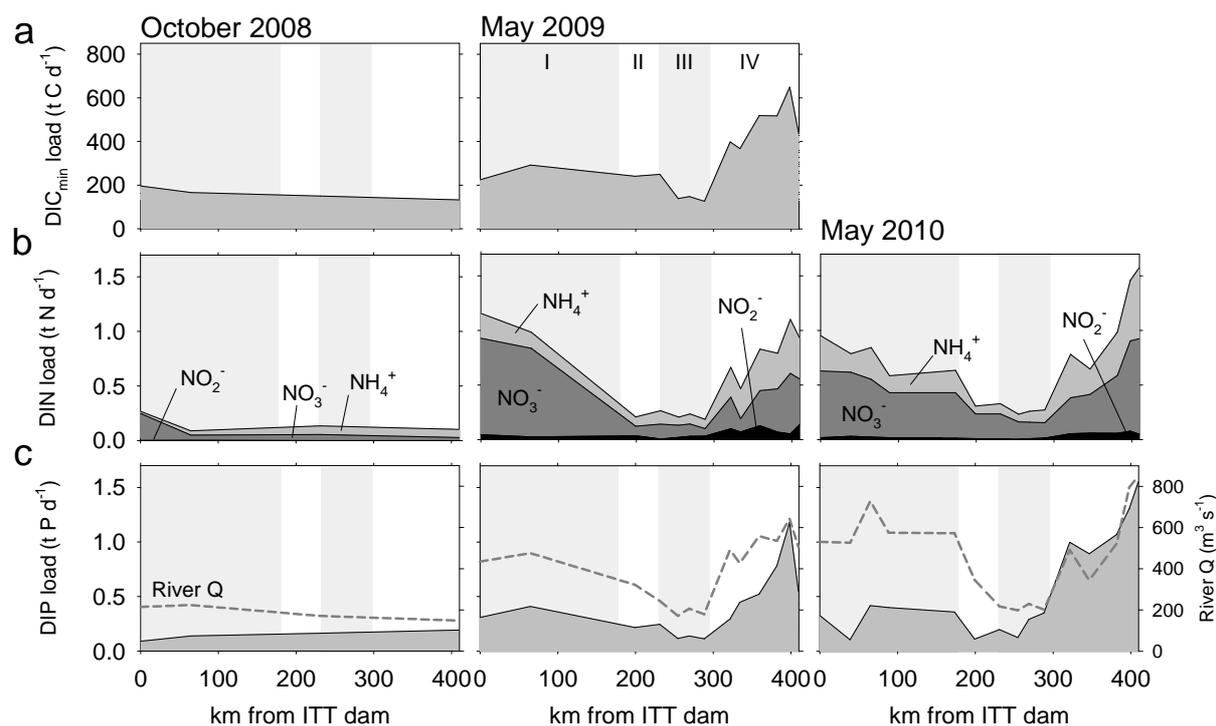


Figure 6. DIC_{min} (a), DIN (b) and DIP (c) loads calculated as concentration \times discharge along the Kafue River in October 2008, May 2009, and May 2010. The dashed gray line in panel (c) shows the river discharge from Zurbrügge et al. (2012b).

Seasonal variability in 2008/09

Over the sampled annual cycle in 2008/09, dissolved oxygen concentrations (Figure 7a) were characterized by the steep concentration drops during flooding period (Figure 2), but also showed persistent low (<100 μM) levels after 250 km. DIC_{min} showed the highest concentrations in August 2008, and elevated levels after 250 km coinciding with the DO minimum (Figure 7b). Similarly, ΔCO_2 concentrations reached the maximum of 162 ± 86 μM at 334 km (supplementary information). Nutrient data (NH_4^+ , NO_3^- and o-PO_4^{3-}) from bimonthly sampling campaign, sampled at 0, 64, 231, 334 and 409 km are discussed in Wamulume et al. (2011) and are provided as supplementary information.

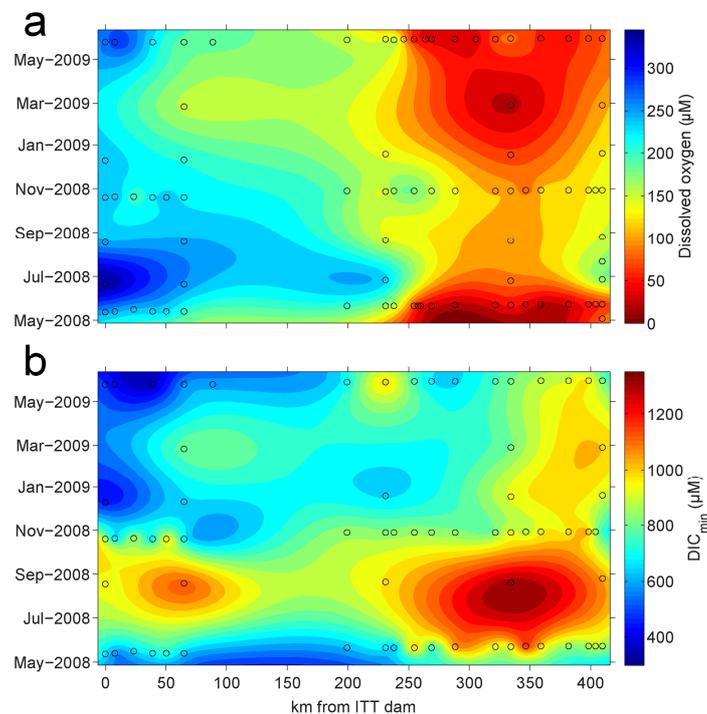


Figure 7. Concentrations of (a) dissolved oxygen, and (b) DIC_{min} along the Kafue River between May 2008 and May 2009. Empty circles represent single measurements.

The annual DIC_{min} , DIN and DIP net exports (= loads at the outflow – loads at outflow; Table 2) were characterized by (1) high exports during the flooding period in May, (2) relatively small positive or negative export fluxes during the falling limb and the dry season (July-December), and (3) high exports of DIN (mainly NH_4^+) during the rainy season in February 2009 (Table 2). The annual net TOC export of $\sim 60,000$ t C yr^{-1} reported during this time period (Wamulume et al. 2011) was approximately twice as large as the net DIC_{min} exports, and the net TN exports of $\sim 1,800$ t Ny^{-1} were approximately 15 times greater than the net DIN exports over the same period.

Discussion

The Kafue Flats are a hydrologically well-defined system, that is, in the absence of significant groundwater inflow and -export incoming water mainly originates from the upstream reservoir, direct precipitation and lateral seasonal tributaries, and leaves the system via the Kafue River or by evapotranspiration (Wamulume et al. 2011). The extensive hypoxia along sections III and IV (Figure 2) of the Kafue River could not be explained by in-stream respiration, but resulted from mineralization in the slowly moving waters of the inundated floodplain and intense river-floodplain exchange (Zurbrügg et al. 2012b). We found that this exchange occurs at two spatial scales: (1) A small-scale lateral exchange with the inundated floodplain was observed at constant discharge along section III and caused a steep decline in DO concentrations. (2) Large-scale exchange was the result of river water being forced into the floodplain along section II and reentering the river along section VI maintaining persistent low riverine DO. As a net result, more than 80% of the water leaving the Kafue Flats during the flooding period had transited the floodplain at a residence time of ~2 months based on its evaporative signal (increase in $\delta^{18}\text{O}\text{-H}_2\text{O}$ and specific conductivity). This leads to two implications: (1) We assumed that this latter, large-scale exchange mechanism also affected nutrient dynamics and the respiration signal in the Kafue River and that the changes of DIC_{min} , DIN and DIP were a result of biogeochemical processes during the floodplain transit. (2) Measuring at bimonthly intervals along the Kafue River's main channel and the outflow (409 km) captured a well-integrated signal of biogeochemical and physical processes occurring in the inundated area and allowed for upscaling of respiration and nutrient release or uptake in the system.

Table 2. Net exports of C, N, and P calculated from the annual sampling campaign.

Campaign	DIC_{min} (t C d ⁻¹)	DIN (t N d ⁻¹)	DIP (t P d ⁻¹)
May 2008	476	0.45	1.54
June 2008	n.a.	n.a.	-0.11
August 2008	107	n.a.	0.17
October 2008	-47	-0.17	0.10
December 2008	139	-0.57	0.05
February 2009	-375	2.47 ^a	-0.02
May 2009	216	-0.13	0.24
Annual net export (t yr ⁻¹)	32,400	129	75.6

^a only NH_4^+ loads.

Quantification of mineralization in the Kafue Flats

We quantified the amount of OC respiration that took place along the flow path of water traveling through the floodplain before re-entering the river and in the river itself for the three spatially intense sampling campaigns (Table 2) and over the annual cycle (Figure 8). The observation of ΔCO_2 close to 0 at the dam wall for October 2008 and May 2009 (Figure 3b) and over an annual cycle (supplementary information) suggests that the reservoir water, after high-turbulence discharge over the dam spillways, was near equilibrium with the atmosphere. The positive ΔCO_2 at the end of the floodplain (409 km) must thus entirely originate from respiration occurring within the river-floodplain system. The respiration of OC was quantified using the production rate of inorganic carbon (“IC production”) and the consumption rate of DO (“DO consumption”).

Quantification of OC respiration by IC production

Organic carbon respiration, calculated as IC production, is the sum of DIC_{min} load increase (Figure 6) along the river and CO_2 outgassing along the river. Outgassing was calculated as the water-air flux of F_{CO_2} :

$$F_{\text{CO}_2} = k \times \Delta\text{CO}_2 \quad (3)$$

The gas transfer velocity k strongly depends on environmental conditions. A recent comparison of gas transfer velocities in the Amazon and the Mekong river basins by Alin et al. (2011) showed that transfer velocities in large rivers ranged from 1.5-7 m d^{-1} (mean $\sim 2.4 \text{ m d}^{-1}$) and largely depend on wind speed rather than other variables. The use of the empirical relationship from Alin et al. (2011) would result in $k = 10 \text{ m d}^{-1}$ for the slowly flowing Kafue River (mean velocity = 0.5 m s^{-1}), which would overestimate gas exchange in this low-turbulence system. For comparison, Richey et al. (2002) derived values of 2.4 m d^{-1} for Amazon tributaries, and 0.65 m d^{-1} for the Amazon floodplains, for which Rudorff et al. (2011) estimated 2.4 m d^{-1} . Bouillon et al. (2007) used a lower estimate of 1.0 m d^{-1} for Tana River estuary (Kenya). We considered a range of $k=2.0\pm 0.8 \text{ m d}^{-1}$ appropriate for the Kafue River.

The total IC production along the main channel in May 2009 was 272-400 t C d^{-1} , whereof approximately half (175 t C d^{-1}) left the system in dissolved form and the remainder (97-225 t C d^{-1}) via CO_2 outgassing. During the dry season, IC production was four times smaller ($\sim 80 \text{ t C d}^{-1}$) and outgassing contributed $\sim 60\%$ (Table 3). Over the annual cycle, we estimate that IC production was 58,000-97,000 t C , based on the increase in DIC_{min} load (29,000 t C) in the water leaving the Kafue Flats and CO_2 outgassing. The largest IC production occurred during peak flooding in May, and the lowest rates were found in August 2008 at the beginning of the dry season.

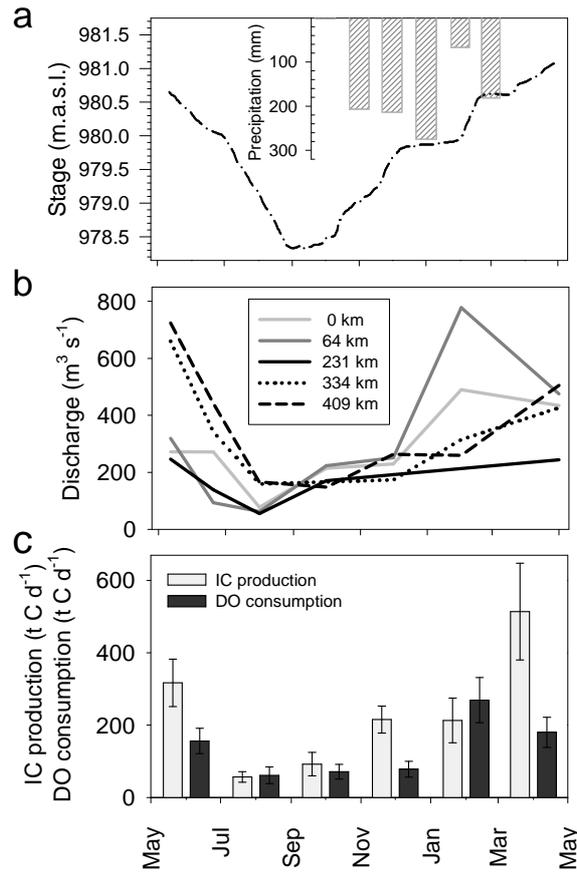


Figure 8. (a) Stage at 230 km (line) and monthly precipitation (bars) in the Kafue Flats between May 2008 and May 2009. (b) Bimonthly discharge measurements at 0, 64, 231, 334 and 409 km from Wamulume et al. (2011). (c) IC production and DO consumption in the Kafue Flats over an annual cycle. Error bars represent the range of applied gas transfer velocities.

Quantification of OC respiration by DO consumption

The second approach to quantify respiration is based on DO levels and a simple box-model at the scale of the river sampling resolution. We calculated the net oxygen consumption rate, R_{O_2} , as the difference in DO concentration at the inflow and outflow of a model box (DO_{in} , DO_{out}) plus the amount of reaeration occurring in the box:

$$R_{O_2} = Q_{avg} \times \left(DO_{out} - DO_{in} + \frac{k_{reaer}}{h} \times AOU \right) \quad (4)$$

whereby k_{reaer} is the oxygen gas transfer velocity of $1.8 \pm 0.7 \text{ m d}^{-1}$, which corresponds to the range of k for CO_2 outgassing, corrected by the diffusivities of O_2 and CO_2 , h is the mean depth and Q_{avg} is the mean flow in the box. The apparent oxygen utilization AOU was defined as the difference between DO saturation (DO_{sat}) and in-situ DO concentration

$$AOU = DO_{sat} - DO \quad (5)$$

The box-model approach for the three spatially intense campaigns provides DO consumption estimates that translate into mineralization rates of the same magnitude as those estimated through IC production (Table 3). Over an annual cycle, the estimated DO consumption corresponded to the respiration of 35,000-58,000 t C which is equal to ~60% the IC production. IC production and DO consumption generally followed the floodplain water level (Figure 8a), with maxima in May and minima during receding floods in August. Overall low IC production during flood recession was also observed in the Amazon floodplains where CO₂ outgassing was reduced 8-fold compared to the dry season, rising and high water (Rudorff et al. 2011), whereby the differences resulted from changes in flooded area, while the gas transfer velocities were very similar for all seasons.

Table 3. Mineralization in the Kafue Flats based on IC production and DO consumption. The range in parentheses results from different gas transfer velocities.

Campaign	IC production			DO consumption
	DIC _{min} increase (t C d ⁻¹)	CO ₂ outgassing (t C d ⁻¹)	Total IC production (t C d ⁻¹)	Net oxygen consumption rate (t C d ⁻¹)
May 2010	n.a.	n.a.	n.a.	206 (161-251)
May 2009	175	161 (97-225)	336 (272-400)	149 (113-185)
October 2008	34	46 (28-65)	80 (62-99)	80 (56-104)

Flooded areas and areal respiration rates

Both IC production and DO consumption calculations considered respiration and gas exchange along the flow path of the water through the Kafue Flats. Because of the intense river-floodplain exchange the river water integrates the respiration signal from the hydrologically-connected floodplain areas. However, given that ~40% of water entering the Kafue Flats annually exits via evapotranspiration (Zurbrügg et al. 2012b), these respiration rates are likely substantial underestimates. The maximum flooded area for the flooding season in 2010 was ~3,000 km² and the minimum inundation of 250 km² was measured in October 2009 based on the inundation model of Meier et al. (2010) (F. Köck, personal communication). To derive areal respiration rates, we used the maximum flooded area for the highest water levels in May 2010. The areal respiration rate in the flooding season calculated from this area was 2.2-3.7 mg C m⁻² h⁻¹ based on IC production, and 1.3-2.2 mg C m⁻² h⁻¹ for DO consumption measurements, respectively. For comparison, estimates of CO₂ outgassing measured by floating chambers from Amazon floodplain range 22-186 mg C m⁻² h⁻¹ over an annual cycle (Rudorff et al. 2011) and 4-325 mg C m⁻² h⁻¹, (mean 91 mg C m⁻² h⁻¹) (Belger et al. 2011). Across the entire Amazon river and wetland system, the mean CO₂ flux derived from floating chambers was 14±3 mg C m⁻² h⁻¹ (Richey et al. 2002), and the total OC respiration was estimated at ~180 mg C m⁻² h⁻¹ (Richey et al. 1988). The mineralization rate estimates of 1-4 C m⁻² h⁻¹ for the

Kafue Flats likely underestimate floodplain CO₂ evasion. An estimate of the areal CO₂ evasion in the Kafue Flats using typical gas transfer velocities of 0.4-0.6 m d⁻¹ for floodplains (Richey et al. 2002; Variano et al. 2009) and an assumed floodplain ΔCO₂ of 120-300 μM, (Figure S3, supplementary information), would be in the range of the literature values (40-130 mg C m⁻² h⁻¹). Scaled to a flooded area of 3,000 km² and over the estimated residence time of floodplain water (~2 months, based on δ¹⁸O-H₂O) (Zurbrügg et al. 2012b), CO₂ evasion from the inundated floodplain would amount to 97,000-360,000 t C yr⁻¹. From this we conclude that measurements in the draining river give appropriate estimates of the increase in DIC_{min}, but capture only a relatively small fraction of the CO₂ outgassing from respiration in the floodplain.

Sources of riverine dissolved inorganic carbon

The apparent deviations between IC production and DO consumption in Fig. 8c require some explanation. The largest differences occurred during peak flooding in May and at the onset of the rainy season in December. The smallest differences were observed during receding flood conditions in August (Figure 8a-b), when mineralization was lowest.

In principle, IC production and thus DIC_{min} can originate from aerobic or different pathways of anaerobic carbon respiration, while DO can also be consumed by chemotrophic oxidation of reduced species (NH₄⁺, Mn, Fe, HS⁻, CH₄). Over a complete flooding/drying cycle, reduced species produced through anaerobic processes during inundation might be re-oxidized by dissolved oxygen when oxic conditions dominate. This would result in a 1:1 stoichiometry for IC production and DO consumption, regardless of the initial electron acceptor. However, at any time point during flooding cycle, this stoichiometry contains information about the redox conditions and respiration processes at the sampling time. If only aerobic respiration prevailed, DO consumption expressed as AOU, and ΔCO₂ should follow the molar 1:1 stoichiometry, corrected by diffusivities of CO₂ and O₂ in water (Figure 9). For low AOU and ΔCO₂, that is high DO concentrations along the first 200 km after Itzhi-Tezhi dam and, samples of all three spatially intense campaigns follow aerobic respiration (Figure 9). For AOU ≤ 150 μM, respiration is aerobic, for stations with higher AOU rather follow the anaerobic line. The oxidation of CH₄ may also contribute to IC production as indicated by the measurements below the 1:1 line (Figure 9).

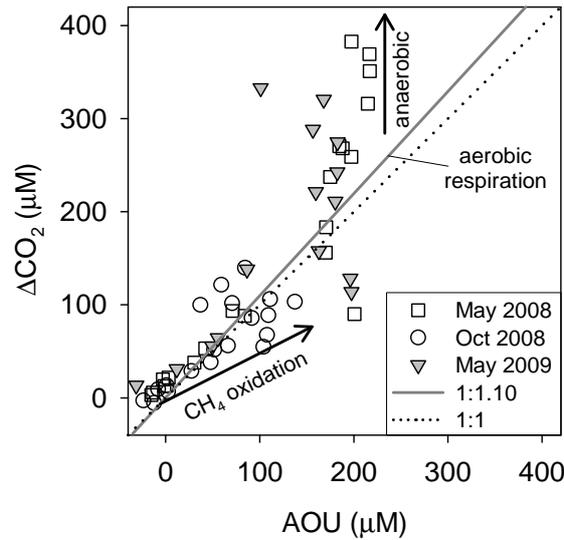


Figure 9. ΔCO_2 vs. AOU for October 2008, May 2009 and the pilot campaign in May 2008. The gray line is the theoretical stoichiometry of aerobic respiration (Devol et al. 1995). The slope of 1.10 results from the correction by the square root of the diffusion coefficients of $2.30 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for CO_2 (Jähne et al. 1987), and $1.91 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ for O_2 (Wise & Houghton 1966), respectively. Waters with a signal of photosynthesis by phytoplankton or macrophytes should follow the same line. Methane oxidation would show a 1:2 stoichiometry and anaerobic OC respiration would show as vertical lines at high AOU. The oxidation of reduced inorganic species would appear as horizontal lines (not shown).

Because of the strongly negative $\delta^{13}\text{C}$ of biogenic methane (-46 to -57‰ in the Kafue Flats, R. Zurbrügg, unpublished data), methane oxidation would leave a distinct negative signal in $\delta^{13}\text{C}_{\text{DIC}}$, which was not observed during the May campaigns. Therefore we conclude that DIC_{min} from methane oxidation cannot be excluded but its contribution might be small. The reduction of SO_4^{2-} could similarly offset the $\text{AOU}/\Delta\text{CO}_2$ ratio. All flooding campaigns showed a net decrease in SO_4^{2-} along the main channel (supplementary information), which suggests high rates of SO_4^{2-} reduction in the floodplain. Based on mass load calculations, SO_4^{2-} -reduction could be equivalent to $\sim 20,000 \text{ t C yr}^{-1}$ and explain 21-34% of the IC production. SO_4^{2-} -reduction can thus explain the stoichiometric deviation between ΔCO_2 and AOU (Figure 9) of 7-15 stations.

The changes in $\delta^{13}\text{C}_{\text{DIC}}$ allow constraining the $\delta^{13}\text{C}$ of the respired OC ($\delta^{13}\text{C}_{\text{OC}}$) by an isotope mixing model, if the amount of DIC from carbonate dissolution ($\text{DIC}-\text{DIC}_{\text{min}}$) and its stable isotopic signature are known.

$$\delta^{13}\text{C}_{\text{OC}} = \frac{\text{DIC} \times (\delta^{13}\text{C}_{\text{DIC}} - \delta^{13}\text{C}_{\text{CO}_3})}{\text{DIC}_{\text{min}}} - \delta^{13}\text{C}_{\text{CO}_3} \quad (6)$$

Because of the carbonate-rich geology in the catchment, $\delta^{13}\text{C}_{\text{DIC}}$ is affected by dissolved carbonates, accounting for $\sim 50\%$ of DIC based in Ca^{2+} and Mg^{2+} concentrations. We used a $\delta^{13}\text{C}$ for carbonates ($\delta^{13}\text{C}_{\text{CO}_3}$) of +3‰, which was measured in dolomite in the Kafue headwaters (Kamona & Friedrich 2007). The mixing model shows, that the additional DIC_{min} produced in the Kafue Flats originated from OC with a $\delta^{13}\text{C}$ of $-14.5 \pm 1.5\%$ for October 2008 and $-16.2 \pm 2.6\%$ for May 2009 (not

considering fractionation during respiration and outgassing). This range is intermediate between measured $\delta^{13}\text{C}$ of soil and sediment OC (-20.0‰) and C_4 -plants (-13.3‰) in the Kafue Flats (Zurbrügg et al. 2012a). C_4 -plants are the dominant vegetation in the areas close to the main channel and C_4 -derived OC could contribute as much as 60-80% to respiration based on the $\delta^{13}\text{C}$ mixing model. This suggests that bioavailable fractions of plant material are mineralized in the floodplain to a high extent.

Release and fate of DIN and DIP

During OM mineralization and an IC production of $\sim 78,000 \pm 19,000 \text{ t C yr}^{-1}$, proportional amounts of DIN and DIP are also liberated. Assuming a constant elemental ratio of the substrate (C:N:P = 180:12:1; W. Blaser, personal communication), 4,500-7,500 t N yr^{-1} and 840-1,400 t P yr^{-1} should have been released during OM mineralization. Compared to actual estimates of DIN and DIP export, only 2-3% of DIN and 5-9% of DIP that originate from mineralization were exported via the Kafue River. The largest fraction of DIN and DIP was retained or lost within the system. Variations in $\text{DIC}_{\text{min}}:\text{DIN}$ and $\text{DIN}:\text{DIP}$ along the river give additional insights into the fate of DIN and DIP. The decrease in NO_3^- after the dam and along section I could be attributed to losses through denitrification in the riverbed and the adjacent floodplain (Figure 4b). Along sections III and IV, increases in NH_4^+ and DIP coincided with the enhanced respiration signal (ΔCO_2 increase) from the floodplain during the May campaigns and suggest that the additional NH_4^+ and DIP was from OM mineralization. Although increases in both DIN and DIP were observed, $\text{DIN}:\text{DIP}$ started decreasing along sections II and III, and reached the lowest values of 1-2 in section IV (Figure 5b). This could be due to preferential losses of N relative to P by plant uptake or denitrification. Such low N:P values indicate strong N depletion in waters exiting the floodplain. Similar low values have been observed in the Orinoco river basin ($\text{DIN}:\text{DIP}=3-8$) (Cotner et al. 2006) and in African river systems ($\text{DIN}:\text{DIP}=1-13$) but reported values for the Amazon were much higher ($\text{DIN}:\text{DIP}=10-100$) (Downing et al. 1999). Similarly, $\text{DIC}_{\text{min}}:\text{DIN}$ was substantially elevated after 200 km during flooding (>700 for May 2009; >1000 for May 2008, supplementary information). For comparison, C:N ratios for particulate OM (POM) were ~ 9 , and for DOM were ~ 22 (Zurbrügg et al. 2012a). The N and P stoichiometries suggest that DIN is taken up more efficiently than P, and N may be the limiting nutrient for large areas in the Kafue Flats.

Despite the efficient retention in the floodplain and apparent N-limitation, the annual DIN yields (export/area) from the Kafue Flats are 13-25 times higher than estimated for the entire Kafue River basin, but comparable to model predictions for the Zambezi River basin and other tropical river basins (Table 4). The yields for the Kafue River Basin were determined by dividing the DIN and DIP export at 409 km by the total area of the basin ($154,000 \text{ km}^2$). For DIP, the Kafue and Zambezi River basin have comparable yields but the contribution of the Kafue Flats to the overall DIP export is 30-170

times higher than for the Kafue River subcatchment. Nutrient yields suggest that the Kafue Flats are a hotspot of nutrient turnover in the Zambezi River basin that has to potential of offset basin-wide nutrient loads, despite contribution of <0.5% of the total area.

Table 4. Modeled DIN and DIP yields in large river basins and measured yields for the Kafue River basin and the Kafue Flats.

River system	Area ($\times 10^3$ km ²)	DIN yield (kg N km ⁻² yr ⁻¹)	DIP yield (kg P km ⁻² yr ⁻¹)
Amazon	5,847	173 ^a	21.6 ^a , 17.3 ^b
Congo	3,694	31.5 ^a , 60-100 ^c	7.8 ^a , 4.4 ^b
Orinoco	1,038	119 ^a	10.3 ^a , 4.1 ^b
Paraná	2,661	43.9 ^a	9.2 ^a , 1.6 ^b
Zambezi	1,362	110-190 ^a , 100-300 ^c	2-5 ^a , 0.37 ^{b,d}
Kafue River basin	154	3.2 ^e	0.9 ^e
Kafue Flats	6.5	43 ^f , 76 ^g	25 ^f , 29-149 ^g

^a Mayorga et al. (2010)

^b Harrison et al. (2005b)

^c Yasin et al. (2010)

^d Harrison et al. (2010) estimated a DIP yield of 1-5 kg P km⁻² yr⁻¹ and a DIP retention of 0.1-5 kg P km⁻² yr⁻¹ for Central Zambia

^e Calculated from annual loads at the outflow of the Kafue Flats which is ~95 km from the outflow of the river basin.

^f Calculated from net exports over an annual cycle, scaled by the maximum flooded area of 3,000 km².

^g During high flows.

Comparison of C, N and P export with primary production

Fate of N: removal and export

The annual net exports of 129 t DIN yr⁻¹ are small compared to the estimated average 6,000 t DIN yr⁻¹ that is released from OM mineralization (based on its C:N ratio) and accounted for ~7% of the total N exports of 1,800 t N yr⁻¹ (Wamulume et al. 2011). This implies that most of the exported N is in organic form. Indeed, the Kafue River waters mobilize large amounts of ON during the floodplain transit, which causes a net export of 6-9 t ON d⁻¹ or 2-4 kg ON km⁻² d⁻¹ (Zurbrügg et al. 2012a). A comparison of the amount of OC and ON that is mineralized in the floodplain with the corresponding amounts that are exported shows that mineralization and export rates are of similar the same magnitude.

$$\frac{\text{OC mineralization (t C d}^{-1}\text{)}}{\text{OC export (t C d}^{-1}\text{)}} = 1.4 \quad \text{and} \quad \frac{\text{ON mineralization (t N d}^{-1}\text{)}}{\text{ON export (t N d}^{-1}\text{)}} = 2.4$$

Apparently, the N-rich fraction in the OM is preferentially mineralized, which is plausible, given the low DIN availability in the system. The ratio of DON to DIN decreased by 70% along the river (data not shown) which suggests that the DIN losses were much higher than any DIN release from

mineralization. Over the maximum flooded area, the mean N removal rate was $\sim 30 \mu\text{mol N m}^{-2} \text{ h}^{-1}$. Field incubation experiments in the floodplains of the Paraná River (Uruguay/Argentina) quantified N-losses by denitrification as $150\text{-}250 \mu\text{mol N m}^{-2} \text{ h}^{-1}$ (Villar et al. 1998). Denitrification in exposed Amazonian floodplain lake sediments were substantially lower, at in-situ rates of $12\text{-}17 \mu\text{mol N m}^{-2} \text{ h}^{-1}$, and potential rates of $>600 \mu\text{mol N m}^{-2} \text{ h}^{-1}$ (Kern et al. 1996). The DIN losses in the Kafue Flats, are in the range of typical denitrification rates for tropical floodplains but there may also be indiscernible sinks for DIN such as storage of N in perennial plant parts (Aerts 1996) and rapid reuptake by the remaining vegetation (Rejmankova 2005). A system scale N budget of the Kafue Flats using N stable isotope and fluxes showed that the annual N deficit of $\sim 21,000 \text{ t N}$ must largely be balanced by N-fixation at rates of $>50 \mu\text{mol m}^{-2} \text{ h}^{-1}$ (Zurbrügg et al. 2012a).

Mineralization relative to net primary production

The aboveground net primary production (NPP) of the Kafue Flats can be approximated by plant biomass derived from Ellenbroek (1987), who measured $1,400\text{-}4,300 \text{ g dry wt m}^{-2} \text{ yr}^{-1}$ for the flooded grass zone adjacent to the main channel. This is substantially higher than for other, more distant vegetation zones, like meadows ($400\text{-}1,000 \text{ g dry wt m}^{-2} \text{ yr}^{-1}$). We approximated the NPP of the flooded area with the values of the productive grassland fringing the Kafue River. Based on C content $40\text{-}47\%$ of tropical macrophytes (Boar 2006; Jones & Muthuri 1997) this corresponds to $800\text{-}2,000 \text{ g C m}^{-2} \text{ yr}^{-1}$. Using a conservative estimate of $800 \text{ g C m}^{-2} \text{ yr}^{-1}$ would imply a NPP of $2.4 \times 10^6 \text{ t C yr}^{-1}$ for the $3,000 \text{ km}^2$ flooded area. A comparison with system-scale respiration estimates shows that $2.4\text{-}4.0\%$ of the NPP was respired in the Kafue Flats and $\sim 2.5\%$ of the NPP was exported as OC (Wamulume et al. 2011). This suggests that $>90\%$ of the NPP in the Kafue Flats is accumulating as plant biomass, buried in soils, burned, or grazed by cattle or wildlife. Typical burial rates in tropical wetlands are $160\text{-}480 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Mitsch et al. 2010) which would be equivalent to $10\text{-}40\%$ of the Kafue Flats' NPP. Besides burial, grazing might be particularly important in this system. The Kafue Flats has a high density of herbivores like the endemic Kafue Lechwe (Rees 1978b). Lechwes can graze vegetation in up to 50 cm water depth (Ellenbroek 1987) and their population in the Kafue Flats was estimated at $\sim 38,000$ over an area of $\sim 6,000 \text{ km}^2$ (Chansa & Kampamba 2010). In addition, cattle from the local population were estimated at $16,000$ which would be equivalent to $55,000$ lechwe (Chansa & Kampamba 2010). Grazing would release N and P from the standing biomass without direct DO consumption and IC production. A detailed analysis on grazing and burial rates and fire will be needed to constrain the fraction of the NPP that remains for microbial degradation.

Dam impacts on mineralization and nutrient loads

Dam operation can affect floodplain nutrient and carbon cycles directly by changing riverine C, N and P loads (Friedl & Wüest 2002) or indirectly by changing the extent and duration of flooding

(Gergel et al. 2005). The construction of the upstream dam substantially reduced N (-50%) and P (-60%) loads to the floodplain (Kunz et al. 2011b). The DIN and DIP loads that are currently discharged from the dam are $210 \pm 110 \text{ t N yr}^{-1}$ and $99 \pm 32 \text{ t P yr}^{-1}$, respectively, which is in the same range as the net exports from the floodplain. The reservoir removes up to $2,400 \text{ t DIN yr}^{-1}$ by denitrification, which suggests that natural DIN inflows to the Kafue Flats may have been substantially higher before dam construction in 1978. Assuming that ~50% of the N lost through denitrification was from allochthonous sources, and thus adding $1,200 \text{ t DIN yr}^{-1}$ to the N export by the Kafue River, would result in an increase in the DIN yields in the Kafue River Basin by a factor of 3.4. An analogous calculation for DIP, assuming 100% allochthonous P, increased the DIP yields by a factor of 2.5. These compensated DIN and DIP yields are still substantially lower than for other tropical catchments (Table 4) which suggests that the KRB is a naturally nutrient-poor catchment. However, the dams have a high potential to modify nutrient loads in this system.

The flow regulation at the upstream Itezhi-Tezhi dam has reduced river-floodplain exchange in the Kafue Flats (Zurbrügg et al. 2012b) and the total flooded area (Mumba & Thompson 2005). The reduction in flooded area may have restricted the highly productive floodplain grass vegetation zones (Ellenbroek 1987). In conjunction with the lower nutrient availability, reduced river-floodplain exchange and thus less mobilization of OM, the overall NPP of the Kafue Flats may have been substantially diminished.

In order to optimize power production, dam operators intend to install turbine facilities at Itezhi-Tezhi dam, which was used as storage reservoir hitherto. Kunz et al. (2011b) calculated that the Kafue Flats could experience a 2-fold increase in DIN, and a 4-fold increase DIP loads accompanied by a more leveled hydrograph from the turbine outlets. The effects of these changes and possible mitigation measures will need a more detailed hydrological and ecological assessment.

Conclusions

In this study we quantified respiration on the scale of the flooded area of a tropical floodplain system. The well-defined hydrology and the intense hydrological river-floodplain exchange allowed constraining floodplain processes from changes in DO, DIC_{min} and nutrient concentrations in the draining river. Based on measurements in the Kafue River at different temporal and spatial scales we calculated that 58,000-97,000 t C yr⁻¹ were respired in the system. The reduction of SO_4^{2-} could explain ~20,000 t C yr⁻¹ of the anaerobic respiration, while we did not observe a distinct signal from CH_4 oxidation. The overall respiration was highest during the flood peak in May and lowest during receding floods in August. Floodplain C₄-grasses could make up >60% of the respired OM.

Over the course of a year, the Kafue Flats were a net source of DIN and DIP, exporting 129 t DIN and 76 t DIP to downstream systems. This corresponds to 43 kg DIN km² yr⁻¹ and 25 kg DIP km² yr⁻¹ which is equivalent to ~2% of the DIN and ~7% of DIP that was released during mineralization in the floodplain. Low DIN concentrations in the system (<2 μM), high $\text{DIC}_{\text{min}}:\text{DIN}$ of >700 and low $\text{DIN}:\text{DIP}$ of <4 along the river suggest efficient N retention in the floodplain probably due to high denitrification and plant uptake rates. Compared to the entire Kafue River basin, the Kafue Flats are an important source of DIN and a hotspot for DIP release in the Zambezi River basin.

The Kafue Flats are a highly productive floodplain but <4% of the net primary production is microbially respired in the system. Small OM exports of <3 % of the NPP suggest that burial in floodplain soils and grazing are more important fates of the biomass. However, the contribution of these processes and the exact flooded areas in the Kafue River require further examination.

Acknowledgements

We thank Jason Wamulume, Griffin Shanungu, Wilma Blaser and the ZAWA wildlife officers at Lochinvar and Blue Lagoon NP for help during field work. Laboratory analyses were supported by Stephan Suter, Kate Ashe, Chantal Freymond, Ruth Stierli and Gijs Nobbe (Eawag), and Moritz Lehmann and Mark Rollog (University of Basel). Institutional support was provided by Imasiku Nyambe (University of Zambia) the Zambia Wildlife Authority, the Zambezi River Authority, Zambia Electricity Supply Corporation (ZESCO). Funding for this study came from the Competence Center for Environment and Sustainability (CCES) of the ETH domain, the Swiss National Science Foundation (Grant No. 128707) and Eawag.

Supplementary information

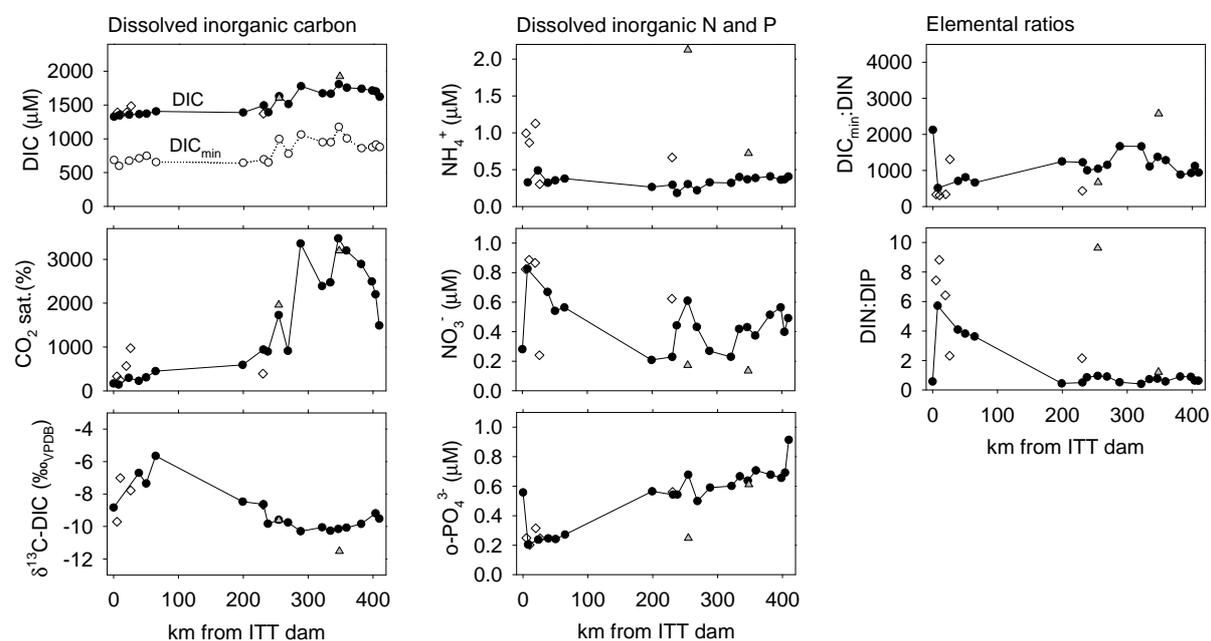


Figure S1. Dissolved inorganic carbon, dissolved inorganic N and P and elemental ratios from the pilot campaign in May 2008. Black circles and lines are stations along the Kafue River, empty circles are floodplain stations and gray triangles mark tributaries.

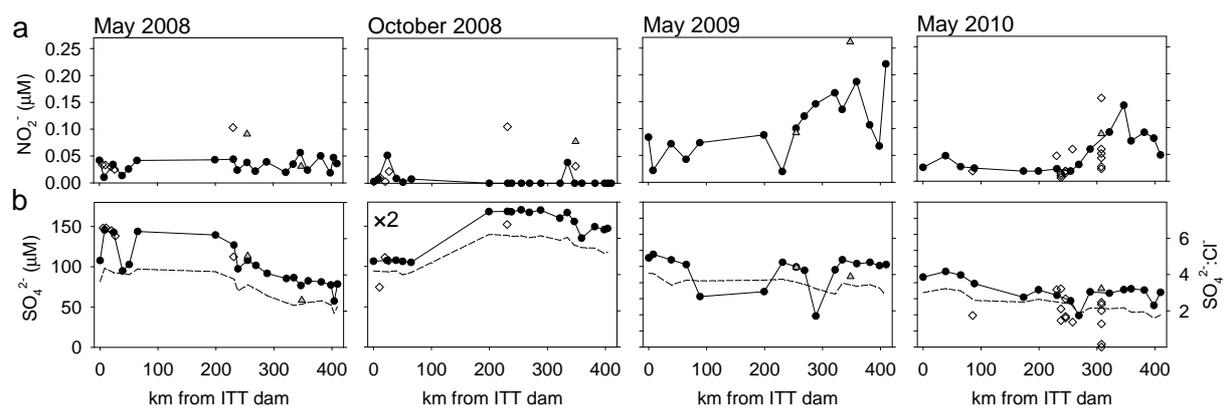


Figure S2. Concentrations of (a) NO_2^- and (b) SO_4^{2-} and molar $\text{SO}_4^{2-}:\text{Cl}^-$ ratio (dashed line) from 2008-2010. The SO_4^{2-} concentration axis in October 2008 is expanded by a factor of 2. Symbols as indicated in Figure S1.

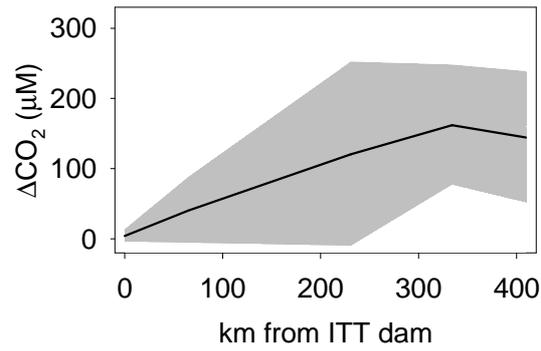


Figure S3. Excess CO_2 (ΔCO_2) along the Kafue River. The black line is the mean the six sampling campaigns between May 2008 and May 2009, the gray shading represents $\pm\text{SD}$.

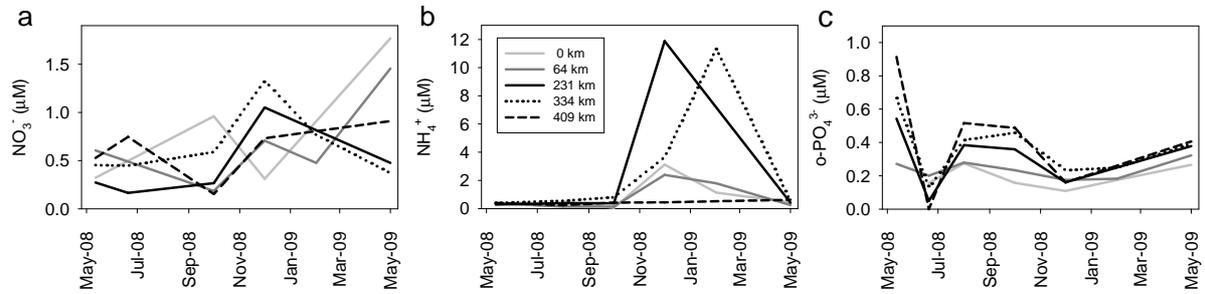


Figure S4. (a) NO_3^- , (b) NH_4^+ , and (c) o-PO_4^{3-} concentrations along the Kafue River over the annual sampling campaign from May 2008 to May 2009. Reprinted from Wamulume et al. (2011).

Conclusions and outlook

Conclusions and outlook

Role of the Kafue Flats for the Kafue River biogeochemistry

The primary goal of this work was to study biogeochemical processes in a dam-impacted tropical floodplain. The Kafue Flats represent a near-ideal study system because of its well-defined hydrology, natural morphology, and low population pressure. In addition, it allowed examining the effects of dam operation in a tropical system, which has rarely been studied.

Organic matter and nutrient fluxes

The detailed surveys during the flooding period showed that the floodplain was a source of OM and nutrients to the river, and caused considerable net exports from the system. Based on flux calculations, the Kafue Flats were a net source of DOM and acted as source or sink of POM, depending on the hydrological conditions of a particular year. The DOM flux entering the river from the floodplain consisted of degraded terrestrial OM but lacked typical plant characteristics. This suggests that plant biomass was largely reworked, buried, burned or grazed on the floodplain and only a small fraction entered the river. The effect of OM mineralization in the floodplain was evident as a decline in DO and a concurrent increase in ΔCO_2 along reaches with high inputs of floodplain water (Chapter 4), which is consistent with the low DO concentrations found in the floodplain. To confine a total C budget of the Kafue Flats a detailed analysis of CO_2 and CH_4 emissions would be required. The analysis of the aquatic fluxes suggest that a relatively small percentage of primary production was respired in the system; thus together with the potentially high burial rates in such systems (Mitsch & Gosselink 2007), the Kafue Flats may be a net sink of CO_2 .

The analysis of the nutrient fluxes indicated that the Kafue Flats were a net source of DIN and DIP. However, only small fractions of DIN and DIP that had been released during OM respiration were exported, while the larger fraction experienced a different fate. The shift in DIN:DIP ratios along floodplain-dominated reaches of the Kafue River showed that DIN experienced stronger retention in the floodplain than DIP. This may be due to two main factors: (1) the Kafue Flats is an N limited system, thus any bioavailable may have been recycled in the floodplain, and (2) the high temperatures, high abundance of OM and DO depletion are favorable conditions for denitrification.

The general paradigm of floodplains as reactors along large rivers also holds for the Kafue Flats. The floodplain system is a biogeochemical hotspot that substantially influences river water quality of the Kafue River and causes C, N and P exports to downstream systems. This influence is strongly linked to the high degree of river-floodplain exchange.

River-floodplain exchange – towards a more comprehensive understanding of floodplain hydrology

River-floodplain exchange is a dominant feature for the biogeochemistry of this system. Studies in South American floodplains have indicated that river-floodplain exchange may affect river chemistry to some degree (Hamilton et al. 1997; Villar et al. 1998), but the extent of river-floodplain exchange has not been quantified. The Kafue Flats are a tropical floodplain system that experiences one flood pulse per year (Chapter 1). The highest water levels were observed after the rainy season, that is, between March and May, which is consistent with the annual flooding and draining of floodplains is described by the “flood pulse concept” (Bayley 1995; Junk et al. 1989). Flooding in temperate lowland or alpine floodplains may be somewhat different than in tropical systems which exhibit a uniform flood pulse (Junk 1999). Tockner et al. (2000) presented a new extended understanding of the flood pulse concept emphasizing the importance of floodplain expansion-contraction below full bank flow (“flow pulses”). Our observations, however, document intense river-floodplain exchange at, or shortly after maximum water levels, which are not addressed by the existing concepts. This exchange happens at two scales (Chapters 2 and 3): water losses and gains over ~200 km as a result of abrupt changes in channel morphology (depicted as section II and IV) and intense exchange at constant flow over ~30 km, promoted by a strongly meandering river channel through a reducing floodplain wetland (section III). Because of its overall importance we propose that river-floodplain studies should be accompanied by a detailed survey of the discharge and channel morphology. River-floodplain exchange should also be quantified by monitoring longitudinal changes in discharge together with hydrological (specific conductivity, $\delta^{18}\text{O-H}_2\text{O}$) or biogeochemical (DO, labile DOC) tracers that help distinguish the river- and floodplain end members (Chapter 2).

Impact of dams on the Kafue Flats

Without doubt, the dams at Itezhi-Tezhi (ITT) and Kafue Gorge have affected the Kafue Flats as an ecosystem. The ecological impacts of the dams along the Kafue River have been widely discussed (Smardon 2009 and references therein), but hydrological alterations have only been analyzed qualitatively hitherto (Mumba & Thompson 2005; Rees 1978a). A spatially explicit model that quantifies the dam-induced changes in flooded areas is in progress (Meier et al. in preparation; Meier et al. 2010).

Hydrology: flooded areas and river-floodplain exchange

Long-term discharge records at several stations in the lower Kafue River basin have demonstrated that dam operation at ITT has increased base flows during the dry season and reduced peak flows (Wamulume et al. 2011). This has increased the permanently flooded area, while the average flooded area was reduced. We found that dam operation at ITT has also substantially reduced the extent of

exchange between the river and the floodplain during the flooding period (Chapter 2). Lateral water flows from the river to the floodplain relative to the river discharge have been reduced by 50% upstream of river-km 230. A similar reduction was observed for water inflows in the floodplain-dominated reach downstream of 230 km.

Biogeochemistry

Compared to the hydrological impacts, dam-induced changes in river and floodplain biogeochemistry are more difficult to elicit, and have not been studied in detail in this system because of the lack of pre-dam data. In general, the dam can affect the floodplain ecosystem via direct changes in water chemistry (DO, nutrients) or indirectly by changing the downstream flooding regime (e.g. Gergel et al. 2005).

a) Direct effects: changes in water chemistry

The direct effects are largely a result of reservoir processes and include an overall reduction in particle loads and DIN and DIP inputs (Kunz et al. 2011b). Because of the efficient trapping of allochthonous POM in the reservoir, and concurrent algal growth, the POM discharged to the Kafue Flats is mainly composed of phytoplankton from the epilimnion of ITT reservoir (Chapter 3). The terrestrial DOM from the upstream catchment passes the reservoir without major changes, implying slow reactivity, while the DOM produced in the reservoir may be rapidly degraded.

Under the current operation rules, water is only released over the spillways. We found that this water was well-oxygenated and relatively nutrient-poor year-round. The low DO concentrations observed along the Kafue River can thus not be a direct effect of upstream dam operation. The overall reduction in nutrient loads might occur during the onset of the rainy season when NH_4^+ concentrations upstream of ITT reservoir were elevated by a factor of 10 relative to the dam outflow (Wamulume et al. 2011) due to a first flush of dry riparian areas. During pre-dam times, these DIN loads would have reached the Kafue Flats. In summary, the direct impact of ITT dam on the water quality is confined to lower nutrient loads and changes in POM quality.

The installation of turbine facilities at ITT dam could substantially alter water chemistry of the dam discharge in the near future (Kunz et al. in preparation). Kunz et al. (2011b) predicted that as much as 60% of the overall dam release could be diverted through the turbine outlet at a capacity of $\sim 300 \text{ m}^3 \text{ s}^{-1}$. Because of the hypolimnetic anoxia ($< 1 \text{ mg L}^{-1}$ DO) that persists for several weeks before oxic water would be released over the spillways, chances are high that DO-free, reducing waters could enter the Kafue Flats. This is in strong contrast to actual conditions where the Kafue River receives DO-saturated water (Chapter 2). Because of the accumulation of NH_4^+ and DIP in the hypolimnion during the reservoir's stratification, low DO-waters could be accompanied by a substantial increase in nutrient loads. Over an annual cycle, DIN loads could increase from 210 to 710 t yr^{-1} , and DIP from 73 to 160 t yr^{-1} (Kunz et al. 2011b). The most critical downstream effect may, however, be related to

the low oxygen levels rather than to higher nutrient loads. Because of slow reaeration and intense river-floodplain exchange, the inflowing low-DO water may affect the DO regime along the entire Kafue River, leading to more pronounced hypoxia. Enhanced DIN and DIP loads may, in turn, enhance in-stream production along the upper parts of the Kafue River, and – as water is diverted to the floodplain – will enhance nutrient availability and productivity in the floodplain.

b) Indirect effects: changes in floodplain hydrology

The indirect dam impacts originate mainly from smaller flooded areas and less river-floodplain exchange. Generally speaking, processes occurring in water-logged soils and standing waters became less dominant relative to in-stream processes. The reduction in river-floodplain exchange may have mitigated the hypoxia in the Kafue River, under the assumption that DO consumption in the flooded area has been similar under pre-dam conditions (Dudley & Scully 1980). In Chapter 2 and 4 we showed that mineralization in the floodplain was more important than in the river based on a mass balance (i.e., the amount of OC respired per time). A decrease in flooded area may thus have resulted in an overall decrease in mineralization. This would imply higher OC burial rates, smaller CO₂ emissions and reduced nutrients loads to downstream systems. The amount of anaerobic respiration would be disproportionally reduced, that is, lower rates of denitrification and methanogenesis on the scale of the entire floodplain system.

The construction of Kafue Gorge dam has affected the hydrology and biogeochemistry of the lower Kafue Flats. An area of 800-1,200 km² (12-18% of the total floodplain area) has been permanently inundated (Obrdlik et al. 1989). This lagoon-like area drains 4-times more slowly than under pre-dam conditions (Chapter 2), and could promote the permanent hypoxia around 300 km (Chapter 4).

Management optimizations and environmental flows

Floodplain ecosystems crucially depend on periodic flooding and the hydrological connection between river and floodplain. Our studies showed that the extent of river-floodplain exchange was nearly at pre-dam levels during wet years, e.g. from 2005-2010 (Chapter 2), but was reduced by up to a factor of four in dry years (2001-2005) compared to the five subsequent years. The flow regime that was established after dam construction included minimum releases of 300 m³ s⁻¹ for four weeks in March (Acreman 1996) and a minimum flow of 40 m³ s⁻¹ throughout the year (Schelle & Pittock 2005). However, the peak discharge at the inflow to ITT reservoir has only been <500 m³ s⁻¹ for three seasons since 1973 (ZESCO, unpublished data) and the minimum discharge was frequently below 20 m³ s⁻¹. In addition, the channel constriction at 230 km causes flooding when the river discharge exceeds 170 m³ s⁻¹ based on previous estimates (Ellenbroek 1987), but measurements indicate that flooding may occur at a discharge of <100 m³ s⁻¹ (Chapter 2). Dam releases at ITT exceeded this discharge in 91% of the days since 1978 (ZESCO, unpublished data), which reveals two major

problems: (1) The current management scheme allows flooding after 230 km even during the dry season, and (2) the minimal flows of $300 \text{ m}^3 \text{ s}^{-1}$ may not cause sufficient flooding to secure ecosystem functioning at more distant floodplain areas. Improving the situation might require (1) to increase minimum flows at ITT, and (2) to establish a maximum flow rate during the dry season to promote drainage of permanently flooded areas along the Kafue River. Environmental flows from ITT dam and other restoration measures in this system need to consider channel morphology in order to predict flooding and lateral exchange between river and floodplain. Any changes in the flooding regime in the permanently flooded areas of the lower Kafue Flats would require changes in dam management at Kafue Gorge dam.

Turbine and spillway operation

Under the current dam operation rules, dam outflows are saturated with respect to DO. At the dam inflow, DO levels were at >80% saturation year-round (Chapter 4). In order to ensure river water quality and ecosystem health, at least 80% DO saturation should be maintained at the dam outflow. This could be achieved by artificial aeration of turbinated low-DO water or by diverting epilimnetic waters or a mix of hypolimnetic/epilimnetic waters to the turbines (Kunz et al. in preparation). A combination of spillway and turbine releases would introduce waters enriched in DIN and DIP, which would mimic natural nutrient loads, e.g., as a “first flush” pulse of nutrients at the beginning of the rainy season. These recommendations need to be completed by results from ecological studies.

Outlook: Further research directions

Tropical floodplains remain poorly studied system relative to the spatial extension. Further research should improve the understanding of the C and N cycles on a system scale.

Sampling strategies

Despite the size of tropical floodplain system, we showed that important processes can occur on small spatial scales and in short time periods. In the Kafue Flats, measurements of physical and chemical parameters at higher temporal resolution but at fewer stations would be beneficial. This could be achieved using automated sampling or measurement systems. The onset of the flood, which was not sampled at high resolution in our studies, has been found to be a “hot moment” for floodplain biogeochemistry (e.g. Mladenov et al. 2005). This period of the hydrological cycle (along with the flooding period) should be a particular focus of studies in this or in other floodplain systems. The detailed survey of discharge and channel morphology with an acoustic Doppler current profiler revealed important information on the hydrology of the system and the driving forces of biogeochemical processes. Finally, remote sensing techniques offer a unique opportunity to cover spatial changes in flooded area and vegetation zones (Arieira et al. 2011; Hess et al. 2003; Munyati

2000). A more comprehensive understanding of the system would benefit from combination of more local process studies (incubations, flux measurements) with spatially distributed data.

Carbon and nitrogen budgets

Tropical wetlands are the largest source of atmospheric CH₄, but studies on CH₄ emissions from tropical floodplains are scarce (Bastviken et al. 2010). A comprehensive C budget of the Kafue Flats (including burial, grazing and burning) would contribute to the growing data base on C cycling in floodplains in general. The combined dam/floodplain system of the Kafue Flats would be an ideal model system for comparative studies on large floodplain systems in South America or Asia. A particularly interesting hypothesis in this context would be: “Dam operation reduces CH₄ emissions of downstream floodplains because of the smaller flooded area and shorter inundation period and thereby overcompensates CH₄ emissions from the reservoir”.

Even more than C budgets, N budgets in tropical floodplains are poorly constrained. Many systems are N limited (Downing et al. 1999) and the source, availability and fate of N are of particular interest. To address this task, denitrification, plant uptake and N-fixation should be quantified using flux and rate measurement techniques, and covering the main vegetation zones and time periods. Besides asymbiotic N-fixation in soils and from free-floating organisms, symbiotic N-fixation should be quantified. This would create a link between plant ecological studies and river-floodplain biogeochemistry.

Integrated modeling

The indirect effects of dam operation on the biogeochemistry are strongly linked to the changes in the flooding patterns. The mineralization of organic matter via aerobic and anaerobic pathways and greenhouse gas emissions depend on the extent and duration of inundation (Rudorff et al. 2011). A state-of-the-art hydrological model to quantify the changes in flooded area, flooding duration and water flows in the floodplain is currently in development (Meier et al. in preparation). The changes in nutrient and organic matter inputs to the Kafue Flats (Kunz et al. 2011b), river floodplain exchange along the river and floodplain mineralization should all be incorporated by a combination of inundation and biogeochemical modeling (e.g. Basu et al. 2011; Tritthart et al. 2011).

In most tropical floodplain studies, hydrological modeling and floodplain biogeochemistry have not been combined. For example in the Okavango delta where different research groups were doing hydrological modeling (Bauer et al. 2006; Milzow et al. 2009) and biogeochemical field studies (Mladenov et al. 2007a; Mladenov et al. 2005) during the same period, but without measurable collaborative outcome. In the Kafue Flats, we provide background data on nutrient and OM concentrations as well as other field measurements which would allow for a meaningful model calibration. A combined hydrological-biogeochemical floodplain model would significantly improve understanding of tropical floodplain biogeochemistry.

Annex

Annex

Water chemistry survey in the Barotse Floodplains: Flood recession and dry season

In order to compare the dam-impacted Kafue Flats to a natural system, we initiated two field campaigns in October 2008 (dry season) and May 2009 (flood recession) to the Barotse Floodplains. The Barotse Plains are a relatively pristine floodplain (~9,000 km²) along the upper Zambezi River in Western Zambia (Figure A1a). We sampled along a 120 km river transect, from South of Mongu to Senanga (Figure A2b). The first sampling station (0 km) is a tributary entering the Zambezi, the following eight stations are along the main stem of the river. Sampling procedures and analyses are described in chapters 2, 3 and 4. The results of the sampling are presented in Figure A2.

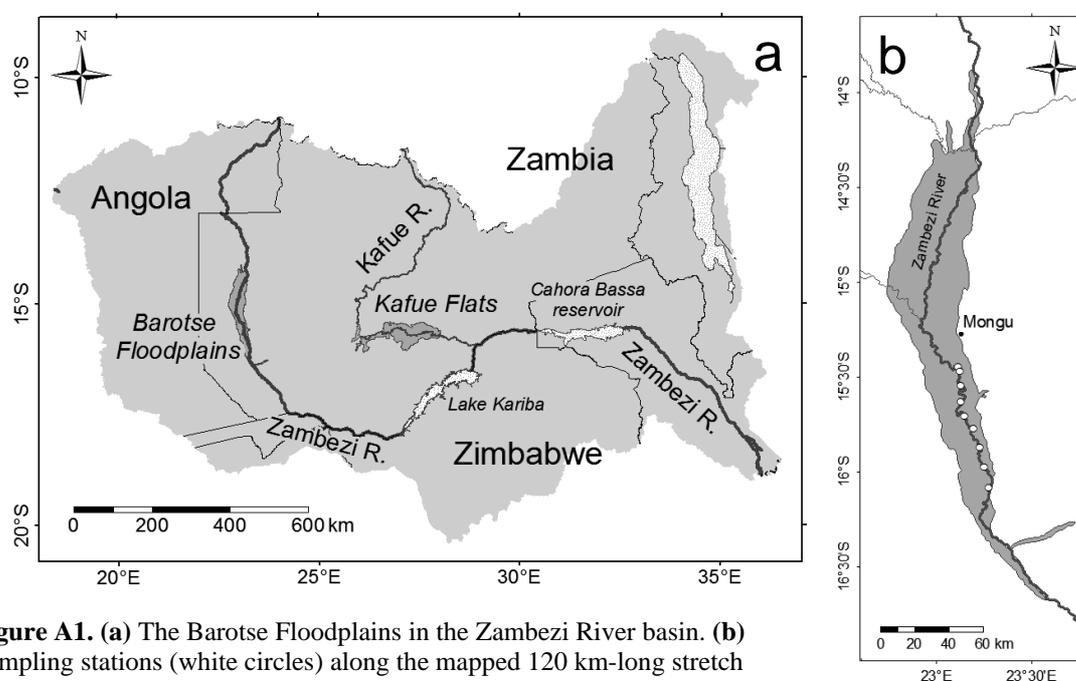


Figure A1. (a) The Barotse Floodplains in the Zambezi River basin. (b) Sampling stations (white circles) along the mapped 120 km-long stretch of the Zambezi River.

In general, only small changes in water chemistry were evident along the sampled reach. Specific conductivity and $\delta^{18}\text{O-H}_2\text{O}$ did not suggest strong floodplain interaction, while dissolved oxygen and pH were suppressed during flood recession, similar to the Kafue Flats. Nutrient, ion, total P and suspended solids concentrations and were overall lower during receding floods, when higher flows diluted the solute concentrations. Total N, total OC and DOC were higher during flood recession, probably as a result of leaching DOM from soils or floodplain vegetation.

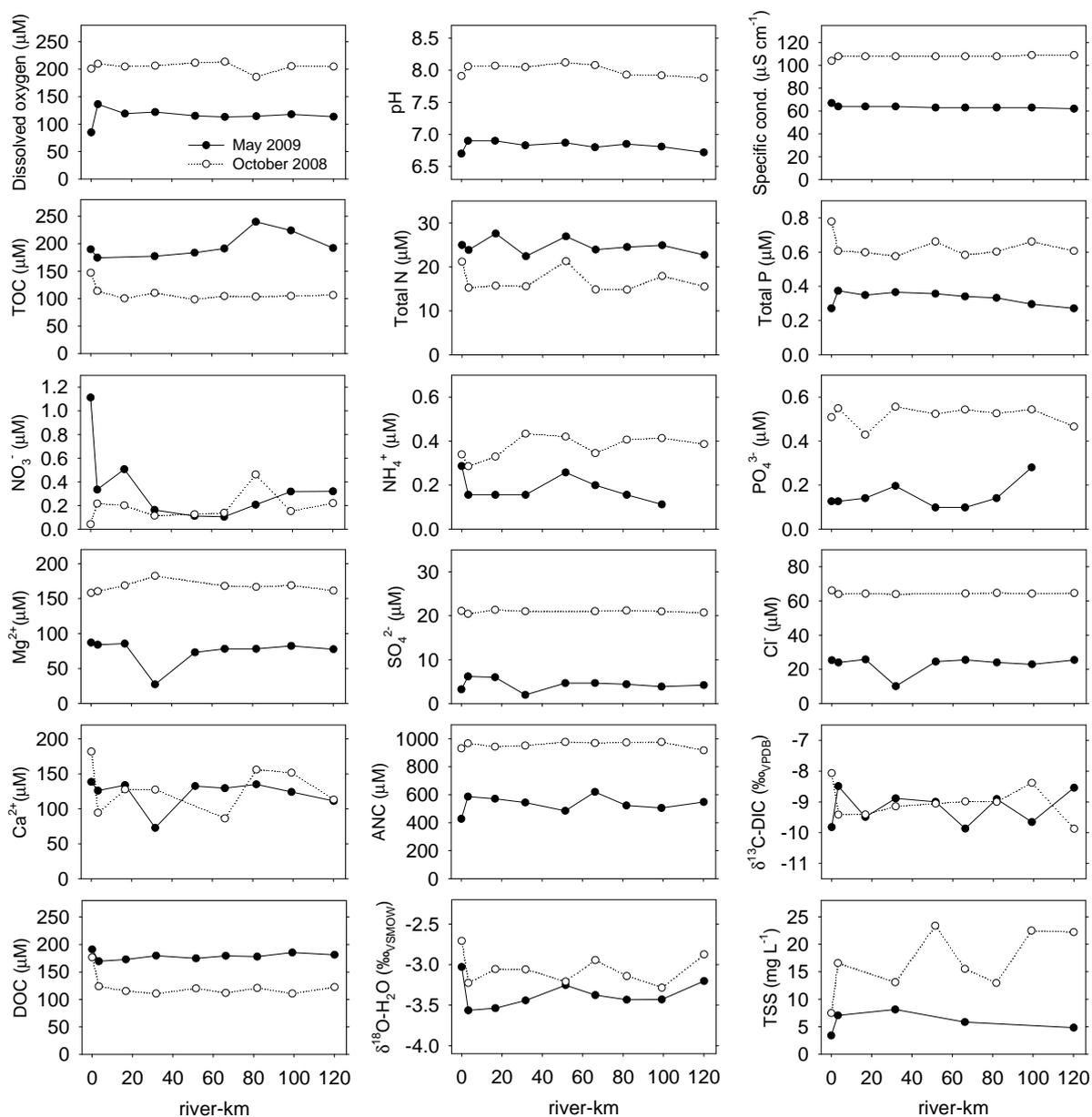


Figure A2. Chemical and physical parameters measured along the Zambezi River flowing through the Barotse Floodplain. Empty circles represent parameters measured during the dry season in October 2008, filled circles measurements during flood recession in May 2009. TOC = total organic carbon, ANC = acid neutralizing capacity, TSS = total suspended solids.

Acknowledgements

Four years of PhD are a long time, long enough to meet many great people in Switzerland and abroad. I would like to thank all of those who supported my research:

- Dave Senn was a really great supervisor! He always supported me, during field campaigns, lab work, paper writing and, most importantly, through the difficult periods of my PhD. I appreciate all of the inspiring discussions and his positive view which always motivated me to take the next steps. His scientific guidance was of great importance for the outcome of this PhD.
- Bernhard Wehrli supported me doing this PhD at ETH and Eawag. He created an atmosphere with a lot of freedom which made work in his group very enjoyable. His experience and scientific input was of great value particularly during the last months of my PhD.
- The field work was the best time of my PhD. I was privileged to have support from fantastic people during my four field campaigns: my two Zambian friends and MSc students Jason Wamulume and Griffin Shanungu, Wilma Blaser, the ZAWA Wildlife Officers at Lochinvar and Blue Lagoon National Park, our boat driver Event Ngandu in particular, and Samuel Mwale from the ZRA who performed ADCP measurements.
- A special thank goes to Nanina Blank and Manuel Kunz. Nanina was MSc student, field assistant, and lab researcher during the period of my PhD; without her help in the field and in the lab, life would have been so much harder. My PhD benefited greatly from Manu's work. Thanks for introducing me to field work in Zambia and sharing your experiences.
- A big thank you to my "office ladies" Simone Peter, Jasmin Mertens, Nuttakan Wongfun, Tonya DelSontro and Lee Bryant for a great time during the last years! And to Sebastian Sobek, my diploma thesis supervisor who introduced me to the world of science.
- A lot of data for this thesis came from the work of MSc and BSc students and interns who helped with lab analysis and modeling: Stephan Suter, Chantal Freymond, Kate Ashe, Stefan Bucher and Jan Landert.
- Thanks to all my ADAPT colleagues for the fruitful collaboration over the last four years, particularly to Philipp Meier and Florian Köck for answering countless emails about data requests and to Harry Olde Venterink for ecological advice.
- The field campaigns were supported by many Zambian Partners: Professor Imasiku Nyambe, Ingrid Muganya, Carol Mweemba (University of Zambia), Chuma Simukonda, Wilbroad Chansa and Francis Samalumo (Zambia Wildlife Authority), Romas Kamanga, Elenestina Mwelwa, Moses Mbuta and Willy Sakala (ZESCO), Evis Siamakocha (Zambezi River Authority), Adam Hussien and Peter Chola (Department of Water Affairs).

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- I would also like to thank my co-examiner Moritz Lehmann whose isotope lab at University of Basel was always open for me. I really appreciated his input on my research, in regard to both daily lab work and also on my OC/ON paper. Thanks to Mark Rollog for his expertise and support during my lab campaigns in Basel.
 - Many people at ETH Zürich and Eawag supported my laboratory work here in Switzerland: Ruth Stierli, Oliver Scheidegger, Gijs Nobbe, Dörte Carstens, Chregu Dinkel and Carsten Schubert (who provided unlimited access to the isotope lab) at Eawag Kastanienbaum, and Britt Peterson, Kurt Barmettler and Soil Chemistry and Environmental Chemistry groups at ETH Zürich.
 - Thanks to my Indian friends Bhaskaran Munaswamy and Kishor Senapati for all the encouragement!
 - Last but not least - möchte ich meiner Familie in Interlaken und meinen Freunden hier in Zürich ganz herzlich danken! Ihr habt mich während der ganzen Zeit unterstützt und seid immer für mich da gewesen.
 - This PhD project was funded by the Competence Center for Environment and Sustainability (CCES) of the ETH domain, the Swiss National Science Foundation (Grant No. 128707) and Eawag.

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Education

03/2008 – 04/2012	Doctoral candidate at ETH Zürich, Institute of Biogeochemistry and Pollutant Dynamics, and Eawag. Advisor: Prof. Bernhard Wehrli. Topic: <i>Biogeochemistry of a large tropical floodplain system (Kafue Flats, Zambia): River-floodplain exchange and dam impacts</i>
11/2007	Diploma in Environmental Sciences (MSc ETH), ETH Zürich, Switzerland.
01/2005 – 06/2005	ERASMUS exchange semester at Lund University, Sweden.
10/2002 – 10/2007	Environmental Science study, ETH Zürich, Switzerland. Major in Chemistry and Microbiology of Aquatic Systems.
1998 – 2002	High school in Interlaken BE, Switzerland. Main subject: Economics and Law.

Work experience

2009 – 2011	Teaching assistant Chemistry lab training, Department of Environmental Sciences, ETH Zürich.
11/2007-02/2008	Associate researcher, Aquatic Chemistry group, Prof. B. Wehrli, ETH Zürich. Project: <i>Role of lake sediments in the global carbon cycle – organic carbon burial and greenhouse gas emissions.</i>
07/2006 – 10/2006	Development cooperation internship in Jharkhand State, India and Allahabad Agricultural Institute: Topic: <i>Drinking water related issues in rural areas in India.</i>
11/2005 – 02/2006	Internship at Givaudan Switzerland Ltd. Dübendorf, Switzerland. Department of Environment, Health and Safety. Project: <i>Establishing a waste water model for the production plants of Givaudan Ltd.</i>
04/2004 – 10/2004	Research assistant (part-time) at the group of Prof. M. Carollo, Institute for Astronomy, Department of Physics, ETH Zürich, Switzerland.

Other training and experience

2008 – 2011	Supervised several MSc and BSc students (ETH Zürich and University of Zambia).
04/2010	Summer School in Quantitative Microbial Risk Assessment, TU Delft, NL.
02/2009 – 06/2009	GIS/Geoinformatics course, Institute of Geodesy and Photogr., ETH Zürich.
since 2009	Assistant teacher at the Swiss Army Environmental Protection Education Center, Spiez, Switzerland.

Publications

- Zurbrügg, R., J. Wamulume, R. Kamanga, B. Wehrli, and D. B. Senn. *River-floodplain exchange and its effects on the fluvial oxygen 1 regime in a large tropical river system (Kafue Flats, Zambia)*. Journal of Geophysical Research – Biogeosciences, 117, 1-12, G03008.
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Selected presentations and posters

- Zurbrügg, R., S. Suter, M. F. Lehmann, B. Wehrli, and D. B. Senn. *Hydrological drivers of organic matter quality, mineralization, and export in a tropical dam-impacted floodplain system*. 9th INTECOL International Wetlands Conference, 3-8 June 2012, Orlando, FL, USA - Presentation
- Zurbrügg, R., S. Suter, M. F. Lehmann, B. Wehrli, and D. B. Senn. *Effect of river-floodplain exchange on OC and ON biogeochemistry in a tropical floodplain system (Kafue Flats, Zambia)*. AGU Fall Meeting 5-9 December 2011, San Francisco, CA, USA - Poster
- Zurbrügg R., J. Wamulume, M. F. Lehmann, I. Nyambe. B. Wehrli, D. B. Senn: *Effects of hydrological river-floodplain exchange on C and N biogeochemistry in the dam-impacted Kafue Flats (Zambia)*. ASLO Aquatic Sciences Meeting, 13-18 February 2011, San Juan, Puerto Rico. - Presentation
- Zurbrügg R., J. Wamulume, B. Wehrli, I. Nyambe, D. B. Senn: *Impact of river-floodplain exchange on river biogeochemistry in the Kafue Flats*. ADAPT Stakeholder Meeting 22 January 2011, Lusaka Zambia - Presentation
- Zurbrügg R., J. Wamulume, D. B. Senn: *Influence of hydrological river-floodplain exchange on the biogeochemistry of the dam-impacted Kafue River, Zambia*. Integrated Water Resources Management Seminar, University of Zambia, School of Mines, Lusaka Zambia, 11 June 2010 - Presentation