Biogeochemical dynamics of a tropical river-floodplain system

A thesis submitted to attain the degree of
DOCTOR OF SCIENCES of ETH ZURICH

(Dr. sc. ETH Zurich)

presented by
ALISSA LUcretia ZUIJDEEst
MSc, Universiteit Utrecht

Born on 28.06.1989
citizen of the Netherlands

Accepted on the recommendation of
Prof. Dr. Bernhard Wehrli
Prof. Dr. Timothy I. Eglinton
Prof. Dr. Nathalie Dubois
Prof. Dr. Steven Bouillion

2017
Summary

Inland waters are increasingly recognized for their potential to alter the fluxes of organic carbon from terrestrial ecosystems to the oceans. Rivers are considered net heterotrophic systems, with large quantities of carbon dioxide emitted to the atmosphere. In the global budgets, tropical rivers are of interest because of the large quantities of terrestrial organic matter they transport and the amounts of greenhouse gases that are being emitted to the atmosphere. Riverine biogeochemistry, especially in tropical rivers with seasonal rainfall patterns, is strongly impacted by interactions of the river with its floodplains. Once a flood pulse spills onto low-lying riparian areas, the flooded floodplain develops distinctly ecological functions that are distinctly different from the bordering river and the terrestrial ecosystems.

In this thesis the biogeochemical functioning of tropical river-floodplain systems was examined, with the largely pristine Barotse Plains along the Zambezi River as the main case study. The research focused on understanding the seasonal patterns of organic matter cycling, linking hydrology and biogeochemical processes, and tracing the origin of riverine organic matter. Considering the increasing anthropogenic pressure on inland waters, it is imperative to understand the impact of dam construction on tropical fluvial biogeochemistry, as dam construction is expected to boom in Africa, South America and Asia. To this end, the biogeochemistry of the Barotse Plains was compared with that of the dam-impacted Kafue Flats. To capture the dynamics of the system, large scale field campaigns were complemented with long-term sensor deployment. Riverine organic matter composition was characterized with regard to carbon and nitrogen content, isotopic compositions, radiocarbon content, and biomarkers.

Particulate and dissolved organic matter in the Barotse Plains exhibited different seasonal trends: maximum loads of particulate organic matter occurred during the initial phases of flooding, while dissolved organic matter loads peaked at the same time as peak flow. During an annual cycle, particles and associated phosphorus were eroded from the floodplain, while organic matter was retained, with varying dynamics between seasons. The seasonal trends are strongly linked
to the balance of primary production and degradation on the floodplain and in
the river, with degradation dominating during initial flooding, primary production
dominating during continued and maximum flooding, and more degradation
during receding water levels.

The interaction between the river and the floodplain is a driving force for
riverine biogeochemistry. A mass balance approach showed that during peak
flow, roughly half of the downstream discharge had spent time on the floodplain.
Furthermore, distinct hysteresis patterns were observed between biogeochemical
parameters and both discharge and travel time of the flood pulse over the
floodplain. At longer travel times, more degradation of organic matter occurred
on the floodplain, making the floodplain a stronger hotspot for greenhouse gas
emissions.

Particulate organic matter in the river carried a distinct soil-derived signature
year-round, but the input from vegetation showed distinct seasonal variations,
as shown using a variety of isotopic and biomarker analyses. During low-water
conditions, organic matter was mostly derived from terrestrial vegetation and
mineral soils. In contrast, when the floodplain was inundated the riverine organic
matter showed large contributions from topsoil and floodplain vegetation.

The dams in the Zambezi catchment trap particles and organic matter and
release easily degradable aquatic biomass, changing the quantity and signature of the
downstream organic matter. Nutrients are retained in the reservoir, and the timing
of and ratio in which nitrogen and phosphorus become available to downstream
ecosystems change. The altered hydrograph also changes flooding dynamics of
downstream ecosystems, which can lead to encroachment of woody plants onto
the floodplain and altered biogeochemical functioning of the floodplain.

The results in this thesis highlight the strong seasonal dynamics of tropical river-
floodplain systems, and how the biogeochemistry is heavily linked to the hydrology
of the system. Understanding these interactions between river, floodplain, and
vegetation is crucial in light of changing climate and altered water balances.
Kurzzusammenfassung


Die Ergebnisse dieser Doktorarbeit verdeutlichen, dass tropische Fluss-
Samenvatting

In de mondiale koolstofkringloop werden rivieren lange tijd beschouwd als simpele transportsystemen, die organisch materiaal van het land naar de oceanen transporteerden. Onderzoek in de laatste decennia heeft echter uitgewezen dat de hoeveelheid en samenstelling van het organisch materiaal in de rivier veranderen tijdens transport van land naar zee. Afbraak van organisch materiaal in de binnenwateren (rivieren, kreken, meren, etc.) leidt tot uitstoot van koolstofdioxide naar de atmosfeer. In tropische rivieren komt het grootste deel van het organisch materiaal van natuurlijke vegetatie en niet van land- en akkerbouw. Afbraak van dit organisch materiaal, in combinatie met relatief langzame algengroei in rivieren, leidt tot een grote potentie voor de uitstoot van broeikasgassen. Deze twee factoren maken tropische rivieren interessant om te bestuderen.

De biogeochemie van rivieren is sterk gekoppeld aan de interactie tussen de rivier en het omliggende land, in het bijzonder overstromingsvlaktes. In tropische regio’s is meestal sprake van seizoensgebonden regen, met een nat en een droog seizoen, waardoor grote overstromingsgebieden ieder jaar onder water komen te staan. Deze seizoensgebonden overstroming leidt tot bijzondere condities op de overstromingsvlaktes, waardoor zich daar nadrukkelijk andere ecosystems vormen dan in de rivier, of op het omliggende land.

In dit proefschrift is de biogeochemie van een tropisch overstromingsgebied onderzocht. Mijn onderzoeksgebied was de Barotse Plains, een groot overstromingsgebied van de Zambezi, dat nauwelijks door menselijk handelen is aangetast. Het onderzoek heeft zich gericht op het begrijpen van de seizoensgebonden biogeochemische variatie in het gebied, het koppelen van de biogeochemie met de hydrologie van de rivier, en het achterhalen van de oorsprong van het organisch materiaal in de rivier.

Het indammen van een rivier heeft nadrukkelijke gevolgen voor de biogeochemie, en in de komende decennia zal het aantal dammen in Afrika sterk toenemen. Het is daarom belangrijk om te de invloed van een dam op de biogeochemie van overstromingsvlaktes te bestuderen. In het stroomgebied van de Zambezi is nog een overstromingsvlakte van vergelijkbare grootte te vinden,
namelijk de Kafue Flats. In tegenstelling tot de Barotse Plains, wordt de Kafue Flats nadrukkelijk beïnvloed door de aanwezigheid van dammen stroomopwaarts en –afwaarts van het gebied.

Om de seizoensgebonden dynamiek van het systeem goed te kunnen meten, zijn veldonderzoeken aangevuld met automatische meetsystemen. De veldonderzoeken vonden plaats op verschillende momenten gedurende het jaar, en richtten zich op de biogeochemie van de rivier op verschillende locaties. De automatische meetsystemen bleven voor ongeveer een jaar op dezelfde plek, en bepaalden meerdere malen per dag een aantal biogeochemische parameters. In het laboratorium werd de samenstelling van het organisch materiaal bepaald door het meten van de koolstof- en stikstofgehaltes, de isotopenverhouding van het koolstof, de ouderdom van het monster, en de biomarkers. Biomarkers kunnen worden beschouwd als moleculaire fossielen, die gebruikt kunnen worden om de oorsprong van het organisch materiaal te achterhalen.

In de rivier kan organisch materiaal gevonden worden in opgeloste vorm, of als deeltjes. Deze twee verschillende vormen van organisch materiaal gedroegen zich niet op dezelfde manier. De grootste hoeveelheid deeltjes werd gemeten gedurende de eerste fase van de jaarlijkse overstroming, terwijl de opgeloste vorm het meest aanwezig was tijdens de maximale afvoer ongeveer twee maanden later. Gedurende een complete overstromingscyclus wordt organisch materiaal achtergelaten op de overstromingsvlakte. Echter, er zijn sterke seizoensgebonden verschillen, en deze zijn gekoppeld aan processen op de overstromingsvlakte. Gedurende de eerste fase van de overstroming worden bodemdeeltjes van de overstromingsvlakte weeggespoeld. Aan deze bodemdeeltjes kleeft ook organisch materiaal, en dat wordt op dit moment afgebroken. In de tweede fase van de overstroming begint er weer vegetatie te groeien op de overstromingsvlakte, waardoor de bodemdeeltjes beter worden vastgehouden. Na het regenseizoen zakt het waterniveau weer, en de planten op de overstromingsvlakte verwelken en worden afgebroken.

Deze interactie tussen het rivierwater en de overstromingsvlakte is zeer belangrijk voor de biogeochemie van de rivier. Tijdens de maximale waterafvoer had ongeveer de helft van het rivierwater tijd doorgebracht op de overstromingsvlakte. De tijd die het water nodig heeft om de overstromingsvlakte te passeren is
variabel gedurende het jaar. De biogeochemie in de rivier is sterk gekoppeld aan deze reistijd, met verschillende patronen tijdens toenemende en afnemende waterniveaus. Hoe meer tijd het water doorbrengt op de overstromingsvlakte, hoe meer afbraak plaatsvindt op de overstromingsvlakte. Als gevolg daarvan neemt de uitstoot van broeikasgassen toe bij een langere verblijftijd van het water op de overstromingsvlakte.

Het organisch materiaal, dat als deeltjes door de rivier wordt getransporteerd, is grotendeels afkomstig van bodems en vegetatie. De bijdrages van bodems en verschillende types vegetatie zijn variabel gedurende het jaar. Tijdens het droge seizoen, met lage waterniveaus, was organisch materiaal in de rivier afkomstig van diepere bodemlagen en van de vegetatie van het omliggende land. Gedurende de overstroming kwam het organisch materiaal in de rivier vooral van de bovenste laag van de bodems en de specifieke vegetatie van de overstromingsvlakte.

In de reservoirs van de verschillende dammen in de Zambezi rivier wordt een groot deel van de rivierdeeltjes opgeslagen op de bodem van het reservoir. De hoeveelheid organisch materiaal dat beschikbaar is voor de ecosystemen stroomafwaarts neemt daardoor af. Daarnaast verandert de samenstelling van het organisch materiaal in het reservoir: het organisch materiaal dat wordt opgevangen wordt vervangen door materiaal afkomstig van algengroei in het reservoir. Behalve organisch materiaal worden ook nutriënten opgeslagen in het reservoir, maar in verschillende hoeveelheden, waardoor de beschikbaarheid stroomafwaarts verandert. Naast deze veranderingen in het organisch materiaal, verandert een dam ook de hydrologie: het sterke seizoensgebonden debiet wordt afgevlakt tot een stabiel debiet voor elektriciteitsopwekking. Dit leidt tot minder sterke seizoensgebonden overstromingen, en als gevolg hiervan kunnen andere planten zich vestigen op de overstromingsvlakte. Dit heeft vervolgens effect op de biogeochemische kringlopen op de overstromingsvlakte.

De resultaten van dit proefschrift laten nadrukkelijk zien dat er een seizoensgebonden dynamiek is in de biogeochemie van tropische overstromingsgebieden en dat deze sterk gekoppeld is aan de hydrologie. Met het oog op klimaatverandering en waterbeschikbaarheid is het belangrijk deze interacties tussen rivier, overstromingsvlakte en vegetatie te begrijpen.
# Table of contents

Summary .......................................................... 1  
Kurzzusammenfassung ......................................... 3  
Samenvatting ...................................................... 7  

Chapter 1 .......................................................... 13  
   General introduction  

Chapter 2 .......................................................... 27  
   Hysteresis effects in organic matter turnover in a tropical floodplain during a flood cycle  

Chapter 3 .......................................................... 61  
   Organic matter dynamics in a tropical river-floodplain system  

Chapter 4 .......................................................... 101  
   How dams and wetlands affect carbon and nutrient fluxes in the Zambezi  

Chapter 5 .......................................................... 131  
   Seasonal dynamics of carbon and nutrients from two contrasting tropical floodplain systems in the Zambezi River Basin  

Chapter 6 .......................................................... 169  
   Conclusions and outlook  

References ......................................................... 181  
Acknowledgements ............................................. 197  
Curriculum Vitae ............................................... 199
Chapter 1

General introduction
Inland waters in the global carbon cycle

Carbon cycling on Earth occurs between the terrestrial and aquatic realms on different spatial and temporal scales, ranging from gas exchange processes on the scales of centimeters and days to organic matter burial in the deep ocean operating on the order of thousands of kilometers and thousands of years. In the last decades, the importance of inland waters in the global carbon cycle is increasingly recognized, and research efforts in understanding the role of rivers, streams, lakes, and wetlands have been intensified (Battin et al., 2009; Melack, 2011). In previous estimates of the carbon cycle, the inland waters were simply considered “plumbing”, i.e., delivering carbon from the terrestrial to the marine realm, whereas newer estimates revealed that inland waters play an important role in the transformation of organic matter, and redistribution of carbon between terrestrial ecosystems (Cole et al., 2007; Aufdenkampe et al., 2011).

In recent years, rivers have been identified as (net) heterotrophic systems (Battin et al., 2008), transferring terrestrially-produced organic matter as carbon dioxide ($CO_2$) to the atmosphere. Estimates of inland-water emissions are on the same order of magnitude as $CO_2$ emissions resulting from land-use change (Raymond et al., 2013). The conditions in large rivers are generally unfavorable for organic matter production, though small niches in the riparian zone can contribute fresh organic matter. Large tropical rivers systems are still highly underrepresented in both modeling studies (e.g., Dumont et al., 2005; Harrison et al., 2005a; Harrison et al., 2005b) and global budgets based on measurements (e.g., Alvarez-Cobelas et al., 2008; Alvarez-Cobelas et al., 2009; Alvarez-Cobelas et al., 2012).

River biogeochemistry in the tropics and subtropics

Tropical rivers transport mainly natural organic matter and little organic matter from anthropogenic sources, and are thus an important contributor in the global carbon cycle. Research efforts into the role of large tropical rivers, however, have only recently increased, with one notable exception: the Amazon is perhaps one of the best-studied large rivers in the world, with investigations into both the composition of the material transported (e.g., Hedges et al., 1986a; Kim et al.,
2012), and the emissions of greenhouse gases from its catchment (e.g., Richey et al., 2002; Melack et al., 2004; Mayorga et al., 2005). Research on African rivers has shown that riparian inputs dominate the fluvially transported particulate organic matter (Marwick et al., 2014b), and that the spatial distribution of land cover (i.e. C$_3$ and C$_4$ vegetation) and hydrological connectivity between rivers and wetlands further determines the quantity and quality of dissolved organic matter (Lambert et al., 2015; Lambert et al., 2016).

Greenhouse-gas emissions from tropical rivers in Africa and in South-America significantly contribute to the global greenhouse gas budget (Richey et al., 2002; Raymond et al., 2013; Borges et al., 2015b). Recently, it has been suggested that the extent of wetlands in a tropical catchment controls the concentration of CO$_2$ in the river water (Borges et al., 2015a). In this case, wetlands were defined as habitats with continuous, seasonal, or periodic standing water or water-saturated soils (Hess et al., 2015). Floodplains are one of such habitats, and fairly common in tropical regions.

**Floodplain dynamics**

When river discharge exceeds the storage capacity of the river channel, the water spills onto the surrounding areas (Fig. 1.1). While in temperate systems this typically happens after extreme rainfall events (e.g., Tockner et al., 1999), in tropical systems this can occur on a regular seasonal basis. Inundated floodplains, especially when they are seasonally flooded, are characterized by soil conditions and vegetation patterns that are distinctly different from their surrounding terrestrial and aquatic ecosystems (Mitsch and Gosselink, 2007). The dynamics of the flood pulse, i.e., the timing and extent, determine the environmental conditions on the floodplain. Spatial and temporal variability in inundation during a flooding event results in environmental gradients from the river onto the floodplain to the dry areas. The effects of inundation on the floodplain vegetation were first described in the Flood Pulse Concept (Junk et al., 1989).
Primary production (photosynthesis, Eq. 1.1), respiration and degradation processes, as well as terrestrial organic matter inputs determine the balance of carbon cycling (net autotrophic of heterotrophic) in a river-floodplain system. River-floodplain systems are known for their high production rates (Mitsch et al., 2010). Typically, the main channel is unfavorable for primary production, and floating macrophytes, periphyton, and floodplain vegetation contribute most to the system’s productivity (Junk et al., 1989). In a well-mixed, oxygenated water column, aerobic respiration rates (Eq. 1.2) may be high due to inputs of eroded terrestrial material (Ward and Stanford, 1995), and result in elevated CO$_2$ concentrations in the water column.

\[
\text{Photosynthesis} \quad 6CO_2 + 6H_2O + \text{sunlight} \rightarrow C_6H_{12}O_6 + 6O_2 \quad (1.1)
\]

\[
\text{Aerobic respiration} \quad C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad (1.2)
\]

\[
\text{Methanogenesis / Fermentation} \quad C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4 \quad (1.3)
\]
In contrast, on the inundated floodplain both primary production and organic matter degradation occur (Fig. 1.2). Floodplain vegetation is typically adapted to the seasonal inundation and low-oxygen conditions: prolonged inundation typically results in low oxygen conditions in the water on the floodplain (Hamilton et al., 1997; Zurbrügg et al., 2012) and leads to anoxic floodplain soils. Under reduced oxygen levels, other anaerobic degradation processes take over the role of aerobic degradation. When all other electron acceptors (such as nitrate, iron, and manganese) are depleted, as is often the case in inundated soils, fermentation (i.e., methanogenesis) of the organic matter will not only produce CO$_2$, but also methane (CH$_4$, Eq. 1.3). Methane is a much more potent greenhouse gas than CO$_2$ (roughly 25 times more effective in trapping the sun’s radiation; IPCC, 2007). And, with oxygen levels in the overlying waters being low, methane is unlikely to be oxidized before escaping from the floodplain to the atmosphere. Tropical floodplains have been found to be hotspots for CO$_2$ and CH$_4$ emissions, and are
globally significant sources of these greenhouse gases (e.g., Richey et al., 2002; Belger et al., 2011; Bass et al., 2014; Borges et al., 2015b).

River-floodplain exchange has been linked with oxygen depletion in various tropical rivers (Hamilton et al., 1995; Hamilton et al., 1997; Zurbrügg et al., 2012). Similarly, the interaction between rivers and floodplains controls sediment dynamics and associated carbon, nutrients, and pollutants (Aalto et al., 2003; Fisher and Acreman, 2004). Floodplains can retain large quantities of suspended particles, but due to erosion and degradation processes only small amounts of the riverine organic carbon are ultimately buried (Omengo et al., 2016b).

**Anthropogenic influences**

Combustion of fossil fuels and land-use changes are well known anthropogenic perturbations of the global carbon cycle. It has led to increased emissions of carbon dioxide and methane (CH$_4$), which enhance the Earth’s greenhouse effect, causing global mean temperatures to rise (IPCC, 2007). However, parts of these emissions are subsequently redistributed between the larger carbon reservoirs on Earth, resulting in secondary effects such as ocean acidification (Doney et al., 2009). The effects of human alterations of inland waters are not as obvious as those from land-use change and fossil fuel emissions, but they may prove significant. A large fraction of the world’s largest river systems has already been affected by human activities to such a degree that biodiversity and ecosystem services are at risk (Syvitski et al., 2005; Vörösmarty et al., 2010). For example, rivers are affected by the construction of hydropower dams (e.g., Van Cappellen and Maavara, 2016), water diversions for irrigation (e.g., Nilsson et al., 2005), and drainage of wastewater into the surface waters.

Any of these changes affect the river biogeochemistry. Water extraction for irrigation alters the discharge to downstream areas and generally removes nutrients from the river (Nilsson et al., 2005), whereas effluents from urban areas deliver large amounts of nutrients and organic matter to aquatic systems (Walsh et al., 2005). The prolonged residence time in hydropower reservoirs creates favorable opportunities for organic matter degradation. As a consequence, most hydropower
reservoirs are hot spots of carbon dioxide and methane emissions to the atmosphere (Abril et al., 2005; Guérin et al., 2006; DelSontro et al., 2011; Kemenes et al., 2011). Increased water residence time also results in retention of carbon and nutrients, and dams can alter nutrient limitation patterns (Van Cappellen and Maavara, 2016). Along with the changes in hydrological functioning of the river, such changes in water biogeochemistry can have severe impacts on downstream ecosystems (Van Cappellen and Maavara, 2016).

**Research questions**

Recent research has revealed riverine organic-matter cycling in the tropics and subtropics to be an important component of the global carbon cycle, but much remains to be studied in more detail. Considering the various anthropogenic disturbances of inland water systems, it is essential to understand the functioning of pristine systems before any large-scale human interference. Catchment-wide studies have highlighted the importance of river-floodplain and river-wetland interactions for (sub-)tropical river biogeochemistry. The overall aim of this thesis is to understand how the riverine biogeochemistry and organic-matter composition are affected by, and linked to river-floodplain processes.

The specific questions are:

1. What are the seasonal patterns of organic-matter cycling along a floodplain? (Chapter 2-5)
2. What is the role of hydrology on river-floodplain biogeochemistry? (Chapter 2 and 4)
3. Which are the sources of riverine organic matter, and how do their relative contributions change throughout the year? (chapter 2, 3, and 4)
4. How does dam construction impact tropical fluvial biogeochemistry? (Chapter 4 and 5)
Outline

To answer these questions, first the study site and scientific approach will be described in this chapter. The following chapters, which are written as individual research articles, provide partial answers to the overarching question. Some of these have already been published together with various co-authors. In chapter 2, which builds on and significantly benefited from the BSc thesis of Simon Baumgartner, I investigate the biogeochemical and hydrological seasonality of the Barotse Plains in more detail. This work led to a hypothesis regarding changing sources of organic matter throughout the year. One of the initial goals of this thesis was to distinguish various inputs to the pool of riverine organic matter using a biomarker approach, which culminated in chapter 3. Sources of the riverine particulate organic matter changed throughout the year, with varying degrees of inputs from soils, floodplain vegetation, and terrestrial vegetation. A synthesis of biogeochemical functioning of floodplains and reservoirs in the Zambezi catchment is presented in chapter 4. Following on the dissertation of Dr. Roland Zurbrügg, chapter 5 focused on the comparison of the hydrology and biogeochemistry of the Barotse Plains and the dam-impacted Kafue Flats. The thesis is concluded with an integrated overview of the main results and conclusions in chapter 6, and highlights directions of future research efforts.

Study site: Zambezi River

The Zambezi catchment in sub-Saharan Africa (Fig. 1.3) provides an excellent study site to answer the above raised questions, as the catchments hosts several large, pristine floodplain areas, and is impacted by a number of (hydropower) dams and reservoirs. One of the large floodplains in the catchment, the Kafue Flats, is bordered by two dams (Itezhi-Tezhi and Kafue Gorge), which makes this an excellent case to study dam-impacts on floodplain biogeochemistry. This has previously been reported in Zurbrügg (2012). In order to better understand the functioning of a pristine floodplain, this thesis has focused on the Barotse Plains in western Zambia.
The Zambezi River is an important freshwater system in sub-Saharan Africa. It has the fourth-largest catchment off all African rivers and is one of the major river systems draining into the Indian Ocean. The catchment spans across 8 different countries. Given its position between 11 and 18˚S, the movements of the Intertropical Convergence Zone dominate the climate of the Zambezi catchment. As a result, the catchment experiences pronounced dry and wet seasons, with the rain falling between December and March. In the undisturbed parts of the catchment, upstream of the major hydropower dams (Fig. 1.3), the seasonality in rainfall is reflected in the discharge patterns, which exhibit peak flows shortly after the conclusion of the rainy season. Energy production at the two hydropower dams and their reservoirs (Lake Kariba and Cahorra Bassa) determines the discharge patterns further downstream, leading to more stable discharges (Fig. 1.4). The combination of large discharge seasonality and the shared catchment introduces the need for sustainable water use among the riparian countries. This
recently became particularly evident in 2015/2016, when an El-Niño-related
drought was responsible for extremely low water levels (FEWSNET, 2016) and
electricity generation from hydropower production was limited.

![Figure 1.4 Discharge in the Zambezi catchment downstream of the Barotse Plains (black dots) and spills from the Kariba Dam turbines (blue triangles). Data from the Zambezi River Authority, 2013-2014.](image)

Previous biogeochemical work in the Zambezi catchment has focused on the Kafue River tributary, with detailed investigations into the biogeochemistry of the Itézhi-Tezhi Reservoir (Kunz et al., 2011b) and the Kafue Flats floodplain (Wamulume et al., 2011; Zurbrügg et al., 2012; Zurbrügg et al., 2013), the hydrology of the flood pulses on the floodplain (e.g., Meier et al., 2010; Cohen Liechti et al., 2014), as well as the ecology of the flora and fauna on the floodplain (Blaser, 2013; Blaser et al., 2013). Research into the hydropower potential and optimization (e.g., Kunz et al., 2013; Spalding-Fecher et al., 2014) has become very important in light of both changing water demands and climate change. Previous catchment-scale investigations have focused on greenhouse gasses (Teodoru et al., 2015) and dissolved organic matter characteristics (Lambert et al., 2016), or are based on sedimentary records off the coast of Mozambique (e.g., Schefuß et al., 2011; Wang et al., 2013). What became evident from these catchment-wide studies is the importance of floodplain and wetland areas for the river biogeochemistry.
Approach

What has become abundantly clear from previous work in tropical floodplain systems is that tropical river-floodplain systems are highly dynamic in both space and time. In order to answer my research questions and to capture the dynamical aspects of the biogeochemical functioning of the floodplain comprehensively, a variety of methods was applied.

Field sampling

A first approach to capture the seasonal dynamics of organic-matter cycling along the floodplain comprised of sampling campaigns at different times during the year. In total, three large-scale campaigns have been conducted in the floodplain and the Zambian part of the Zambezi catchment. During these campaigns, in-situ measurements were performed and samples were collected at multiple locations upstream of, along, and downstream of the Barotse Plains. Field campaigns, however, can only capture snapshots of the annual cycle.

Hence, a second method to study the seasonal dynamics involved the long-term deployment of multi-probe devices. These instruments are designed to operate with little to no maintenance and no external power supply, and are thus perfectly suited for deployment in remote places such as Barotse Plains. The instruments were installed during one of the larger campaigns, and two additional, shorter field trips were conducted for maintenance and retrieval. Each probe measured physicochemical parameters (temperature, conductivity, pH, oxygen, fluorescent dissolved organic matter, and turbidity) every hour for a period of several months. Combining the continuous measurements of the multi-probes with discrete measurements obtained during the field campaigns allowed for quantification of the intra-annual biogeochemical dynamics. The long-term deployment was combined with water-level records from a local partner (the Zambezi River Authority) in order to link the biogeochemistry to the hydrology of the Zambezi River.
Tracing riverine organic matter

In river-floodplain systems, most of the organic matter transported downstream is produced outside of the main channel. Different sources of organic matter to the river include sedimentary bedrock, soils, and vegetation. The chemical characteristics of organic matter derived from these sources differ, and such changes in the composition of the organic matter can be used to trace its origin. Large volumes of river water were filtered during the field campaigns to obtain samples for the characterization of suspended material. In addition, soil and vegetation samples were collected.

Bulk properties

As a first step, bulk organic carbon-to-nitrogen ratios can be considered. Carbon-to-nitrogen (C:N) ratios can be useful to identify the origin of the suspended organic matter. Terrestrial sources typically have higher C:N ratios than phytoplankton (Elser et al., 2000), with soil values generally falling somewhere in between the two. Even more informative are measurements of the carbon-to-nitrogen ratio in combination with those of the isotopic composition of the organic matter. Phytoplankton and higher plants have different ways of assimilating carbon dioxide from the water or atmosphere, respectively, and these different pathways result in different carbon isotope fractionation factors. Phytoplankton-derived organic matter is characterized by depleted $\delta^{13}$C values (around -30‰), whereas a much larger variability is observed in the stable isotopic signature of terrestrial plants. Different groups of terrestrial plants use either the C$_3$ and the C$_4$ pathway for photosynthesis, which result in carbon isotopic values for plant biomass of around -30‰ or -12‰, respectively. In addition to the stable carbon isotopic value, the radiocarbon content of a sample can provide information on the age of a sample. For tracing the active carbon cycle, the $^{14}$C content is generally used, which can be expressed in various ways. In this thesis, the radiocarbon signature of organic matter is presented as the fraction modern ($F_{^{14}C}$, which divides the fractionation-normalized $^{14}$C activity of the sample by the normalized activity of an international standard: NIST oxalic acid).
**Biomarkers**

Biomarkers can be used as a powerful tool when more detailed insights into the organic matter composition are desired. Biomarkers can be considered molecular fossils, or molecular puzzle pieces. Each plant, every alga has a specific molecular signature, which is closely related to the signatures of similar organisms. To be useful as a biomarker, it has to be distinctly different from other groups of organisms. Additionally, the molecular composition should be robust, and not degraded upon death of the organism, so that the signature will be preserved and similar to the original signature. Several of those biomarkers can provide information about different vegetation and soil input, which have been used in this thesis to identify sources of organic matter in the Zambezi River (Fig. 1.5).

![Molecular structures](image)

**Figure 1.5** Molecular structures of a C$_{25}$ n-alkane, a C$_{24}$ saturated, straight-chain fatty acid, and GDGT-Ia as an example of branched GDGTs.

Plant waxes (n-alkanes) on leaves of higher-order terrestrial plants typically have a length between C$_{25}$ and C$_{35}$, and the signal is dominated by the odd-numbered homologues. Algae on the other hand typically have shorter chain lengths. Fatty acids are typically found as polar lipids, with a strong even predominance. Higher plants produce mainly longer, straight-chain, saturated fatty acids (C$_{24}$-C$_{30}$), while algae and bacteria produce shorter chain lengths (C$_{14}$-C$_{20}$) in larger abundances. Several indices have been developed over the years for both n-alkanes and fatty acids to give a quick overview of the plant wax composition.
Soil bacteria and archaea produce specific membrane lipids, called branched glycerol dialkyl glycerol tetraethers (GDGTs). These GDGTs are found in a variety of environments, but are commonly considered a tracer for terrestrial organic matter (Hopmans et al., 2004). The exact composition of the membrane lipids has been found to change with mean annual air temperature and soil pH (Weijers et al., 2006; Weijers et al., 2007; Peterse et al., 2012; Schouten et al., 2013b).
Chapter 2

Hysteresis effects in organic matter turnover in a tropical floodplain during a flood cycle

Alissa Zuijdgeest
Simon Baumgartner
Bernhard Wehrli

Biogeochemistry, 2016
doi: 10.1007/s10533-016-0263-z
Abstract

Tropical inland waters are increasingly recognized for their role in the global carbon cycle, but uncertainty about the effects of such systems on the transported organic matter remains. The seasonal interactions between river, floodplain, and vegetation result in highly dynamic systems, which can exhibit markedly different biogeochemical patterns throughout a flood cycle. In this study, we determined rates and governing processes of organic matter turnover. Multi-probes in the Barotse Plains, a pristine floodplain in the Upper Zambezi River (Zambia), provided a high-resolution data set over the course of a hydrological cycle. The concentrations of oxygen, carbon dioxide, dissolved organic carbon, and suspended particulate matter in the main channel showed clear hysteresis trends with expanding and receding water on the floodplain. Lower oxygen and suspended matter concentrations prevailed at longer travel times of water in the floodplain, while carbon dioxide and dissolved organic carbon concentrations were higher when the water spent more time on the floodplain. Maxima of particulate loads occurred before highest water levels, whereas the maximum in dissolved organic carbon load occurred during the transition of flooding and flood recession. Degradation of terrestrial organic matter occurred mainly on the floodplain at increased floodplain residence times. Our data suggest that floodplains become more intense hotspots at prolonged travel time of the flood pulse over the floodplain.
Introduction

In light of increased atmospheric carbon dioxide (CO₂) concentrations, research is focusing on the role of the different compartments in the global carbon cycle. Inland waters have traditionally been somewhat neglected, being treated as plumbing to transport terrestrial carbon to the oceans (Melack, 2011). Streams, rivers, artificial and natural lakes, wetlands, and floodplains, which cover approximately 4.6 million km² or >3% of the terrestrial realm (Downing et al., 2006), have been identified as important biogeochemical reactors within the global cycle (Raymond et al., 2013). Recent work has emphasized that inland waters remove carbon via burial (Battin et al., 2009) and emissions to the atmosphere (Raymond et al., 2013). Global budgets are still lacking important contributions from tropical inland waters, specifically in Africa.

In Africa, heavy seasonal rainfall, associated with monsoons or the Intertropical Convergence Zone, inundates large floodplain areas along most tropical rivers. Such floodplains are characterized by distinct hydrology, soil conditions, and vegetation, and they support significantly different ecosystems at the border of terrestrial and aquatic zones (Mitsch and Gosselink, 2007). After the onset of the rains, discharge increases, and water from the main channel (henceforth referred to as river water) is forced onto the floodplain, causing a flooding event (Ward and Stanford, 1995). The interaction between the flood pulse and the floodplain creates transition zones between terrestrial and aquatic habitats (Junk et al., 1989). The return of floodplain water into the main channel delivers organic matter, particles, and nutrients that were released from the floodplain soils into the water on the floodplain, which can sustain high aquatic productivity in the river-floodplain system (Ward and Stanford, 1995; Robertson et al., 1999).

The temporal variability in inundation and hence aquatic and terrestrial habitats leads to distinct vegetation patterns on floodplains, first summarized in the Flood Pulse Concept (Junk et al., 1989). Whereas the rapid water flow in the main channel is typically unfavorable for intense primary production, aquatic macrophytes and periphyton in the riparian zone and on the floodplain usually contribute to high primary production rates. In slow-flowing tropical rivers, floating macrophytes
could have greater importance (Junk et al., 1989). Rivers and streams are on a global scale net heterotrophic, even without considering bordering floodplains and wetlands (Battin et al., 2008). On various floodplains the initial flood pulse resulted in high respiration rates (Marcarelli et al., 2010; Gallardo et al., 2012; Chaparro et al., 2014), while production of biomass accumulated during dryer periods (Gallardo et al., 2012). The seasonal flooding results in highly dynamic, temporally and spatially variant interactions between the riparian terrestrial ecosystems and the river.

Floodplains in the Okavango delta are considered sources of dissolved organic carbon (DOC), particularly during the annual flood (Mladenov et al., 2005). Leaching of DOC from vegetation, particularly leaf litter, occurs rapidly after the vegetation is first wetted (O'Connell et al., 2000). Based on studies in five different river-floodplain systems in the U.S.A, Peru, and Venezuela, inputs of terrestrial organic matter were more important to the aquatic food webs during high flow (Roach et al., 2014). In contrast, in the Amazon organic matter was exported from the river onto the floodplain during rising water levels, whereas organic matter produced by phytoplankton and macrophytes on the floodplain was transferred back to the river during high and falling water levels (Moreira-Turcq et al., 2013). Interactions between a flood pulse and the river's floodplains have been shown to alter the dissolved organic carbon concentrations and sources throughout the year.

River-floodplain exchange has also been found to affect the in-stream oxygen concentrations. Inputs of oxygen-depleted floodplain water significantly lowered the oxygen concentrations at the downstream end of a large floodplain in Zambia (Zurbrügg et al., 2012). Similarly, low oxygen concentrations were found on the floodplains in the Paraguay River Basin (Hamilton et al., 1995). The Atchafalaya River, a tributary of the Mississippi, experiences low dissolved oxygen concentrations along one of its floodplain areas during receding water levels (Kaller et al., 2015). Higher respiration rates in floodplain areas and decreasing oxygen concentrations in the downstream direction were also found in the Macquarie River in Australia (Kobayashi et al., 2011). In general, higher respiration rates on the floodplain are responsible for low oxygen conditions in the floodplain water, which in turn affects the oxygen concentration in the river water at downstream locations.

Floodplain systems are also hotspots in terms of greenhouse gas emissions
(Raymond et al., 2013). In the Amazon catchment, floodplain areas were found to be emitting larger quantities of CO$_2$ to the atmosphere than previously considered for tropical systems (Richey et al., 2002). Similar to the flooded forests of the Central Amazon Basin, inter-fluvial wetlands in the Negro River catchment emitted CO$_2$ to the atmosphere (Belger et al., 2011), showing that high evasive fluxes can be expected from any type of flooded ecosystem. In a tropical wetland in Australia, emissions of CO$_2$ varied among different habitats (Bass et al., 2014). The high emission rates in the Amazon catchment led to revised global budgets (Raymond et al., 2013).

The importance of river-floodplain interactions for different components of the river biogeochemistry has been highlighted and studied, but an integrative view of the effects in tropical floodplains is still lacking. Due to the high anthropogenic burden on many tropical systems, it is imperative to gain a mechanistic understanding of the biogeochemical cycling in remaining pristine systems, before these disappear altogether.

To gain such a holistic overview of river-floodplain interactions, we continuously observed water quality parameters up- and downstream of the Barotse Plains in the upper Zambezi basin, a large, pristine floodplain at high temporal resolution over a flooding cycle with deployed multi-probes. This procedure allows estimating the biogeochemical transformations occurring in the floodplain system as a function of time. The temporal resolution of our data set allows characterization of seasonal patterns, instead of capturing only snapshots in time. We aim to (1) determine the seasonal patterns of organic matter cycling during a hydrological cycle, (2) understand which processes are responsible for these patterns, and (3) evaluate on which time scales these processes affect the river biogeochemistry.
Methods

Study site

The Zambezi River Basin is the fourth largest in Africa at $1.4 \times 10^6$ km$^2$, and the only one of the major African rivers draining into the Indian Ocean. Due to its location in the Southern Hemisphere, the catchment experiences a pronounced wet season during the passage of the Inter Tropical Convergence zone from December to March followed by a dry season from April to November. The Barotse Plains are a near-pristine floodplain area with low population density of roughly 6 people per km$^2$ (Euroconsult Mott MacDonald, 2007) in the upstream part of the Zambezi River in Western Zambia (Fig. 2.1). The main body of the floodplain area is estimated around 7,700 km$^2$ (Hughes and Hughes, 1992). The hydrograph in the Barotse Plains shows peak flow in April - May and low-flow conditions between July and November.

Figure 2.1 Map of the Zambezi catchment, with the extension of the Barotse floodplain and the locations of the sensors shown in the insert.
Previous research in the Zambezi basin has shown that the catchment exports large quantities of DOC at very high flow (Zurbrügg et al., 2013; Lambert et al., 2016), and that the organic matter cycling is strongly impacted by the presence of hydropower dams in the catchment (Kunz et al., 2011a; Kunz et al., 2011b; Wamulume et al., 2011; Zurbrügg et al., 2013). Emissions of greenhouse gases have been linked to natural barriers (waterfalls), and hydropower reservoirs (DelSontro et al., 2011), and the presence of floodplain areas, with highest concentrations of CO₂ and methane found just downstream of extensive floodplain areas (Teodoru et al., 2015). Temporal variations of concentrations and trends in dissolved and particulate organic carbon (DOC and POC, respectively) and greenhouse gases in the river system have been observed between periods of high and low flows (Zurbrügg et al., 2013; Teodoru et al., 2015; Zuijdgeest et al., 2015).

Probes deployment
At two locations in the Zambezi River Basin (Fig. 2.1) we have deployed WTW EXO2 probes, at the upstream end of the Barotse Plains, just south of Lukulu (14.5340S, 23.1466E) and at the downstream end in Senanga (16.0994S, 23.2963E). At Lukulu, the probe was deployed in the middle of one of two branches of the river, which both carry water year-round. Previous research (not published) showed there was little variation in biogeochemical composition of the water in the two branches. The probe in Senanga was deployed from a floating jetty, roughly 5m from an outer bend of the river. The Zambezi was horizontally well-mixed (Zuijdgeest et al., 2015). Though there typically is some flooding upstream of the first sensor location, the bulk of the seasonal flooding occurs between these two locations. At both locations, daily water level measurements are available from the Zambezi River Authority. At Senanga the water level data can easily be correlated to discharge measurements at Ngonye Falls, somewhat further downstream of the floodplain.

At hourly intervals, the instruments logged for 60 seconds temperature, conductivity, pH, dissolved oxygen, fluorescent dissolved organic matter (fDOM),
and turbidity. Automated wiping of the sensors with a small brush prior to measurement ensured high-quality data from the sensors. Both probes were deployed in early November 2013, serviced in April 2014 and the measurement interval was set to 9h for the remainder of the deployment, and retrieved in September 2014. Service included new batteries and recalibration of the sensors, though the observed drifting was minimal. Unfortunately, both probes have experienced interrupted data collection: in Lukulu the measurements after service were not recorded properly, and in Senanga the period between March 11 and service (April 12) is missing due to a short-circuit in the temperature/conductivity sensor.

At the times of deployment, service, and retrieval, additional water samples were collected before stopping the deployment. Samples for alkalinity were stored cold and determined in the laboratory by end-point titration. Filtered water (GF/F, 0.7µm; Whatman) was collected in 12mL Exetainer vials and poisoned with CuCl\textsubscript{2} for analysis of dissolved inorganic carbon (DIC) and in 40mL glass vials and acidified with 100µL 2M HCl for analysis of dissolved organic carbon. Both were analyzed in the laboratory on a Shimadzu TOC-L Analyzer. Suspended particulate matter (SPM) concentrations were determined by weight difference on GF/F filters (0.7µm; Whatman) after freeze-drying for at least 24 hours. During various other sampling campaigns in the Zambezi catchment (October 2013, June 2015), the same kind of samples have been collected simultaneous with discrete measurements with an EXO2 probe.

**Calibrations and calculations for organic matter and the carbonate system**

During the field campaigns and servicing trips related to the deployment, simultaneous measurements with the EXO2 probe and water samples for laboratory analysis were collected. From this data set, we determined correlations between fluorescent dissolved organic matter and DOC (Fig. 2.2a), and between turbidity and SPM (Fig. 2.2b). High-turbidity values (>20 FNU) were filtered out of the data set because of uncertainty about measurement accuracy. We used
the conductivity record to calculate the alkalinity changes over time (Fig. 2.2c). Correlations between conductivity and alkalinity result from natural geological and climatic controls and are often used to assess anthropogenic impacts on streams or rivers (Stewart, 2001; Kney and Brandes, 2007; Thompson et al., 2012). Preliminary data from the upstream catchment of the Zambezi (upstream of Lake Kariba) indicated a strong correlation between conductivity and alkalinity during high water levels (April 2013). The initial data has been expanded with additional measurements at the sampling locations, and measurements by Teodoru et al. (2015), confirming a clear correlation between conductivity and alkalinity (Fig. 2.2c; more details in Appendix 2.2). By combining the conductivity-based alkalinity data with measured pH, temperature, and salinity, the entire carbonate system was calculated with the CO2SYS Excel sheet (Pierrot et al., 2006), using the dissociation constants compiled by Millero, 1979.

![Figure 2.2](image)

**Figure 2.2** Correlations based on samples from November 2013, April 2014, and June 2015 between a) fluorescent dissolved organic matter (fDOM) and DOC ($r = 0.722$, $p = 7.16e-4$), b) turbidity and SPM ($r = 0.869$, $p = 2.92e-6$), and c) conductivity and alkalinity ($r = 0.966$, $p < 2.2e-16$).

**Calculating process rates from sensor data**

Using the hourly oxygen recordings, we applied the diel oxygen method as outlined by Staehr et al. (2010) to calculate gross primary production (GPP), net primary production (NPP), and respiration rates in the river. The underlying assumption in this method is that the change in oxygen concentration over a daily cycle is mainly governed by GPP, respiration, and the diffusive flux. The
diffusive flux was calculated using the temperature-dependent oxygen saturation concentration and wind speed data from a nearby meteorological station. During the night no GPP occurs, so from the change in oxygen concentration observed during those hours the respiration rate could be determined, correcting for the diffusive O$_2$ flux. This respiration rate was assumed to be constant throughout the day as well, allowing the calculation of the contribution of primary production to the change in oxygen concentrations over time during daylight hours. These calculations were not possible for the second half of our deployment, because the longer (9h) time intervals between measurements did not guarantee two measurements during both day and night.

**Inundation dynamics**

Visual consideration of the two water level records (Fig. 2.3a) suggested that the downstream record was a time-shifted version of the upstream record. However, because the shift was not constant, a more sophisticated method was needed to calculate the residence time of water in the floodplain area. For this purpose, the dynamic time warping package “dtw” in R (Giorgino, 2009) was used. This procedure stretches and compresses two time series to maximize the correlation between the two (Giorgino, 2009). The water level time series at Lukulu was set as the query, to be compressed and stretched to represent the time series at Senanga, the reference. Water level records were first normalized to the mean water level for each record, for ease of calculation and comparison. Calculation was performed using different step patterns, but the mori2006 pattern (Mori et al., 2006) yielded results that matched visual observations best (see Appendix 2.3), and the results from this procedure were used in this study.

Visual comparison of the water level records and the dynamic time warping procedure did not correspond well in the first months of the time series, with negative travel times being calculated. This was probably due to calculation artifacts relating to the boundaries of the time series and small variations in the two records. The travel time at the end of the dry season was therefore manually adjusted to a smooth increase from 3 to 8 days, where the minimum of 3 days
is determined based on acoustic Doppler current profiler flow measurements at several locations along the Barotse Plains from April 2013 (Zuijdgeest et al., 2015). At the end of the year, travel times were again set manually to 3 days to match the observations and correct for boundary-related calculation artifacts (Appendix 2.3). Unfortunately, it was not possible to obtain water level records for a longer time period, to minimize the boundary effects for the time period of the study. While the algorithm produced robust results over the time of the flood peak and its recession, its accuracy seems to be limited at the boundaries of the time-series. Future methodological tests on multi-year time series could help to clarify and constrain this limitation.

**Figure 2.3** a) Temporal changes in water levels at Lukulu and Senanga and precipitation at Kalabo (in the middle of the floodplain; data from www.biota-africa.org). b) Temporal changes in travel time of the flood pulse over the floodplain. The first peak in travel time is replaced by a gradual increase based on visual observations, minimum travel times are set to 3 days based on ADCP data from April 2013. c) Relationship between travel time and discharge at Senanga.
Results

Hydrology and inundation dynamics

Shortly after the onset of the rains, travel time over the floodplain increased markedly (Fig. 2.3b). Towards the end of the rainy season prolonged travel times were following larger rain events. Travel times remained high during receding water (May-July) and only started to decline rapidly at the end of July.

Plotting travel time of the flood pulse over the wetlands against discharge at Senanga revealed a counter-clockwise hysteresis effect (Fig. 2.3c). The travel time of water between Lukulu and Senanga increased with rising water levels, reaching maximum travel times of approximately 35 days at roughly 1300 m$^3$s$^{-1}$, well before peak flow. During the remaining wet season, travel time decreased again to a steady 20 days until peak flow was reached. Contrastingly, during receding water levels travel time rose again and remained at a maximum of roughly 30 days until discharge dropped below 1000 m$^3$s$^{-1}$. At high discharge, the travel time was distinctly shorter during rising water levels than during receding water levels.

Seasonal patterns of organic matter parameters

The records from Lukulu and Senanga showed distinct temporal shifts in carbon dynamics: while oxygen concentrations decreased earlier in the year in Senanga, peak concentrations in CO$_2$ and DOC were observed roughly 1.5 month earlier in Lukulu compared to Senanga. CO$_2$ concentrations almost doubled between the upstream and downstream locations. From mid-May to early-July, the CO$_2$ concentrations in Senanga increased again to a smaller, second peak, as conductivity (i.e. alkalinity; Appendix 2.4) rose while pH remained stable. Suspended matter concentrations in Senanga were high at the end of the dry season and the first months of the wet season, but decreased with increasing discharge (Fig. 2.4d). Towards the end of our time series a small increase in SPM concentrations was observed. In Lukulu the SPM concentrations were lower than in Senanga throughout the year, and with a less distinct pattern: small maxima were observed mid-December, early January, and early March without any clear seasonal pattern.
The load of suspended particulate matter peaked earliest in the year, around February, followed by maximum CO$_2$ loads in early March (Fig. 2.4). Oxygen and DOC peaked somewhat later, around May and early April, respectively.

![Figure 2.4](image)

**Figure 2.4** Temporal changes in oxygen, carbon dioxide, dissolved organic carbon, and suspended particulate matter concentrations and loads throughout the year. Data for Lukulu lacking after servicing in April, recording gap in Senanga between March 11 and April 12.

**Hydrology and river biogeochemistry**

The observed delay between peaks in CO$_2$ and DOC at Lukulu and Senanga (Fig. 2.4) clearly showed that processes on the floodplain impacted the biogeochemistry of the downstream location. Correlations with discharge showed hysteresis patterns, with distinctly different regimes during rising and falling water levels: O$_2$ exhibited anti-clockwise hysteresis (Fig. 2.5a), whereas clockwise hysteresis was observed for CO$_2$ (Fig. 2.5b) and DOC (Fig. 2.5c). Remarkably, SPM concentrations did not show a clear hysteresis pattern: in general, concentrations decreased with increasing discharge, and increased along the same trend when water levels decreased again (Fig. 2.5d).
The concentration of oxygen showed a distinct anti-clockwise hysteresis versus travel time (Fig. 2.6a), in contrast to the clockwise hysteresis observed in CO$_2$ (Fig. 2.6b) and DOC concentrations (not shown). DOC concentrations exhibited a pattern similar to CO$_2$, though with more variable concentrations at short travel time (Fig. 2.6c). SPM, on the other hand, showed high concentrations at short travel times, and lower concentrations when the water spent more time on the floodplain (Fig. 2.6d). During receding waters, SPM concentrations were generally lower than during rising water levels.

**Figure 2.5** Relationships between oxygen, carbon dioxide, dissolved organic carbon, and suspended matter concentrations in Senanga and discharge. Note the recording gap in Senanga between March 11 and April 12, which resulted in the two disjointed lines.
Figure 2.6 Relationships between oxygen, carbon dioxide, dissolved organic carbon, and suspended matter concentrations in Senanga and travel time of the flood pulse over the floodplain. Note the recording gap in Senanga between March 11 and April 12, which resulted in the two disjointed lines.

In-stream primary production and respiration

Calculated net primary production in the water column in Senanga (Fig. 2.7a) decreased from the onset of the deployment, with minimum values towards the end of December. Once productivity reached this minimum, oxygen concentrations started declining. During the remainder of the rainy season, NPP varied without any clear relationship with oxygen concentrations. Respiration rates increased between November and mid-January, and peaked around the time that oxygen concentrations started to drop (Fig. 2.7b). During the second half of the rainy season, respiration rates declined again, with oxygen concentrations rising when respiration rates fell. Though we were only able to calculate NPP and respiration rates during the first half of our deployment, that period did see the largest variability in oxygen concentrations in the river water. There was no correlation
between river oxygen concentrations and either NPP or respiration (correlation coefficient $r = 0.155$ and 0.165, respectively).

![Figure 2.7](image)

**Figure 2.7** Oxygen concentrations and a) NPP and b) respiration rates at Senanga between November 2014 and April 2014. No rates were calculated for the remainder of the year due to longer intervals between measurements.

**Discussion**

In order to further explore the connections between hydrology and biogeochemistry in the Barotse Plains, we suggest three phases of the seasonal flooding cycle, during which different processes dominate organic matter cycling. This concept can be used to guide future field research on organic matter cycling and particle mobilization. The travel time of water over the floodplain will be identified as a useful parameter to define model equations for water quality in spatially explicit hydrological models. The travel-time concept offers the potential to generalize the dynamics of floodplain processes across different systems.
Phase 1 - Expansion

During the initial phases of the flooding season, increasing loads of CO$_2$ and DOC, and decreasing oxygen concentrations in the river were observed. The peak SPM load preceded the maximum of the CO$_2$ load, indicating that the physical soil erosion was triggered by river flow over previously dry soils, whereas the onset of mineralization processes and the subsequent diffusive transport of CO$_2$ from the soil pore space into the flood water required more time. Alternatively, degradation of mineral-bound organic matter could occur in the water column. We hypothesize that the first phase, one of initial flooding, was characterized by intense floodplain soil mobilization, as a consequence of the unprotected floodplain soils at the end of the dry season. Erosion resulted in peak suspended matter loads around February. During the dry season, vegetation on the floodplain shrivels due to lack of water, and typically the biomass is burned before the onset of the rains, to foster new vegetation growth (Andreae, 1991; Mitsch et al., 2010). This agricultural practice leaves the floodplain vulnerable to soil mobilization during the first flood pulse. The peak SPM load preceding peak flow has previously been attributed to exhaustion of the sediment source in other highly seasonal systems (Rovira and Batalla, 2006;
Oeurng et al., 2011). Continued flooding of the Barotse Plains exhausted the initial source of suspended matter, and as flooding spread, progressively smaller amounts of loose floodplain soil were available for mobilization.

**Phase 2 - Maximum**

As the wet season progressed, the whole floodplain was inundated and the discharge reached its maximum. With diminishing inflows, the travel time of water over the floodplain increased again to its maximum value (Fig. 2.8). As a consequence of the maximum travel times, in-stream oxygen concentrations reached minimum values and increasing DOC concentrations were observed. Around March, carbon dioxide and SPM concentrations and loads decreased, whereas oxygen concentrations rose. It is important to notice that the particles behaved differently from the solutes. We suggest that during this second phase, the controlling regime shifted from flooding to stabilization of the floodplain soils. Continued stabilization of the floodplain soils by wetland vegetation also shifted the dominant regime on the floodplain from respiration to primary production, resulting in the uptake of CO$_2$, production of DOC and O$_2$, and minimization of the source of SPM. This would have led to the maximum oxygen loads observed around peak flow, simultaneously with DOC.

The characteristic features of the second phase correspond well to trends recorded for other tropical systems. Strong increases in pCO$_2$ downstream of the Barotse Plains and other flooded systems in the Zambezi catchment have also been observed during the rainy season (Teodoru et al., 2015). The Barotse Plains showed high DOC and low SPM concentrations during peak flow in 2013 (Zuijdgeest et al., 2015). Retention of particulate organic matter and net export of dissolved organic matter indicated degradation processes dominated over primary production in April 2013 (Zuijdgeest et al., 2015). DOC concentrations in the Okavango delta peaked two to four weeks before peak flood (Mladenov et al., 2005). The source of the DOC changed from vascular plant inputs during rising water levels to DOC from the microbial degradation of dissolved organic matter derived from vascular plants during receding water levels (Mladenov et al., 2005).
During high and falling water levels, input of organic matter that was produced on the floodplain has been observed in the Amazon (Moreira-Turcq et al., 2013).

**Phase 3 - Contraction**

During declining water levels, CO\(_2\) levels remained elevated compared to the minimum observed at the end of the dry season and the water column remained well oxygenated. Dissolved organic matter concentrations and loads decreased significantly, but SPM started to rise again sporadically towards the end of the dry season. The observed decrease in O\(_2\) concentration and rise in CO\(_2\) around July was less extensive than during phase 1.

During the third phase, we propose that the floodplain sediment source (i.e. bare soil) was mostly depleted, but there was a continuous input of organic matter from the floodplain vegetation to the river, as connectivity between the river and its floodplain remained. Vegetation debris contributed to the suspended pool, and degradation of this source of organic matter kept CO\(_2\) levels elevated. The more extensive oxygen consumption at the onset of flooding could be the result washing out of accumulated degradation products soil-associated organic matter, or simply the effect of a larger pool of organic matter to start with. As the lateral connectivity between the floodplain and the river decreases, conditions change towards a rather well confined flow channel typical for the dry season. During this period of only channelized flow, which was not fully captured by our data, we suggest that SPM input came from atmospheric inputs or biomass burning at the end of the dry season.

**Travel time as determining factor for riverine biogeochemistry**

Travel time of the river water from Lukulu to Senanga was used here as a quantitative indicator for analyzing the biogeochemical effects of water retention on the floodplain. Discharge measurements showed that water flowing through the main channel would reach the downstream end of the floodplain in roughly 3 days during peak flow (April 2013; Zuijdgeest et al., 2015) and in approximately
6 days during receding water levels (June 2015; unpublished data). However, the offset between water level records at Lukulu and Senanga indicated that the flood pulse took three to four weeks to reach the downstream end of the floodplain. This was slightly faster than a previous estimate of flood attenuation, estimating 4-6 weeks between Lukulu and Senanga (Beilfuss, 2012). The long travel times corresponded well with investigations on the seasonal variation in flooded area, as previously shown for the Kafue Flats (Meier et al., 2010), and with estimations of the river discharge spending time on the floodplain (Zurbrügg et al., 2012). Compared to these approaches, using the water level records to calculate the residence time of water on the floodplain has the advantage that (1) water level records are much more easily obtained than the size of flooded areas, (2) recording is not affected by cloud cover, which often limits satellite approaches, and (3) it is not sensitive to spatial sampling variability along the floodplain. In previous efforts to define the interaction between river and floodplain in the Zambezi catchment, bankfull capacity along the river was used to determine locations of floodplain filling and draining (Zurbrügg et al., 2012; Zuijdgeest et al., 2015). As it is generally not feasible to determine bankfull capacity continuously, the precision of the locations is clearly impacted by the spatial sampling resolution. As the travel-time approach results in an integrated view of the river-floodplain interactions, this is not dependent on spatial sampling resolution.

Spatially explicit hydrological modeling of floodplain processes remains a challenge, but for the Zambezi catchment distinct progress has been made, e.g. Cohen Liechti et al. (2014). As a future step, these authors suggested to include equations for water quality parameters. Quantification of the correlations between travel time of the water over the floodplain and the observed concentrations in the main channel at Senanga could provide such equations. To this end, the data were fitted with trend lines that describe how respective concentration is impacted by prolonged residence time on the floodplain during rising and falling water levels (Table 2.1). During rising water levels, the oxygen concentrations were exponentially linked to the travel time, whereas CO\textsubscript{2} and DOC were both well described by the natural logarithm of the travel time. During falling water levels, oxygen was dependent on the natural logarithm, while the increase in CO\textsubscript{2} with increasing
travel time was best described by an exponential function. No statistical trends could be discerned for DOC during falling water levels, and SPM concentrations throughout the year. The time since the onset of the flood was more crucial in determining the SPM concentrations in the river. These different dynamics of particulate and dissolved phases should be noted, and in future carbon and nutrient budgets, this clear difference needs to be considered. At present, these equations are location-specific to the Barotse Plains, but their more general applicability should be tested via analysis of other tropical floodplain systems.

**Table 2.1** Fitted trend lines for $O_2$, $CO_2$, DOC, and SPM concentrations as a function of travel time (TT) during rising and falling water levels. The residual standard error gives the average error of calculating the concentration based on the travel time. For example, for $O_2$ during rising water levels: on average, using the regression line to predict the concentration from the travel time, this results in an error of 0.39 mg L$^{-1}$.

<table>
<thead>
<tr>
<th>Water levels</th>
<th>Formula</th>
<th>Residual standard error</th>
<th>Achieved convergence tolerance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2$ (mg L$^{-1}$)</td>
<td>Rising: $O_2 = -9.62 + 22.0 \times TT^{-0.173}$</td>
<td>0.389</td>
<td>5.82e-07</td>
</tr>
<tr>
<td></td>
<td>Falling: $O_2 = 4.37 + 0.43 \times \ln (34 - TT)$</td>
<td>0.454</td>
<td>6.36e-08</td>
</tr>
<tr>
<td>$CO_2$ (ppm)</td>
<td>Rising: $CO_2 = -6.37e4 + 5.84e3 \times \ln (1e4 \times TT - 5.30)$</td>
<td>823</td>
<td>7.76e-08</td>
</tr>
<tr>
<td></td>
<td>Falling: $CO_2 = 2.17e3 + 4.49e-2 \times TT^{3.11}$</td>
<td>642</td>
<td>9.71e-06</td>
</tr>
<tr>
<td>DOC (µM)</td>
<td>Rising: $DOC = 204 + 127 \times \ln (TT - 5.3)$</td>
<td>70.5</td>
<td>3.49e-09</td>
</tr>
<tr>
<td></td>
<td>Falling: No significant correlation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPM (mg L$^{-1}$)</td>
<td>Rising: No significant correlation</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Falling: No significant correlation</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Greenhouse gas emissions from floodplains**

Wetlands and floodplains are often considered and described as hotspots or biogeochemical reactors, with large potential of greenhouse gas emissions (Raymond et al., 2013). Varying patterns of organic matter respiration and consequent fluxes of $CO_2$ and methane have been reported for various (sub-) tropical floodplains. These variations have not yet been linked to a governing mechanism. In rivers, hydrological storage and increased residence times have been identified as factors increasing aquatic respiration (Battin et al., 2008).
In the Barotse Plains, the lack of correlation between O$_2$ concentration and NPP and respiration strongly suggested that the changes in oxygen concentration in the river were not caused by in-stream respiration processes, but were dominated by the mixing with oxygen-depleted floodplain water. This has previously been shown to cause in-stream oxygen conditions to drop along the Kafue Flats (Zurbrügg et al., 2012). During rising water levels, oxygen concentrations decreased and carbon dioxide concentrations increased simultaneously as a function of the travel time over the floodplain (Fig. 2.9). During receding water levels, longer travel times still led to lower oxygen concentrations and raised pCO$_2$, though they were not of the magnitude as observed during rising water levels. A negative correlation between oxygen and carbon dioxide concentrations has previously been reported for the Zambezi, with lowest oxygen values observed downstream of floodplain systems (Teodoru et al., 2015).

![Figure 2.9 Relationship between oxygen and carbon dioxide concentrations in the river at Senanga, as a function of travel time over the floodplain. Data missing between March 11 and April 12 due to instrument malfunction.](image)

Considering these observations, we suggest that travel time of the flood pulse could be a determining factor for the extent of organic matter degradation in river-floodplain systems. We hypothesize that at short travel times, organic matter is simply transferred from the floodplain to the river to be degraded further downstream, whereas at longer travel times the degradation processes are occurring on the floodplain. As such, riverine CO$_2$ emissions would also shift from the floodplain system to downstream ecosystems as travel times get shorter.
To test this hypothesis for other systems, seasonal information on both hydrology and biogeochemistry is needed, which is somewhat scarce for (sub-) tropical floodplains and wetlands. In floodplains and marshes in the Murray-Darling Basin (Australia), respiration rates were found to be higher than the rates measured in the river channel (Kobayashi et al., 2013). This is in contrast to Amazonian floodplains, where Richey et al. (2002) proposed that in-stream respiration of terrestrially-derived organic matter was driving CO$_2$ evasion rates. A more detailed analysis of travel times could possibly reconcile such divergent observations. The floodplain and swamp areas in the Murray-Darling basin have limited connectivity to the main channel, so there would be very little delivery of organic matter to the main channel. At these very long travel times, emissions of greenhouse gases linked to organic matter degradation originate from the floodplain. At the downstream end of Richey et al.’s (2002) study area in the Amazon catchment, simulated water levels were estimated to be ahead of the observed water levels by 15-25 days (Paiva et al., 2013). This discrepancy was caused by the flood retention by the floodplain.

These studies suggested different locations where organic-matter degradation occurred, and we suggest that this can be explained by the varying travel times over these three floodplain systems. In the Amazon, at shorter travel times, degradation was assumed to occur in the main channel, whereas in the Murray-Darling, at very long travel times, degradation of organic matter and emissions of CO$_2$ occurred on the floodplain. So in general, during times of short and intermediate travel times (roughly up to three weeks), a larger fraction of terrestrially-derived organic matter would be degraded in the main channel of a tropical river, as was found in the Amazon catchment and at shorter travel times in the Zambezi. This means that emissions from floodplains are smaller at such times, but that downstream systems could have uncharacteristically high emission rates due to floodplain inputs of labile organic matter at shorter travel times. At longer travel times, degradation occurs on the floodplain, and high emissions of greenhouse gasses can be found there, as in the Murray-Darling study.

This preliminary comparison shows that a more detailed analysis based on travel times could potentially reconcile apparently conflicting spatial patterns in different floodplain systems and therefore contribute to a general understanding
of tropical floodplain dynamics. This concept provides a governing mechanism for the trend of increasing riverine \( p\text{CO}_2 \) values with increasing wetland coverage in tropical catchments (Borges et al., 2015a). Recent work showed how the retention time of water in freshwater ecosystems is driving the remineralization rates of organic matter, and suggested a strong connection between catchment hydrology and carbon processes in inland waters (Catalan et al., 2016). Our results further highlight this connection between flood cycles and river-floodplain greenhouse gas emissions.

Conclusions

Our data highlights the need for time series, rather than snap shots to improve our understanding of highly dynamic river-floodplain systems. We showed that the calibrated data of DOC, SPM, and \( \text{CO}_2 \) concentrations from high-resolution sensor data can be obtained for full flooding cycles in remote areas, and that such approaches provide opportunities to reveal patterns and processes.

Oxygen, DOC, \( \text{CO}_2 \), and SPM concentrations in the river exhibit hysteresis behavior in relation to discharge and travel time of the water over the floodplain. There are distinctly different regimes during rising and falling water levels, with potentially different sources of organic matter. We propose three phases to describe these different regimes, from expansion to maximum to contraction. Relationships between travel time of the flood pulse and oxygen and carbon dioxide concentrations highlight how hydrological conditions drive the biogeochemistry in tropical river-floodplain systems. This interaction between hydrology and biogeochemistry implies that floodplains become more intense hotspots for greenhouse gases at longer travel times of the flood pulse.
Acknowledgements

The authors thank Christian Dinkel and Kristina Peterson for fieldwork assistance. A big thank you to Gerard and Graham from Barotse Tiger Camp and to Mr. Charles from Senanga Safaris for hosting the probes. Discussions with Christian Teodoru were very much appreciated, and comments from Marie-Sophie Maier, our editor Chris Evans, and two anonymous reviewers helped improve the manuscript. Prof. Imasiku Nyambe (University of Zambia and its Integrated Water Resource Management Center), the Zambia Wildlife Authority, and the Zambezi River Authority (specifically Mr. Sakala) provided institutional support. Funding for this study came from the Competence Center for Environment and Sustainability (CCES) of the ETH domain, the Swiss National Science Foundation (Grants No. 128707 and 157750) and Eawag.
Appendices

Appendix 2.1: Deployment Description

The WTW EXO2 multi-probes were deployed early November 2013, at Barotse Tiger Camp (GPS S14°32.016’ / E023°08.790’) and Senanga Safaris Lodge (GPS S16°05.972’ / E025°17.777). At Barotse Tiger Camp, the probe was kept floating by two buoys (empty containers), and kept in place above the deepest area of the channel by rope connections to the shore and to poles on a sandbank. At Senanga Safaris Lodge, the probe was deployed underneath a floating jetty, on the outer curve of the river. Both probes were set to measure at hourly intervals for one minute, which would be averaged to obtain a single value. A brush wiped the sensors before each in order to remove biofouling and ensure optimal performance of the optical sensors.

The probes were operated on 4 large (D) batteries, which would last roughly 200 days. Servicing was done in April 2014 at both locations. Servicing involved retrieving the data, replacing the batteries, removing biofouling, and recalibration of the pH probe. In Senanga, recording had ceased early March (March 11). The temperature and conductivity sensor was clearly malfunctioning when new batteries were inserted, giving values of several millions degrees Celsius. We assume that a tree log or some other big piece of debris hit the probe, which has caused the temperature/conductivity sensor to short-circuit. During servicing, a new temperature/conductivity sensor was installed.

For the remainder of the year, the probe was (accidentally) set up to measure every 9 hours. In Senanga, the probe was still functioning upon retrieval (September 2014), but had become trapped on land. The floating jetty had been hauled ashore, without regards for the probe deployed underneath. Luckily, the muddy environment affected the oxygen probe, which made it very easy to spot the exact moment that the probe had come ashore, end of July 2014. In Lukulu, the probe disappeared early September 2014, and was found (without its ropes, cables, and buoys) discarded in the bush several kilometers further downstream several weeks later. There has been no data recorded on the probe; whether this is due to the theft or an error in deployment cannot be traced.
Figure S2.1 Pictures of the probe after 5 months deployment: organisms have colonized the outside of the sensors, while the brush has prevented biofouling of the optical sensors.
Appendix 2.2: Performance of the conductivity-alkalinity correlation and error propagation

To test the performance of the correlation between conductivity and alkalinity, we’ve calculated the ratio between the correlation alkalinity value and the measured or DIC-calculated value (Table S2.1). In addition, we have also looked how this ratio might be improved if we separate our data back into the two different seasons (Fig. S2.2). While using one correlation increases the strength of the correlation ($r^2$), but the overestimation is slightly larger (Table S2.1). The difference during the dry season is very minimal and probably not significant. However, we did decide to go with only one correlation, because there is no mechanistic understanding why we would have the division between the two correlations at 100 µS cm$^{-1}$. In addition, the fact that we have only sampled the extreme seasons (so far) makes this cut-off value somewhat random, and disregards the dynamics during the more dynamic periods of the hydrograph.

While the correlation between conductivity and alkalinity is fairly strong, it is definitely not perfect. The higher conductivity (and alkalinity) values of the dry season have a strong influence on the correlation, leading to an overestimation of alkalinity values during the wet season. The ratio between correlation-derived values and the measured or DIC-calculated alkalinity values varies between 0.95 and 2.10 during the wet season (mean 1.30; median 1.20), and between 0.91 and 1.05 during the dry season (mean 0.97; median 0.98; see above). Such an overestimation would propagate throughout the subsequent calculations, resulting in larger concentrations and evasive fluxes of CO$_2$. However, we estimate the highest CO$_2$ concentrations during high conductivity conditions. Therefore, error propagation from the conductivity-alkalinity correlation would be most noticeable at receding flows, when we actually report lowest CO$_2$ concentrations, which could be even more depleted due to this overestimation.
Figure S2.2 Separate correlations between alkalinity and conductivity for the wet season (circles) and the dry season (triangles), more details of which can be found in Table S2.1.

Table S2.1 Performance of one correlation (including both seasons) and two correlations (division at 100 µS cm\(^{-1}\)) between conductivity and alkalinity, expressed as the ratio between correlated alkalinity values and measured or DIC-calculated alkalinity values, and the correlation properties.

<table>
<thead>
<tr>
<th></th>
<th>Mean</th>
<th>Med.</th>
<th>Min.</th>
<th>Max.</th>
<th>Slope</th>
<th>Intercept</th>
<th>(r^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>One correlation</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet season</td>
<td>1.29</td>
<td>1.20</td>
<td>0.95</td>
<td>2.10</td>
<td>0.011</td>
<td>-0.156</td>
<td>0.93</td>
</tr>
<tr>
<td>Dry season</td>
<td>0.98</td>
<td>0.99</td>
<td>0.91</td>
<td>1.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Two correlations</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet season</td>
<td>1.17</td>
<td>1.09</td>
<td>0.85</td>
<td>1.96</td>
<td>0.010</td>
<td>-0.137</td>
<td>0.85</td>
</tr>
<tr>
<td>Dry season</td>
<td>0.99</td>
<td>1.02</td>
<td>0.85</td>
<td>1.07</td>
<td>0.010</td>
<td>-0.041</td>
<td>0.94</td>
</tr>
</tbody>
</table>
Appendix 2.3: Dynamic Time Warping

At the two measurement locations, water level is determined daily by the Zambezi River Authority. As a consequence of flooding over the riverbank during high discharge, there are no rating/gauging curves available for these two stations. Based on visual observations it is clear that there is a lag period between the two records, and that this lag is not constant through time. In order to gain a quantitative measure of this lag period, or in other words the time the flood pulse needs to travel from Lukulu to Senanga, we have applied a Dynamic Time Warping procedure to the data, using the \texttt{dtw} package in \texttt{R} (Giorgino, 2009). Application of different step patterns yielded somewhat different results (Fig. S2.3): based on visual matching we have decided to use the data generated using the mori2006 step pattern (Mori et al., 2006) to calculate the lag times presented in the manuscript.

The peak in travel time during the first few months seems also to be to some extent caused by calculation artifacts: there are a lot of small wiggles in the normalized water level records, which the program tries to link (Fig. S2.3). This leads to unrealistically high travel times at the start of our time series. To counteract this calculation artifact, we have manually altered the record, to increase from a travel time of 3 days (based on April 2013 ADCP measurements) to the 8 days observed at the saddle point between the first two extremes.

Besides unrealistically high travel times in the first months, some of the calculation procedures also result in negative travel times, most noticeable in the “Symmetric2” step pattern. Additionally, travel times drop to zero at the end of the record. This is due to settings at the beginning and end. Still, this was visually still the best fit.
Figure S2.3 Dynamic Time Warping analysis, comparison of four different step patterns: symmetric1, symmetric2, asymmetric, mori2006, which were all calculated with closed beginnings and ends. Solid black line represents the normalized water level at Lukulu, the dotted red line represents the record at Senanga.
Appendix 2.4: Seasonal behavior of conductivity and pH, affecting CO$_2$ concentrations

Conductivity shows a clockwise hysteresis effect, with values decreasing with increasing discharge (Fig. S2.4a). During falling water levels, the conductivity of the river water increases slowly again towards the maximum values observed at the end of the dry season. Unfortunately, due to the deployment issues (see different section), we are lacking data between August and early November, during which period the strongest increase in conductivity is expected.

![Conductivity vs. Discharge](image1)

**Figure S2.4** Relationships between conductivity and discharge and pH and discharge at Senanga.

Since conductivity measures the conductance, which increases with higher ion concentrations, it makes sense that the conductivity would decrease with increasing discharge. Increasing discharge results in a dilution of the initial water mass, leading to lower ion concentrations (e.g. Ca$^{2+}$ 91 µM during peak flow, 360 µM during lowest flow in Lukulu). During falling water levels, the fraction of upstream river water (groundwater derived) slowly increases relative to the fraction of floodplain water. This mixing of high-conductivity water from the upstream river and low-conductivity, diluted water from the floodplain slowly decreases the conductivity in the main river. Similar conductivity patterns, with lowest values around peak flood, have also been observed in the Okavango delta (Mladenov et al., 2005).
pH on the other hand shows no hysteresis effect, but is simply decreasing with increasing discharge, and increasing at the same pace when water levels drop (Fig. S2.4b). Devol et al. (1995) already recognized similar seasonal behavior of pH in the Orinoco and Amazon Rivers (their data and of Lewis and Saunders, 1989), with minimum pH occurring at maximum discharge and maximum pH at low flows. These authors speculated that the link between dissolved gas concentration and river depth could be a common feature of large, tropical rivers with extensive floodplain areas. The contrasting patterns in conductivity and pH lead to a second, smaller maximum in CO$_2$ concentrations around July.
Chapter 3
Organic matter dynamics in a tropical river-floodplain system

Alissa Zuijdgeest
Negar Haghipour
Lukas Wacker
Francien Peterse
Bernhard Wehrli
Tim Eglinton

in preparation for publication
Abstract

In global estimates there remains large uncertainty about the composition of organic carbon transported by tropical and subtropical large river systems. Floodplain systems have been recognized for their potential to alter fluvial carbon fluxes and emit greenhouse gases, but little comprehensive work has been done on the role of large African floodplains on the composition of the fluvial organic matter. In this study, we investigate the composition of the particulate organic matter transported by the Zambezi River during its passage through the Barotse floodplain under different hydrological conditions to determine whether, how, and when river-floodplain interactions alter the composition of the organic matter. The composition of the particulate organic matter is characterized by bulk properties, including stable and radiocarbon content, along with several biomarkers to study contributions of plant waxes and soil microbial lipids. Distinct differences can be observed in abundances and patterns along the floodplain during different times of the hydrograph. However, during all seasons, soil-derived organic matter contributes significantly to the fluvial organic matter. During times of inundation, this material mostly derived from topsoils, whereas during periods of low flow deeper mineral soils are the likely source. In addition, contributions from vegetation change from floodplain vegetation during inundation to terrestrial plants at low-water conditions. Degradation along the floodplain occurred during falling and low water. The composition of the fluvial organic matter changed markedly along the floodplain and these signals persist downstream until the river flows into the Kariba reservoir.
Introduction

On a global scale, tropical rivers exert important controls on the flux and transformation of terrestrial organic matter that is delivered to the oceans. On regional scales, these large rivers are highly dynamic systems that millions of people depend upon for their livelihoods. Because of the strong seasonality in rainfall and resulting fluvial discharge, large expanses of low-lying terrain regularly flood, forming extensive floodplain areas bordering the river. Such extensive floodplain systems tend to occur in river systems developed on passive margins (Blair and Aller, 2012). Seasonal inundation of the river-floodplain system results in complex hydrological and biochemical processes that create distinct soil conditions and vegetation patterns, differing markedly from terrestrial and aquatic ecosystems bordering the floodplain (Mitsch and Gosselink, 2007). Tropical floodplains are sites of enhanced biological productivity (Mitsch et al., 2010). The temporal cycle of inundation and resultant biological activity has been described in the Flood Pulse Concept (Junk et al., 1989). Floodplains are considered regions of extensive carbon remineralization (e.g. Abril et al., 2014; Borges et al., 2015a) and hotspots of organic matter exchange between the aquatic and terrestrial ecosystems (Galy et al., 2008).

As a consequence of the high temporal variability in floodplain characteristics, the river transports material from different sources throughout the year. Understanding the sources and composition of the particulate matter transported by rivers is important in order to understand the role of fluvial systems in the global carbon cycle and the origin of organic matter signals preserved in river-proximal sediment records. For example in the Amazon, exchange between the river and its floodplain changes the composition of the particulate organic matter transported downstream (Moreira-Turcq et al., 2013). In a floodplain system within the Okavango delta, dissolved organic matter inputs changed from plant-leached material during rising water levels to microbially-derived sources during flood recession (Mladenov et al., 2005). Though the Epulu River in Congo is bordered by swampy forests instead of actual floodplains, this river is characterized by higher inputs of vascular plant material to the riverine dissolved organic matter
during high water levels (Spencer et al., 2010).

In tropical and subtropical rivers, riverine organic matter generally has a young radiocarbon age, suggesting a predominant origin from recently synthesized biomass and/or rapid carbon turnover of source materials. From both a global and a tropical perspective, the age of the riverine organic matter tends to increase with increasing concentration of suspended particles in the river (Marwick et al., 2015). In the Amazon, radiocarbon contents of suspended organic matter suggests that a mixture of present-day plant debris (coarse suspended matter, 65-3000µm) and soil organic carbon (fine suspended matter, 0.5-65µm) is transported by the river (Hedges et al., 1986c). More recently, it has been suggested based on research in the Amazon basin that in humid regions a small, and rapidly cycling pool of young organic matter (< 5 years), likely originating primarily from riparian and floodplain \( \text{C}_4 \) grasses, is responsible for large carbon dioxide fluxes from major river systems to the atmosphere (Mayorga et al., 2005).

Different sources of organic matter can be further disentangled using diagnostic molecular signatures. Various biomarker proxies are based on the abundance and distribution of source-specific biomolecular tracer compounds such as higher plant waxes (\( n \)-alkanes) or membrane lipids of soil microorganisms (glycerol dialkyl glycerol tetraethers, GDGTs). For example, \( n \)-alkane \( C_{31}/C_{27} \) ratios can be used to differentiate between tree/shrub-dominated ecosystems \( (C_{27}) \) and grass/herb-dominated ecosystems \( (Zech et al., 2010) \). Similarly, the relative proportion of mid-chain \( (C_{23}, C_{25}) \) to long-chain \( n \)-alkanes \( (C_{29}, C_{31}) \) has been used to determine the inputs of aquatic macrophytes \( (Ficken et al., 2000) \). Branched GDGTs dominate in soils, and it has been hypothesized that they are produced by anaerobic microorganisms in anoxic micro-habitats \( (Weijers et al., 2006) \). Methanogens in anoxic soils have been found to produce GDGT-0, but no crenarchaeol \( (Blaga et al., 2009) \).

However, while the organic matter dynamics in the expansive Amazon floodplain has been relatively well-studied, much less is known about the molecular composition and sources of organic matter in (sub)tropical rivers and their floodplains in Africa, and in particular about the role of floodplains in modulating materials exported from these systems. Most studies in the latter have focused on
a specific suite of markers (e.g., lignin-derived phenols), or have relied on stable or radiocarbon isotopes of the particulate matter to deduce organic matter sources (e.g. Alin et al., 2008, Bird et al., 1994, Marwick et al., 2014a, and Spencer et al., 2010). In contrast, multiple studies have used biomarkers to reconstruct paleo-environmental conditions in different parts of Africa from sediment records (e.g. Castañeda et al., 2016; Schefuß et al., 2011; Schefuß et al., 2016). Recent work in the Congo basin (Hemingway et al., 2016) has shown catchment-integrated seasonal variations in biomarker contents exported from this major river system. However, to our knowledge, little comprehensive biomarker research has been performed inside these African river-floodplain systems, or any (sub)tropical floodplain system outside of the Amazon basin.

In working towards closing this information gap, we have examined the evolution of fluvial suspended particulate organic matter composition during its transit through a pristine floodplain system (Barotse Plains) within the Zambezi catchment. Previous research in this area has highlighted the importance of river-floodplain interactions for organic matter remineralization and CO$_2$ respiration during downstream transport (Zuijdgeest et al., 2015; Zuijdgeest et al., 2016). In addition, it has been hypothesized recently (Zuijdgeest et al., 2016) that during the dry season and early flooding stages the input to the suspended matter mainly originates from dry soil material and withered vegetation, whereas after peak flow the newly sprouted vegetation is mostly responsible for the organic matter transported downstream by the river.

In this study, we examine a suite of biomarker signatures in order to investigate the origin of the particulate organic matter transported by the Zambezi River during its passage through the Barotse floodplain under different hydrological conditions, and to determine whether, how, and under which hydrologic conditions floodplain processes attenuate, modify and/or augment the river main stem signals.
Methods

Study site

Of the four largest fluvial systems in Africa, the Zambezi River \(1.4 \times 10^6 \text{ km}^2\) is the only river draining into the Indian Ocean. The catchment area spans eight different countries between 10° and 20°S. This location ensures yearly wet (December-March) and dry seasons (April-November). As a consequence, discharge is highly variable during the year and at various locations large floodplain areas are inundated seasonally. The Barotse Plains in western Zambia is one of these large floodplain areas in the Zambezi catchment that seasonally inundate, with a maximum inundated area of roughly 7,700 km² (Hughes and Hughes, 1992).

The Barotse Plains extend roughly from Lukulu to Senanga, slightly more than 200km in length, with a maximum inundation width of 40 km. The floodplain area and most of the upstream catchment is underlain by Kalahari sandstone, though further downstream outcrops of basalt can also be observed. The vegetation in the upstream part of the catchment has been qualified as a mixture of deciduous forest, grasslands, and so-called Miombo woodlands (Fig. 1; Timberlake, 2000). On the floodplain, extensive grasslands are interspersed with occasional clumps of trees (Timberlake, 2000; Zambezi Society, 2000). The specific floodplain vegetation includes papyrus, rushes, and reeds, along with introduced species like water hyacinths, water lettuce, and water fern. Around floodplain seeps, peaty soils contain a richer flora and support vegetable cultivation (Zambezi Society, 2000). Soils in the floodplain are mainly gleysols (water-logged soils that are not salty) and arenosols (sandy soils with little profile development), according to the soil map from FAO/UNESCO from 1992, as presented by Gerrits (2005).
Figure 3.1 Zambezi River Basin vegetation map (SADC/SARDC and others, 2012), with the Barotse Plains outlined in black.

Sample collection

During various field campaigns (April 2013 (high water HW), October 2013 (low water LW), and June 2015 (falling water FW)), surface water (2.5 - 14 L) has been filtered through pre-combusted 90mm GF/F filters (0.7µm, Whatman) to obtain the suspended matter transported by the river. Samples were collected just upstream of and along the Barotse Plains, and included several tributaries (Fig. 3.2). Additional topsoil and plant samples were collected at various locations. All samples were freeze-dried before analysis. All plots in this manuscript will show samples upstream of the defined floodplain area from the Zambezi and the Lungwebungo and Luanginga tributaries, with the first floodplain sample collected downstream from the zone of mixing of the Zambezi and the Lungwebungo (based on field observations).
Figure 3.2 Map of the Zambezi catchment with the Barotse Plains expanded in the insert. Sampling stations during the low-water campaign are shown as circles, sampling stations visited during high and falling water levels are shown with stars. An additional sample at Senanga was collected during falling water. The samples downstream of the dam differ in location between high water and the other two seasons: during the former it was collected at Chirundu, during the latter it was collected roughly 5km downstream of the dam.
Laboratory analyses

**Bulk analyses**

Bulk carbon and nitrogen content and carbon and nitrogen stable isotopic composition of the samples were determined by elemental analyzer isotope ratio mass spectrometer (EA-IRMS; ThermoFinnigan FlashEA 1112 coupled to a DeltaV Advantage Continuous-Flow IRMS) and calibrated against in-house standards ($\delta^{13}$C: −15 to −30 ‰VPDB; $\delta^{15}$N: −3 to +6 ‰air). For radiocarbon content, the filters were fumigated with 37% hydrochloric acid for 72 hours at 60°C. Acid fumes were removed using sodium hydroxide (48 h) and samples were stored in a desiccator until analysis. From each sample, 4 cm$^2$ was cut out, which corresponded to 100-500 µg C. Analysis was performed on an EA-Accelerator Mass Spectrometer (AMS) system (Micadas) at ETH Zürich (Christl et al., 2013). Several blank filters and blank filters spiked with standards (oxalic acid HOxII, F$^{14}$C = 1.34 and phthalic anhydride, F$^{14}$C = 0) were included to assess the blank contamination (Appendix 1). Soil pH was determined after thoroughly mixing 10 grams of freeze-dried bulk soil samples with 25 mL of de-ionized water.

**Biomarker analysis – plant waxes**

Samples for biomarker analysis were extracted in 9:1 dichloromethane:methanol (DCM:MeOH) in a CEM Mars Xpress Microwave. Resulting solvent extracts were saponified and separated by liquid-liquid extraction into a neutral fraction (hexane) and, after acidification to pH 2, an acid fraction (Hexane:DCM 4:1). The neutral fraction was split into an apolar (n-alkanes; Hexane:DCM 9:1) and a polar fraction (GDGTs; DCM:MeOH 1:1) by eluting over a silica gel column (2-5% deactivated). The apolar fraction was analyzed on a gas chromatograph equipped with flame ionization detection (GC-FID; Agilent Technologies 7890A GC system, HP5 column 30m x 0.320mm i.d., 0.25 µm film thickness) and quantified against an external standard mixture (Fluka C$_{21}$-C$_{40}$ alkanes). The acid fraction was derivatized with boron trifluoride (BF$_3$)-MeOH (30min, 80°C), and resulting fatty acid methyl esters (FAMEs) purified by elution over a silica gel column topped with NaSO$_4$.
The FAMEs were eluted using 4mL Hexane:DCM (4:1), analyzed by GC-FID and quantified against an external standard (Supelco C₄-C₂₄ even-carbon-numbered FAMEs).

A small subset of samples, upstream and downstream of the floodplain during the three different seasons, was also subjected to compound-specific stable carbon isotopic analysis of alkanes and fatty acids using a Thermo Scientific Trace GC Ultra coupled to a Delta V isotope ratio MS. Due to lack of isotopic measurement of the BF₃-MeOH, no correction for the methylation could be applied, so reported d¹³C data for the fatty acids are internally consistent but are not absolute.

Proxies

We calculated the average chain length (ACL) from the weight-averaged number of carbon atoms in higher plant C₂₇-₃₅ n-alkanes and C₂₄-₃₄ n-fatty (alkanoic) acids. The n-alkane C₃₁/C₂₇ ratios can be used to differentiate between tree/shrub-dominated ecosystems (C₂₇) and grass/herb-dominated ecosystems (Zech et al., 2010). Using the differences in most abundant n-alkane chain lengths found in different types of vegetation, the P.aq ratio (Ficken et al., 2000) can be used to trace inputs of terrestrial, emergent, and submerged vegetation. It is defined as the relative proportion of the C₂₃ and C₂₅ homologues compared to C₂₉ and C₃₁. The carbon preference index (CPI) shows the odd-over-even dominance of a sample, and can provide an indication of petrogenic or anthropogenic hydrocarbon contamination, or the extent of degradation of plant input materials. Changes in the terrigenous/aquatic mixture of fatty acids can be described using the TARₚₐ ratio (Bourbonniere and Meyers, 1996). The molecular isotopic signature of the C₃₁ n-alkane can be used to estimate the woody plant cover and the ecosystem type when soil organic matter has a δ¹³C value between -22 and -40‰ (Magill et al., 2013).
Table 3.1 Alkane and fatty acid proxies

<table>
<thead>
<tr>
<th>Proxy calculation</th>
<th>Eq.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ACL_{\text{alkanes},27-35} = \frac{\sum^{m}<em>{i=3}(2i+1) \cdot [C</em>{2i+1}]}{\sum^{m}<em>{i=3}[C</em>{2i+1}]} ) with ( n = 13, m = 17 )</td>
<td>(3.1)</td>
<td></td>
</tr>
<tr>
<td>( ACL_{\text{fatty acids},24-34} = \frac{\sum^{m}<em>{i=3}2i \cdot [C</em>{2i}]}{\sum^{m}<em>{i=3}[C</em>{2i}]} ) with ( n = 12, m = 17 )</td>
<td>(3.2)</td>
<td></td>
</tr>
<tr>
<td>( CPI = \frac{\sum \text{odd } C_{21-35}}{\sum \text{even } C_{20-34} + \sum \text{even } C_{22-36}} )</td>
<td>(3.3)</td>
<td></td>
</tr>
<tr>
<td>( TAR_{FA} = \frac{C_{24} + C_{26} + C_{28}}{C_{12} + C_{14} + C_{16}} )</td>
<td>(3.4)</td>
<td>a</td>
</tr>
<tr>
<td>( P.\text{aq} = \frac{C_{23} + C_{25}}{C_{23} + C_{25} + C_{29} + C_{31}} )</td>
<td>(3.5)</td>
<td>b</td>
</tr>
<tr>
<td>( f_{\text{woody}} = (\sin(-1.3530 - 0.08538 \cdot \delta^{13}C_{31}))^2 )</td>
<td>(3.6)</td>
<td>c</td>
</tr>
</tbody>
</table>


Biomarker analysis – GDGTs

The polar fraction, containing the GDGTs, was analyzed after filtration through a 0.45µm PTFE filter using a modified version (Schouten et al., 2007, as described by Peterse et al., 2012) on a high performance liquid chromatography/atmospheric pressure chemical ionization-mass spectrometry (HPLC/APCI-MS; Agilent Technologies 1260 Infinity coupled to a 6130 Quadrupole MS, Grace Prevail cyano column (150 mm x 2.1 mm, 3 µm), preceded with a guard column with the same packing). Quantification was obtained using an internal standard (\( C_{46} \) GDGT internal standard (m/z 744)). A small subset of samples, upstream and downstream of the floodplain during the three different seasons, was measured using the novel GDGT method with improved chromatography (Hopmans et al., 2016) in the Organic Geochemistry laboratory at Utrecht University (Ultra High Performance Liquid Chromatograph Agilent 1290 coupled to an Agilent 6310 quadrupole MS; two silica Waters Acquity UPLC HEB Hilic (1.7µm, 2.1x150mm) columns with a guard column of the same material). Based on the results from the subset measured with improved chromatography (Appendix 2), we conclude that values returned from the traditional approach provide a reasonable approximation of environmental conditions, though care is needed when comparing abundances determined using the two different methods.
Proxies

The branched isoprenoid tetraether (BIT) index (Hopmans et al., 2004) has been used to trace the contribution of soil-derived organic matter to marine sediments, and while crenarchaeol is also present in soils, corresponding BIT values are typically >0.90 (Weijers et al., 2006). A correlation between soil pH and the degree of cyclisation in the soil GDGTs has been found (Weijers et al., 2007), so that we can use the relative abundances of the GDGTs to trace back soil pH, with the cyclisation ratio of branched tetraethers (CBT) defined as in Weijers et al. (2007). Similarly, strong correlations between soil GDGT composition and mean annual air temperature (MAT) were recognized (Weijers et al., 2007). These correlations have been updated since, with a more extensive dataset (Peterse et al., 2012). For the CBT and pH reconstructions, we use the definitions of Weijers et al. (2007) while the original dataset contained a larger fraction of tropical soils. For the MAT reconstructions, we used the simplified definitions from Peterse et al. (2012).

Table 3.2 GDGT proxies.

<table>
<thead>
<tr>
<th>Proxy calculation</th>
<th>Eq.</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIT index = [\frac{[GDGT - Ia] + [GDGT - IIa] + [GDGT - IIIa]}{[Crenarchaeol] + [GDGT - Ia] + [GDGT - IIa] + [GDGT - IIIa]}]</td>
<td>(3.7)</td>
<td>a</td>
</tr>
<tr>
<td>CBT = [-\log{\left(\frac{[GDGT - Ib] + [GDGT - IIB]}{[GDGT - Ia] + [GDGT - IIa]}\right)}]</td>
<td>(3.8)</td>
<td>b</td>
</tr>
<tr>
<td>CBT = 3.33 - 0.38 * pH</td>
<td>(3.9)</td>
<td>b</td>
</tr>
<tr>
<td>MBT' = [\frac{[Ia] + [Ib] + [Ic]}{[Ia] + [Ib][Ic] + [IIa] + [IIb] + [IIc] + [IIIa]}]</td>
<td>(3.10)</td>
<td>c</td>
</tr>
<tr>
<td>MAT = 0.81 - 5.67 * CBT + 31.0 * MBT'</td>
<td>(3.11)</td>
<td>c</td>
</tr>
</tbody>
</table>

Results

Floodplain trends

Bulk properties

Along the course of the floodplain, particulate organic carbon (POC) concentrations decreased during high water and increased during low water (Fig. 3.3a). During falling water levels, there was little variation between the concentrations upstream and downstream of the floodplain, but a clear maximum was observed in the middle of the floodplain. The molar ratio of POC to particulate nitrogen (PN) varied between 8 and 14 during the different seasons (Fig. 3.3b). During high water, the ratio decreased shortly after the river entered the floodplain, and remained around 10 at downstream locations. During falling and low water, higher POC:PN ratios were observed roughly halfway along the floodplain, but the values at the downstream end were around 10, similar to high-water conditions.

The stable carbon isotopic composition (d^{13}C values) of POC varied between -30 and -24‰, with highest values observed during falling water and at the downstream end of the floodplain (Fig. 3.3c). Lowest d^{13}C values were observed during low water. While no clear longitudinal trend was present during high water, during the other two seasons the signature of the organic matter moved towards heavier values in downstream direction. The radiocarbon age of the POC varied little along the floodplain, or between high- and falling-water conditions (Fig. 3.3d). However, corresponding F^{14}C values were distinctly lower during periods of low flow, indicating transport of older organic matter.
Figure 3.3 Bulk properties of the suspended particulate matter along the Barotse Plains during high water (blue squares), falling water (orange circles), and low water (green triangles). a) particulate organic carbon concentrations; b) molar ratio between particulate organic carbon and particulate nitrogen; c) stable isotopic signal of the organic carbon; d) fraction modern of the organic carbon. Colored symbols represent SPM from the main channel, open symbols SPM from tributaries.

**Plant waxes**

The abundance of long-chain \(n\)-alkanes to total organic carbon was low during high water conditions (Fig. 3.4a). During falling water levels, the abundance was higher and showed a clear decreasing trend with distance along the floodplain. Abundance was highest during low water conditions. Between the upstream and downstream ends of the floodplain, alkane average chain length (ACL) was largely invariant across all seasons, with values typically between 28 and 29 (Fig. 3.4b). However, minimum values were observed at different distances along the floodplain during the different seasons: during high water the minimum ACL was observed at the second-to-last station, whereas during falling water the minimum was found roughly in the middle of the floodplain. During low water, sampling resolution was too low to discern a pattern. The \(C_{31}/C_{27}\) ratio, which varies between 0.4 and 2.8, suggests that the organic matter transported by the Zambezi
along the Barotse Plains derives from a mixture of grasses and other terrestrial vegetation (shrubs, trees) year-round (Fig. 3.4c). During high water levels, the contribution of tree inputs exhibits a slight increase downstream, and there was one location fairly upstream with high grass inputs. During falling water levels, the $C_{31}/C_{27}$ ratio decreased where the river entered the floodplain and remained stable in the downstream direction. The $P_{aq}$ value was well above 0.1 during all seasons, indicating significant contributions of aquatic vegetation (Fig. 3.4d). The $P_{aq}$ value during the dry season was around 0.3, in the range of emergent macrophytes. In the middle of the floodplain, values increased to 0.6. During high water levels, values at the upstream end of the floodplain were in the range of emergent macrophytes, and increased downstream to reach values characteristic of submerged macrophytes. When water levels fell, the $P_{aq}$ value increased slightly along the floodplain, reaching values around 0.4. Such values are at the boundary between emergent and submerged macrophytes (Ficken et al., 2000).

The contribution of long-chain (i.e., $> C_{24}$) fatty acids to the organic carbon transported increased along the floodplain during high water conditions, from 0.2 to 1.5 mg/gC, and a much smaller increase was observed during low water (Fig. 3.4e). The average chain length of the long-chain fatty acids was even more stable than the corresponding ratio of the alkanes (Fig. 3.4f), with values varying between 26 and 28. During falling water levels, the abundance of long-chain fatty acids decreased along the floodplain. The $TAR_{FA}$ ratio was lowest during low-water conditions, but with an increasing trend along the floodplain (Fig. 3.4g). No clear trend was visible during periods of high or falling water. Values during high water varied around 0.4 and around 0.2 during falling water.
Figure 3.4 Characteristics of the plant waxes in the suspended particular matter along the Barotse Plains during high water (blue squares), falling water (orange circles), and low water conditions (green triangles). a) Abundance of long-chained \( n \)-alkanes (C\(_{27}\)-C\(_{35}\)); b) Average Chain Length of the long-chain alkanes; c) ratio of C\(_{31}\) over C\(_{27}\) alkanes; d) Paq ratio; e) abundance of long-chained fatty acids (C\(_{24}\)-C\(_{34}\)); f) Average Chain Length of the long-chain fatty acids; g) TAR\(_{FA}\) ratio. Colored symbols represent SPM from the main channel, open symbols SPM from tributaries. A comparison between normalization per gram carbon or per gram sediment is presented in Appendix 3.
Compound-specific stable carbon isotopic signatures

The stable carbon isotopic composition of individual long-chain \((C_{24+})\) fatty acids became more \(^{13}\)C-enriched (higher \(\delta^{13}\)C values) along the floodplain, while corresponding abundances of the long-chain fatty acids decreased (Fig. 3.5). \(\delta^{13}\)C values also increased with increasing carbon number. The abundance-weighted FAME-\(\delta^{13}\)C values increased along the floodplain from -35.0 to -29.2‰, while the summed concentration of long-chain fatty acids decreased (Appendix 4). The abundance-weighted isotopic signal of the long-chain fatty acids also increased along the floodplain during all seasons, but how the different seasons compare at one location varied. Except for the upstream location, falling-water samples had the most enriched \(\delta^{13}\)C signature. In the upstream part of the floodplain, values were most depleted during low water, while in the downstream part the high-water measurements showed lowest \(\delta^{13}\)C values.

**Figure 3.5** Abundance (bars) and stable carbon isotopic signature of long-chain fatty acids (circles) at 4 locations upstream, downstream and within (Lukulu, Senanga) the Barotse Plains. Dashed line represents the abundance-weighted \(\delta^{13}\)C signal of the long-chain fatty acids.
In corresponding \( n \)-alkane fractions, some homologues were of insufficient concentration for reliable stable carbon isotopic determination, and no clear downstream trend could be discerned from the analyzed samples. However, based of \( \delta^{13}C \) values of \( n \)-\( C_{31} \) alkane, the fraction woody (Magill et al., 2013) decreased from 0.55 (woodland) to 0.41 (wooded grassland) from the upstream sampling location to Lukulu at the head of the floodplain.

**Soil microbial lipids**

During low water, total GDGT concentrations remained stable along the floodplain, ranging between 200-300 \( \mu g/gC \) (Fig. 3.6a). Total GDGT amounts at the upstream end of the floodplain during high water were lower than during low water, but showed a strong increase along the floodplain, approaching 500 \( \mu g/gC \). When water levels fell after high water, GDGT abundances were greater in the upstream part of the floodplain, but decreased to levels similar to those observed during low-water conditions in the downstream part of the floodplain.

The GDGT pool was dominated by branched GDGTs year-round, with patterns closely resembling the patterns observed in total GDGT concentrations (Fig. 3.6b). Among the isoprenoidal GDGTs, GDGT-0 showed a four-fold increase in abundance, similar to the branched GDGTs during high water (Fig. 3.6c). The other isoprenoidal GDGTs showed only a small increase along the floodplain as well during this season, with concentrations remaining below 5 \( \mu g/gC \) (not shown). The BIT index varied between 0.96 and 1.00 along the floodplain during all seasons (Fig. 3.6d), implying soil inputs dominate the GDGT signatures. The isomer ratios of penta- and hexamethylated 6-Me brGDTs (Sinninghe Damsté, 2016) were on average 0.55 and 0.65, respectively. One outlier was observed, upstream of the floodplain during low water.
Figure 3.6 Downstream trends in GDGT abundances along the Barotse Plains during high water (blue squares), falling water (orange circles), and low water conditions (green triangles). a) Total GDGTs; b) branched GDGTs; c) GDGT-0; d) BIT index. Colored symbols represent SPM from the main channel, open symbols SPM from tributaries. A comparison between normalization per gram carbon or per gram sediment is presented in Appendix 3.

Downstream of the floodplain

Not all changes along the floodplain persisted further downstream, and downstream of the Kariba reservoir the organic matter exhibited a largely different signature (Fig. 3.7). The carbon stable isotopic signal of POC remained fairly stable downstream of the floodplain towards Livingstone, but was distinctly more depleted after exiting the reservoir before increasing again towards Chirundu. Significant variations in the radiocarbon content of POC (expressed as fraction modern C) are only apparent during low water, with a minimum of 0.58 observed just downstream of the Kariba reservoir.

Plant wax signatures showed no clear downstream trend during high water: while the C_{31}/C_{27} ratio increased at Sesheke, a low value for P.aq was observed. During falling and low water, little variation was observed, except for a strong increase in C_{31}/C_{27} ratio just downstream of the reservoir. Concentrations of branched GDGTs increased along the floodplain during high water, but decreased
further downstream, whereas the opposite trend was observed during falling water. The BIT index remained high downstream of the floodplain, but dropped to values below 0.5 downstream of Lake Kariba.

Figure 3.7 Trends of several bulk and biomarker properties of the suspended matter downstream of the floodplain (Senanga) during high water (blue squares), falling water (orange circles), and low water conditions (green triangles). a) Stable carbon isotopic signature; b) fraction modern, c) alkane $C_{31}/C_{27}$ ratio; d) Paq ratio; e) branched GDGTs; f) BIT index.
Discussion

Sampling limitations

While this dataset provides valuable spatial and temporal information about the provenance of the riverine-transported particulate organic matter, there are a few issues that should be considered. First, the spatial coverage differed between the different seasons: sampling resolution during low-water conditions was distinctly lower than during the other two seasons due to issues of accessibility (logistical constraints). Second, most samples during low-water conditions were collected from the river bank, rather than from the middle of the channel due to logistical constraints, which influences measured parameters. For example, the high P_\text{aq} in the middle of the floodplain could be the result of sampling from the bank rather than from the middle of the channel. Similar sampling artifacts could be responsible for the outliers in alkane proxies at Sesheke during high water, and the high BIT index at Chirundu during high water. Third, few samples have been collected of the different organic matter end members contributing to the suspended pool. More extensive vegetation and soil sampling would provide valuable information in this type of study. Despite these limitations, the relatively systematic variations observed as a function of location and hydrologic conditions suggests that key facets of the river-floodplain interactions have been captured.

Radiocarbon composition of riverine organic matter in the Zambezi

During high and falling water levels, the observed radiocarbon values were comparable to previously reported numbers for the Zambezi catchment. Average radiocarbon values during rising water levels were previously reported at F^{14}C of 0.996±0.017, with a value of 1.058 measured at Livingstone (i.e., closest to the floodplain; Marwick et al., 2015). However, values during the dry season were distinctly lower, suggesting a different source of organic matter at that time. It is generally perceived that terrestrial organic carbon derives from three pools: (1) recently synthesized organic matter from terrestrial and/or aquatic primary production, (2) older and diagenetically-altered organic matter from deeper
soil horizons, and (3) fossil, radiocarbon-dead organic material from weathered bedrock (Blair and Aller, 2012). During higher water levels, the organic matter clearly had a recent signature, indicative of plant material, while during low water material was likely derived from deeper soil horizons or fossil organic matter from the sandstone bedrock in the catchment.

Changing sources of organic matter throughout the year

During low-water conditions, higher C-normalized concentrations of long-chain plant wax-derived \( n \)-alkanes corresponded to lower \( ^{14} \text{C} \) contents (older ages) of POC and low concentrations of branched GDGTs (Fig 8). In contrast, during higher water conditions, higher concentrations of long-chain plant waxes (esp. fatty acids) corresponded with higher brGDGT concentrations, and younger organic matter. These patterns confirm that different sources contribute to particulate organic matter carried by the Zambezi throughout the year. In general, organic matter sources during high and falling water are similar, but they differ during the dry season. Throughout the year, inputs of organic matter from discrete vascular plant debris or from aquatic primary producers must exist given higher OC contents of riverine suspended matter (6-17%) compared to those of the limited suite of soil samples analyzed (0.2-7%). Because of the high BIT values and low aquatic primary production rates (Zuijdgeest et al., 2016), it seems unlikely that aquatic production would be a large source to the riverine organic matter, and therefore we suspect higher-plant detritus is a major contributor.

The lack of correlation between radiocarbon age and C-normalized plant wax abundance indicated that during high and falling water organic matter originated from fresh vegetation or potentially topsoil. During low water, the inverse correlations between plant wax (esp. \( n \)-alkane) abundance and \( ^{14} \text{C} \) lead to the conclusion that older plant residues, most likely derived from deeper mineral soils, is transported by the river during this period. It is unlikely that the low values of fraction modern were caused by petroleum contamination, based on the lack of correlation between \( n \)-alkane CPI and \( ^{14} \text{C} \) (see Appendix 5).
The patterns observed in the bulk samples during low water could be a consequence of mobilization of deeper soil organic matter that is introduced to the river. It has been shown in Swiss soils, that the brGDGT abundance in soils decreased exponentially with depth (van der Voort et al., in preparation a). While such information is lacking for Zambezi basin soil profiles, the low abundance of branched GDGTs during low water could imply mobilization of deeper soil material from the floodplain, possibly from riverbank erosion. It has previously been suggested that in large river systems, organic matter aged in soils and floodplains contributes to the riverine load (Galy and Eglinton, 2011; Bouchez et al., 2014). At the same time, older mineral soil organic carbon is typically enriched in long chain \( n \)-alkanes (van der Voort et al., in preparation b). These older mineral soils would also have lower radiocarbon content.
Nevertheless, since the organic matter content of the suspended matter is higher than for top-soils sampled in the catchment, this points to an additional source of plant material. Stable carbon isotopic mass-balance calculations (not shown) imply an input of organic matter with a $\delta^{13}$C value of -27‰ for POC during low water. Six tree species bordering the floodplain were found to have an average isotopic signature of -28.3 ± 1.22‰ (Zuijdgeest et al., 2015), supporting the idea that an initial source of organic matter could come from direct terrestrial inputs during low-water conditions. The lower dry season $\delta^{13}$C values observed (Fig. 3.3) fall into the upper range of modern African woodland C$_3$ dicots (Vogts et al., 2009) whereas the heavier values, found during periods of inundation and falling water, correspond to a mixture of C$_3$ dicots and C$_4$ grasses (Rommerskirchen et al., 2006). During higher water levels, the direct inputs would likely come from entrainment of floodplain vegetation carrying a young radiocarbon signature. Schefuss et al. (2011) report that the contribution of C$_4$ material to the organic matter exported by the Zambezi River to the Indian Ocean increased during historically wet periods. On the shorter timescales examined in this study, this difference between wetter and drier conditions also appears to manifest itself. However, direct inputs from terrestrial vegetation cannot explain the decreased radiocarbon content during low-water conditions. While older organic matter could be eroded in the catchment, we lack evidence of active erosion during low flow. However, most of the geology in the vicinity of the Barotse Plains is comprised of sandstones, which are known for their low organic carbon content. In summary, it seems most likely that during low-water conditions organic matter inputs derive from deeper soil horizons.

In sharp contrast to the $n$-alkanes, the concentration of fatty acids was markedly higher during periods of inundation compared to low water. Moreover, their concentrations strongly co-vary with those of brGDGTs ($r = 0.867$), especially during high and falling water. This implies a strong (top) soil contribution, and supply of terrestrial OC that is not strongly associated with (deeper) mineral soils. The contrasting trends in higher plant-derived alkane and fatty acids might be linked to the type and growth cycle (Jetter et al., 2006) of the source vegetation in the floodplain and upstream locations, although such information is currently unavailable for the Barotse Plains. Alternatively, it may reflect differing reactivity
and particle associations of these two compound classes. Further work is needed in order to fully explain these observations.

Soil inputs

It appeared that the nature of the soil input did not change much between high and falling water, as indicated by correlations between brGDGTs and GDGT-0 (Appendix 6). During low water, concentrations of both brGDGTs and GDGT-0 were much lower but these appear to follow a similar trend. The increase in GDGT-0 provides further evidence for inputs of floodplain soils as it has been previously linked to methanogenic activity (Blaga et al., 2009). Methanogenesis would be most prevalent in more quiescent locations of the inundated floodplain characterized by water-saturated soils that promote in anoxic conditions. An increase in GDGT-0 in SPM from the main channel could thus be due to mobilization of those waterlogged soils.

The marked variations in branched GDGT concentrations and downstream patterns are comparable to those observed in the Amazon River, where highest brGDGT concentrations were found during high water, followed by falling water, with lowest concentrations during low water (Zell et al., 2013). In the downstream half of the Zambezi floodplain during high water, where previous strong decreases in oxygen and increases in organic matter concentrations were linked to inflows of floodplain water (Zuijdgeest et al., 2015), GDGT concentrations rose to more than 400 µg/gC. This provides strong evidence for floodplain-derived soil organic matter entering the river.

Combining results from the current study with data from previous work (Zuijdgeest et al., 2016) allows for a closer examination of soil-river interactions. Measured soil pH for floodplain soils varied between pH 5 and 7, whereas river-water pH varied roughly between 6.5 and 8 (Fig. 3.9a). The observed trend, with higher pH at the end of the dry season, was evident in samples from both field campaigns and from the sensor deployment. However, it should be kept in mind that the field campaigns and the sensor deployment did not capture the same year, so it is not possible to exclude the possibility of inter-annual variability. Since the
brGDGT-based estimates of pH (CBT values) from the suspended matter fell well within the pH range measured on our soil samples from the floodplain, this supports the inference of soil-associated organic matter as a dominant component of the riverine suspended carbon load. In general, soil pH increases with depth, so the seasonal patterns of riverine and GDGT-calculated pH also point to inputs from greater soil depths, which were unfortunately not sampled.

![Boxplots: SPM CBT−pH](image)

**Figure 3.9** Seasonal trends of pH and temperature in the Barotse Plains. a) Compared data include sensor-measured river water pH (Zuijgeest et al., 2016), soil pH, and CBT-calculated pH for both soils and suspended matter. The boxplots represent all the data measured along the floodplain, showing first and third quartiles and the median. b) Compared data include weather data from www.biota-africa.org for Kalabo, in the middle of the floodplain, sensor-measured river water temperature, and MAT reconstructions based on GDGTs using both the classic method and the improved chromatography. All MAT samples shown are all from the downstream end of the floodplain, measured using both methods.
The reconstructions of air temperature based on GDGT abundances from the classic method yielded higher values than using the improved chromatography, as discussed previously. Both reconstructed values were distinctly lower than air temperature (Fig 9b). Water temperature was higher than air temperature, likely due to the large daily fluctuations in air temperature. During the wet season, both measured and reconstructed MAT were fairly stable, and temperatures dropped after the rains ended. Since the proxy-MAT values were distinctly lower than the water temperature, it seems unlikely that in-situ produced GDGTs contributed significantly to the suspended particulate GDGT pool. Further evidence for minimal influences from in-situ GDGT production comes from the isomer ratios, which were very stable throughout the year. Only during low water, the isomer ratio was higher at the upstream end of the floodplain. At this time, water levels at the upstream end of the floodplain were generally less than one meter, and the riverbed was clearly visible. This was a different setting from the other sampling times, when the water was deeper and more turbid. As aquatic primary production rates in the Zambezi are low (Zuijdgeest et al., 2016), it may be possible that due to the shallow water depth and low turbidity, some benthic production was occurring at this point, leading to the increased isomer ratios.

Degradation of organic matter

Changes in organic matter characteristics may not only reflect different sources, but also reflect degradation processes. Degradation during high water levels has also been inferred from the loads of organic matter and nutrients (Zuijdgeest et al., 2015). Further evidence for degradation of organic matter during both high and falling water comes from consumption of oxygen along the floodplain (unpublished results). Decreases in POC contribution to the suspended matter can be interpreted as indicative of organic matter decomposition and transformation during river transport (e.g. Bouillon et al., 2009). We therefore consider potential changes in organic matter characteristics in the context of potential (preferential) degradation processes, though these could also arise from different contributions of different endmembers. During all three seasons, and most notably during falling
and low water, a decrease in radiocarbon contents of POC was accompanied by decreasing POC/SPM ratios (Fig. 3.10). This relationship suggests that younger organic matter is subject to preferential degradation. Moreover, during high and falling water levels, POC $\delta^{13}$C values decrease with increasing degradation, while during low water, they increased with decreasing POC/SPM ratios (Fig. 3.13). The latter may imply preferential degradation of more enriched fractions of the biomass, such as plant waxes or material derived from $C_4$ vegetation, during higher water levels, and selective degradation of more depleted fractions during low water, which could comprise of lignin or material from $C_3$ vegetation. There were no clear patterns of $\%$POC/SPM with the POC:PN ratio, brGDGTs, or the sums of the terrestrial plant waxes (not shown).

![Figure 3.10](image)

**Figure 3.10** Covariation between contribution of particulate organic carbon to the suspended matter ($\%$POC/SPM) and radiocarbon and stable isotopic carbon composition of POC along the floodplain.

Based on its stable carbon isotopic characteristics (Fig. 3.11), suspended POC in the Barotse Plains appears to be dominated by inputs from $C_3$ vegetation. Since most of the corresponding fraction-modern values fall somewhat below current atmospheric radiocarbon content, this indicates that it is at least partially pre-aged and likely originates from soils. While we cannot exclude some small inputs from fossil C sources (kerogen), the coherence in $\delta^{13}$C signatures implies a predominant ($C_3$) plant-derived origin.
Additional evidence for degradation along the floodplain can be found in the biomarker distributions. The varying CPI values (range 1.5-12), while indicative of plant-derived sources of organic matter, imply some degree of degradation. Also, during falling and low water levels, the abundance of both GDGTs (Fig. 3.6) and plant waxes (Fig. 3.4), dropped near the terminus of the floodplain. At the same time, the long-chain fatty acids exhibit higher $\delta^{13}\text{C}$ values. During high water, the isotopic signature increased along the floodplain as well, but so did the abundances. Increased $\delta^{13}\text{C}$ of soil organic matter has previously been attributed to degradation (Wynn, 2007). The combined observations of decreased abundance and $^{13}\text{C}$-enrichment are therefore consistent with degradation of plant material during low and falling water. During high water, inputs of $\text{C}_4$ vegetation from the floodplain would also result in higher $\delta^{13}\text{C}$ values, and along with contributions of longer-chain plant waxes. This suggests different regimes during high water and the other two seasons.
Floodplain organic-matter interactions

For the Barotse Plains, we find that during the (wet) growing season, young plant material comprises a major fraction of the POC transported by the Zambezi. Additionally, we have found that maximum carbon dioxide oversaturation (and hence fluxes) occurred during rising water levels (Zuijdgeest et al., 2016), and it has been suggested that this reflects respiration of dried, above-ground plant debris from the prior year’s growing season. Along with the potential of preferential degradation of more enriched organic matter (potential derived from C₄ vegetation) during high water (Fig. 3.10), these two lines of evidence suggest that, similar to conditions in the Amazon (Mayorga et al., 2005), inputs of young organic matter, carrying a distinct signature of C₄ grasses, are responsible for outgassing of CO₂ from the floodplain.

A trend has been observed between increasing age of the particulate organic matter and increasing suspended matter concentrations (Marwick et al., 2015). For the Zambezi, higher suspended matter concentrations were observed during low water conditions (Zuijdgeest et al., 2016), at which time we also found older organic matter. This trend of younger material being transported at periods of high flow has also been derived from paleo-records from the Congo basin, based on sedimentary analyses (Schefuß et al., 2016). These authors suggested that during periods of higher discharge, rapid transfer of plant debris occurred, leading to younger radiocarbon ages. On the other hand, during periods of lower flow, and hence a smaller extent of wetlands in the river catchment, older material was transported downstream. On longer timescales, the age of terrestrial carbon in tropical rivers may therefore reflect retention processes in the basin that in turn are controlled by continental hydrology (Schefuß et al., 2016). On the smaller spatial and shorter temporal scales examined here, a similar pattern emerged: younger material is transported during periods of high flow compared to periods of low flow. Nevertheless, it is important to keep in mind that modern samples may be affected by radiocarbon inputs from nuclear weapons testing that can mask the original age (Schefuß et al., 2016).
Several of the proxies and parameters shown demonstrate that there is only limited input of aquatic primary production, and that fluvial organic matter in the Zambezi is dominated by terrestrial and floodplain inputs. Carbon-to-nitrogen ratios are elevated compared to those typically observed in algae, BIT values are close to one, and short-chain n-alkanes were only present in small quantities (not shown). In addition, the isomer ratios of GDGTs show values similar to those previously reported for tropical soils, suggesting little input of aquatically-produced GDGTs.

Overall, several lines of evidence lead to the interpretation that during low flow, organic matter input derives from deeper soil layers and aged OC derives from terrestrial vegetation, whereas during periods of higher flow, organic matter derives from fresh organic matter produced during recent growing season(s) on the floodplain. This supports previous interpretations concerning biogeochemical processes in the Barotse Plains (Zuijdgeest et al., 2016).

**Downstream transport and organic matter inputs**

Based on isotopic considerations, it has been previously inferred that plant-wax signals exported from the Zambezi to the Indian Ocean mainly originated from the floodplain area in the lower reach of the river (Schefuß et al., 2011). This floodplain area, located in the Rift Valley, is dominated by Cyperus papyrus (C₄ plant), with lesser contributions of C₃ reeds (Schefuß et al., 2011). During wet conditions, the C₄ material dominated the exported organic matter, whereas during arid conditions C₃-plant-derived organic matter from proximal coastal areas was exported. Such shifts between C₃ woody vegetation and C₄ savanna grasses have also been described elsewhere (Wang et al., 2013).

In the upper reaches of the Zambezi catchment, clear differences in organic matter signatures were observed upstream and downstream of the Kariba reservoir, though few changes were observed immediately downstream of the floodplain. The largest change downstream of the floodplain manifested itself as a decrease in F¹⁴C, which may be linked to inputs of petrogenic carbon. Downstream of the reservoir, the δ¹³C signal was notably depleted compared to upstream, potentially
indicative of phytoplankton production in the reservoir (as in the Tana river; Bouillon et al., 2009). Furthermore, the \( C_{31}/C_{27} \) signal showed that downstream of the reservoir inputs from grasses and herbs dominated the alkane signal, and the contribution of branched GDGTs during high and falling water levels dropped to values observed during low water conditions. We suspect that, if not for the presence of the reservoir, the signals emerging from the floodplain could be subject to longer-range transport.

**Conclusions**

Throughout the year, soil inputs contribute significantly to the organic matter transported downstream by the Zambezi. During times of inundation, the organic matter derives from topsoil and floodplain vegetation, whereas during low-water conditions the material most likely derives from a mixture of direct inputs from terrestrial vegetation and from deeper mineral soils. Degradation along the floodplain occurred during falling and low water, whereas during high water a shift in fatty acid isotopic composition appeared to arise from inputs from \( C_4 \) vegetation. The composition of the fluvial organic matter changed markedly along the floodplain, and these signals persist downstream, until the river flows into the Kariba reservoir.

**Acknowledgements**

The authors thank Renata Fulcri, Ivo Indergand, Kristina Peterson, Cristian Teodoru, and Severin Wiens for fieldwork assistance. Work in the laboratory was supported by Stewart Bishop, Thomas Blattman, Hannah Gies, Madalina Jaggi, and Daniel Montluçon. Institutional support was provided by Imasiku Nyambe (University of Zambia and its Integrated Water Resource Management Center), the Zambia Wildlife Authority, the Zambezi River Authority, and the Laboratory of Ion Beam Physics (LIP) at ETH Zurich. Discussions with Chantal Freymond, Clay Magill, and Tessa van der Voort were much appreciated.
Appendices

Appendix 3.1: Blank correction for radiocarbon

Results from the blank filters spiked with either oxalic acid or phthalic anhydride showed that the (blank) filter contained on average 4.84µg C (max 5.42µg C) with a F$^{14}$C value of 0.665 (95% confidence intervals 0.551-0.779, Fig. S3.1). Sample measurements were corrected based on mass-balance calculations of the fractions of the measured organic carbon that came from the filter and the suspended matter. Taking into account the confidence intervals on the blank assessment, the F$^{14}$C values showed a deviation of less than 0.01. Replicate measurements showed standard deviations in their F$^{14}$C between 0.00 and 0.13.

![Fraction modern of spiked filters against the inverse of the amount of carbon added to the filter.](image)

**Figure S3.1** Fraction modern of spiked filters against the inverse of the amount of carbon added to the filter.
Appendix 3.2: GDGT method comparison

Branched GDGTs have traditionally been linked to soil environments, but in recent years it has been found that they are also produced in aquatic environments (e.g. Tierney and Russell, 2009; De Jonge et al., 2014b; Weber et al., 2015). Recent improvements in chromatography (De Jonge et al., 2014a; Hopmans et al., 2016) have been able to separate previously co-eluting compounds, which were found to have the methyl group at a different positions (De Jonge et al., 2014a). A small subset of samples, upstream and downstream of the floodplain during the three different seasons, was also measured using the newer GDGT method with improved chromatography (Hopmans et al., 2016) in the Organic Geochemistry laboratory at Utrecht University.

There were notable discrepancies in the abundance of individual compounds between the two methods, with the new method measuring 10-70% of the values measured using the old method. The discrepancy, however, varied both between samples and between compounds. Nevertheless, the relative abundances (i.e. the distribution of the GDGTs) were very comparable between the two methods. Differences in BIT values and reconstructed MAT and pH between the two
methods (Fig. S3.2, Table S3.1) show very comparable trends to those previously shown for fluvial sediments in the Danube catchment (Freymond et al., 2017). However, while they found slightly higher MAT values from the improved method, we observe lower reconstructed MAT with the improved method. This may be due to the differences in temperature between the Zambezi and Danube catchments.

Both for our samples and the Danube study, the classic method yielded higher concentrations, which may reflect irreversible binding of the GDGTs to the HPLC column phases. Since the proxy values are very comparable, and there are strong linear correlations between the two methods (r values for our data between 0.75 and 0.99), it seems unlikely that the differences are caused by different response factors of the two mass spectrometers (Schouten et al., 2013a). Freymond et al. (2017) concluded that the improved chromatography led to more accurate reconstruction of local environmental conditions.

**Table S3.1** GDGT proxies using the improved chromatography, as in De Jonge et al. (2014a).

<table>
<thead>
<tr>
<th>Proxy calculation</th>
<th>Eq.</th>
</tr>
</thead>
</table>
| BIT index = \[
\frac{[Ila] + [IIla'] + [IIa] + [Ila'] + [la]}
{[Crenarchaeol] + [IIla] + [IIla'] + [IIa] + [IIa'] + [la]}\]
| (S3.1)                                                 |             |
| CBT' = \log \left( \frac{rel \cdot Ic + rel \cdot IIa' + rel \cdot IIb' + rel \cdot IIc' + rel \cdot IIIa' + rel \cdot IIIb' + rel \cdot IIIc'}{rel \cdot Ia + rel \cdot IIa + rel \cdot IIIa} \right) |
| (S3.2)                                                 |             |
| pH = 7.15 + 1.59 * CBT'                                 | (S3.3)      |
| MAT\text{pr} = 7.17 + 17.1 * rel \cdot Ia + 25.9 * rel \cdot IIb + 34.4 * rel \cdot IIc - 28.6 * rel \cdot IIIa |
| (S3.4)                                                 |             |

\(rel \cdot x\) stands for the abundance of specific GDGT x, normalized to the total brGDGT concentration.
Appendix 3.3: Biomarker contributions to organic carbon

The patterns of biomarker abundance along the floodplain vary slightly when considering normalization versus gram sediment, instead of gram carbon (Fig. S3.3). When considering the abundances per gram sediment, hydrodynamics and hence particle sizes affect the patterns. At larger flow velocities, larger particles can be suspended in the river water, which typically have lower carbon content per gram than smaller particles. By normalizing to gram carbon, such impacts are disregarded, and the resultant patterns show how the composition of the characterizable organic matter changes.

Figure S3.3 Comparison of normalization versus gram sediment and gram carbon of abundances of long-chain alkanes and fatty acids, as well as brGDGTs during high water (HW, blue squares), falling water (FW, orange triangles), and low water conditions (LW, green triangles). All concentrations are in µg biomarker per g sediment or gram carbon.
Appendix 3.4: Fatty acid isotope composition

The stable carbon isotopic composition of individual fatty acids increased to heavier values along the floodplain, while corresponding abundances of the long-chained fatty acids decreased (Fig. S3.4).

![Graph showing weighted FAME $\delta^{13}$C and long-chain FAME abundance along the floodplain during high water (blue squares), falling water (orange circles), and low water (green triangles).](image)

Figure S3.4 Abundance-weighted FAME $\delta^{13}$C and long-chain FAME abundance along the floodplain during high water (blue squares), falling water (orange circles), and low water (green triangles).

Along the floodplain, the abundance-weighted FAME-$\delta^{13}$C values increased during all seasons. However, simultaneous trends in plant waxes, F$^{14}$C, and branched GDGTs varied between the field campaigns (Fig. S5). During low water, no clear trend could be observed with any of these other parameters. During high water, the abundances of long-chain fatty acids and branched GDGTs increased with increasing weighted $\delta^{13}$C. Along with the increase in isotopic composition of the fatty acids during falling water, we observed decreases in carbon-normalized plant wax and brGDGT abundances. This suggests that during high water, organic matter with a depleted signature entered the river, while during falling water the material transported was undergoing degradation along the floodplain, and may have been diluted with non-characterizable organic matter inputs.
Figure S3.5 Cross-plots between abundance-weighted FAME-$\delta^{13}$C and abundance of long-chain plant waxes, fraction modern of POC, and branched GDGTs in the suspended matter in the floodplain.
Appendix 3.5: CPI versus fraction modern

The combined information from the n-alkane carbon preference index (CPI) and fraction modern (F\textsuperscript{14}C) shows that the organic matter is composed of relatively young plant material during high and falling water, but the lower CPI values indicates enhanced degradation (Fig. S3.6).

![Figure S3.6 Cross-plot of n-alkane carbon preference index (CPI) and fraction modern (F\textsuperscript{14}C) of the suspended matter](image-url)
Appendix 3.6: Composition of soil inputs

Covariation between branched GDGTs and GDGT-0 indicated inputs from anoxic soils, most likely located on the floodplain.

**Figure S3.7** Covariation between branched GDGTs and GDGT-0 in the suspended matter in the floodplain during high water (blue squares), falling water (orange circles) and low water (green triangles; downstream samples until Livingstone included). Colored symbols represent SPM from the main channel, open symbols SPM from tributaries.
Chapter 4

How dams and wetlands affect carbon and nutrient fluxes in the Zambezi

Alissa Zuijdgeest
Bernhard Wehrli

submitted to Chemical Geology
Abstract

Inland waters are under increasing anthropogenic stresses. In the last century, roughly two thirds of the world’s wetland area disappeared, and so many dams have been constructed that currently 50% of river water passes through dams before reaching the ocean. Large river systems in tropical and subtropical areas often develop extensive floodplain areas that will suffer from modifications in the flow regime as another boom in dam construction is under way. In the Zambezi catchment, we developed a comparative analysis of the biogeochemical effects of floodplains (Barotse Plains) and reservoirs (Lake Kariba) on tropical river biogeochemistry, to provide a basis to assess the net effect of eliminating wetland areas and transforming rivers into artificial lakes. In addition, we propose the combination of discrete analyses with sensor deployments to capture the seasonality of fluxes over large regional scales in remote areas.

Dams and reservoirs alter the riverine biogeochemistry in distinct, and often different ways. While the Barotse Plains floodplain releases particles during a flood cycle, this suspended material is effectively trapped in Kariba reservoir. Seasonal production of biomass on the floodplain binds nutrients in the form of organic matter that sustains biological productivity in downstream ecosystems. Degradation of the biomass can lead to significant greenhouse gas emissions from the floodplain. The reservoir traps particles and nutrients, but carbon burial (120·10^3 t C per year) is offset by annual emissions of methane to the atmosphere with about 3000·10^3 t C-CO_2-equivalents.
Introduction

Over the last centuries global river systems have been subject to dramatic changes. Channels and dikes for flood protection and navigation now disconnect large fractions of the river corridors, dry up wetlands and reduce the later connectivity in floodplains. In his recent review, Davidson (2014) estimated that up to 87% of global wetland area has been lost over the last 300 years, with losses in the 20th century alone diminishing the area present in 1900 by 64-71%. Wetlands are hotspots of biodiversity, and their disappearance has been accelerating the dramatic decline in freshwater biodiversity worldwide (Vörösmarty et al., 2010). In addition, wetland ecosystems provide important ecosystem services such as flood mitigation, particle trapping for reducing erosion, and uptake and transformation of nutrient flows. The biogeochemical impact of disappearing riparian wetlands has not been quantitatively analyzed so far on a global scale (Gell et al., 2016 and references cited therein), but it is safe to assume that the average residence time of global runoff spent in wetland areas has been shortened in parallel to the decline of wetland area. The loss of lateral connectivity to wetlands as important parts of the river corridor now limits the biogeochemical functions of riparian wetlands as “filter” systems for nutrients (Verhoeven et al., 2006) which are then transferred in the form of organic nutrients to downstream food chains (Durisch-Kaiser et al., 2011).

Dam construction is the second major driver for global change in river systems. The number of large dams started a steady increase in the 1920s, the expansion stagnated in the last two decades, but planning in many regions of Africa, South America and Asia indicates a “second wave” of dam construction (Zarfl et al., 2015). More than 3,700 hydropower dams with a capacity large than 1 MW are currently planned or under construction. At present, about 50% of river water released to the oceans is passing through dams and if current trends continue, this will increase to 90% by 2030 (Van Cappellen and Maavara, 2016). Prolonged residence time in reservoirs generally leads to stratification and distinctly different biogeochemical processes than in the mainstem river. These processes not only alter the quantity of material transported downstream, but also their characteristics. In
addition, the flow regulation can alter the timing of carbon and nutrient delivery to downstream ecosystems (Van Cappellen and Maavara, 2016). It has been estimated that 12% of the global river phosphorus load was trapped in reservoirs in 2000, with this number likely increasing to 17% by 2030 due to the increasing damming of the world’s rivers (Maavara et al., 2015). From a biogeochemical perspective, the transformation of running waters into lakes adds a new reactor system to the aquatic continuum with sediments as semi-permanent deposits of both terrestrial as well as aquatic particles (Vörösmarty et al., 2003). Under high nutrient loads aquatic photosynthesis might enhance carbon storage in sediments. On the other hand, reservoir sediments with high carbon accumulation rates will develop methanogenic conditions that release methane to the atmosphere (Barros et al., 2011). The process often occurs via direct ebullition in the form of gas bubbles (DelSontro et al., 2010), and has now been estimated to represent a significant contribution of 0.5 – 1.2 Pg C equivalents per year to the anthropogenic emissions (Deemer et al., 2016).

Large tropical and subtropical rivers are often characterized by their strong connection with extensive riparian wetlands (e.g., Abril et al., 2014; Kummu et al., 2014; Melack et al., 2009). In many regions the strong seasonality in rainfall favors the formation of extensive floodplain systems with seasonal inundation dynamics. The ongoing and planned expansion of hydropower production will have profound impacts on the structure and function of these tropical wetlands (Zarfl et al., 2015). A biogeochemical assessment of such massive alteration of tropical river systems should be based on comparative studies of the biogeochemical function of both wetlands and dams. Quantifying the transformation, burial and emissions rates of carbon and nutrients by wetlands and dams in similar hydro-climatic environments provides a basis to assess the net effect of eliminating wetland areas and transforming rivers into artificial lakes.

In this context, our study follows two main objectives. First, we use the Zambezi River basin as a test site to develop a comparative analysis of the biogeochemical effects of the Barotse Plains and Lake Kariba on carbon and nutrient fluxes. Second, we propose a combination of discrete chemical analyses and sensor deployments to cope with the significant seasonality of fluxes over
large regional scales in remote areas. As a recent global survey of water quality data has shown, the tropical region shows a severe lack of data (UNEP, 2016). In our biogeochemical analysis we specifically address the questions how large wetlands and hydropower reservoirs change the seasonality and overall availability of nutrients to downstream ecosystems. We develop and present specific budgets and fluxes for carbon and nutrients concentrations, and their ratios for the pristine Barotse Plains and the Lake Kariba reservoir, and combine these new interpretations with previously published results. On a methodological level, we demonstrate how sensor deployments that record annual flood cycles significantly improve mass balance models for wetlands and dams.

Methods

Study sites

The Zambezi catchment in sub-Saharan Africa (Fig. 4.1) is one of the major river systems draining into the Indian Ocean. The source of the river is found in the north-west of Zambia at 1585 m.a.s.l., and over the course of roughly 2,500 km the river flows mainly through forest and bush until it reaches the Indian Ocean (Davies, 1986; SADC/SARDC and others, 2012). In 2008, the Zambezi catchment was home to roughly 40 million people. The region upstream of Victoria Falls is sparsely populated with limited agricultural activities, and the highest population densities in the basin are found in the Copperbelt region in the Northern part of the Kafue catchment and in the Eastern parts of the basin in Malawi and Mozambique. Mining and agriculture, are the most important anthropogenic activities emitting nutrients and pollutants to surface waters (SADC/SARDC and others, 2012).

The Zambezi represents an ideal case study area for investigating the effects of floodplains and dams on carbon and nutrient transfer along the aquatic continuum. The catchment hosts several large, pristine floodplain areas. One of the riparian wetlands in the catchment, the Kafue Flats, is bordered by two dams, which makes this an excellent case to study dam impacts on floodplain biogeochemistry.
(Wamulume et al., 2011; Zurbrügg et al., 2012; Zurbrügg et al., 2013; Zuijdgeest et al., 2015). In the upstream region of the Zambezi, the Barotse Plains is a still largely pristine landscape that undergoes seasonal flooding. In the mainstem of the Zambezi, two large hydropower dams have been constructed between Zambia and Zimbabwe (Kariba – 1959) and in Mozambique (Cahora Bassa – 1974), and more are planned (SADC/SARDC and others, 2012). Previous research has focused on the biogeochemistry of Lake Kariba (DelSontro et al., 2011; Kunz et al., 2011a) and the Itezhi-Tezhi reservoir in the Kafue tributary (Kunz et al., 2011b; Kunz et al., 2013). The remarkable size and hydrological characteristics of these mayor dams and wetlands in the Zambezi Basin are outlined in Table 4.1.

Table 4.1 Physical characteristics of the large floodplains and reservoirs in the Zambezi catchment.

<table>
<thead>
<tr>
<th>System</th>
<th>Length (km)</th>
<th>Surface area (km²)</th>
<th>Volume (km³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barotse Plains</td>
<td>240 a</td>
<td>7700 a</td>
<td></td>
</tr>
<tr>
<td>Kafue Flats</td>
<td>256 a</td>
<td>5660 a</td>
<td></td>
</tr>
<tr>
<td>Lake Kariba</td>
<td>277 b</td>
<td>5364 b</td>
<td>156.5 b</td>
</tr>
<tr>
<td>Cahora Bassa</td>
<td>250 c</td>
<td>2739 d</td>
<td>63 d</td>
</tr>
</tbody>
</table>

Due to its location south of the Equator between 11 and 18°S, the movements of the Intertropical Convergence Zone dominate the climate of the Zambezi catchment. As a result, the catchment experiences pronounced dry and wet seasons, with the rains falling between December and March. The seasonality in rainfall is reflected in the discharge patterns in the undisturbed parts of the catchment, upstream of the major hydropower dams (Fig. 4.2). During the 2013/2014 rainy season, this area exhibited flooding (discharge > 1000 m³ s⁻¹) from February 2 until July 31, with peak flows (discharge > 2500 m³ s⁻¹, March 21 – May 31) towards the end and shortly after the rainy season (November 7 – April 12). The Barotse Plains are flooded annually during the rainy season, when runoff exceeds bankfull discharge. Rather constant energy production at the two hydropower stations (Kariba and Cahora Bassa) determines the uniform discharge patterns further downstream (Fig. 4.2). Lake Kariba also exhibits annual flooding between November and May (Karenge and Kolding, 1995).
period, deep convective mixing is generally triggered in July. Afterwards, thermal
stratification re-establishes. The combination of large discharge seasonality and the
shared catchment (8 riparian countries) introduces the need for sustainable water
use among the riparian countries. This has become evident in 2015/2016, when an
El-Niño-related drought was responsible for low water levels (FEWSNET, 2016)
and hydropower production was limited.

Figure 4.2 Hydrological characteristics of the Zambezi catchment in 2013-2014.
Discharge in the Zambezi catchment downstream of the Barotse Plains (dots) and
spills from the Kariba Dam turbines (triangles), data from the Zambezi River Authority,
2013-2014. Precipitation (grey line) in Kalabo, in the middle of the floodplain (data
from www.biota-africa.org). The rainy season is defined by a black arrow. Flooding
season (blue area) is defined as discharge > 1000 m$^3$ s$^{-1}$, peak flow (shaded area) as
discharge > 2500 m$^3$ s$^{-1}$. Diamonds represent the different campaigns in different
years: orange for low water (LW, October 2013), blue for high water (HW, April 2013),
and green for falling water (FW, June 2015).
Sample collection and measurements

During recent years, a large-scale interdisciplinary project has been conducted in the Zambezi River basin which included specialists in hydraulic engineering, natural as well as social sciences (Mertens et al., 2013). This synthesis builds on the biogeochemical analyses conducted during this project and focuses on the individual and combined effects of the pristine Barotse Plains in the upstream part of the Zambezi and the large Kariba reservoir downstream of Victoria Falls (Table 4.2). We used a combination of discrete chemical analyses and sensor deployments to cope with the significant seasonality of fluxes over large regional scales in the Zambezi catchment. An overview of the data sources for this study is presented in Table 4.2. In short, traditional field campaigns (for both river, reservoir, and sediment sampling) were supplemented with long-term deployment of multi-probes upstream and downstream of the floodplain. For more details regarding sample collection and analysis, we refer to the relevant publications.

Table 4.2 Data sources of measurements in the Zambezi catchment.

<table>
<thead>
<tr>
<th>Location(s)</th>
<th>Sampling method</th>
<th>Parameters</th>
<th>Observation times</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barotse Plains, upstream of Kariba</td>
<td>Field sampling, water</td>
<td>POC, PN, PP, DOC, DON, DOP,</td>
<td>04/2013 (HW)</td>
<td>a</td>
</tr>
<tr>
<td></td>
<td>surface</td>
<td>SPM, multi-probe</td>
<td>10/2013 (LW)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sensor deployment</td>
<td>Temperature, conductivity,</td>
<td>Upstream</td>
<td>b</td>
</tr>
<tr>
<td></td>
<td>(WTW EXO 2)</td>
<td>pH, dissolved O2, fDOM,</td>
<td>11/2013-04/2014</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>turbidity</td>
<td>Downstream</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11/2013-07/2014 (hiatus</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>03/2014)</td>
<td></td>
</tr>
<tr>
<td>Lake Kariba</td>
<td>Field sampling, sediment</td>
<td>POC, PN, PP</td>
<td>07/2007, 05/2008, 02/2009</td>
<td>c</td>
</tr>
<tr>
<td></td>
<td>cores</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Field sampling</td>
<td>CH₄ emissions</td>
<td>07/2007, 05/2008, 02/2009</td>
<td>d</td>
</tr>
<tr>
<td>Downstream of Kariba</td>
<td>Field sampling, water</td>
<td>POC, PN, PP, DOC, DON, DOP,</td>
<td>04/2013 (HW)</td>
<td>#</td>
</tr>
<tr>
<td></td>
<td>surface</td>
<td>SPM, multi-probe</td>
<td>10/2013 (LW)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>06/2015 (FW)</td>
<td></td>
</tr>
<tr>
<td>Zambezi catchment</td>
<td>Field sampling</td>
<td>CO₂, CH₄ emissions</td>
<td>02/2012, 02/2013, 10/2013</td>
<td>e</td>
</tr>
</tbody>
</table>

References: a) Zuijdgeest et al. (2015); b) Zuijdgeest et al. (2016); c) Kunz et al. (2011a); d) DelSontro et al. (2011); e) Teodoru et al. (2015); #) unpublished results.
Improving sensor correlations

Obtaining high-resolution temporal data in remote areas is often limited by logistical challenges, but deployment of autonomous measurement systems can provide valuable information. Standard sensor packages can now record continuous data sets of important water quality parameters such as conductivity, pH, oxygen, and fluorescent dissolved organic matter (fDOM) over periods of several months (Snazelle, 2015). The concentrations and fluxes of nutrients and inorganic carbon are best measured by wet chemical methods in the laboratory. This remains a significant challenge for remote field sites with limited infrastructure. Here we explore a different approach: in our previous study we linked sensor-derived parameters to biogeochemical species of interest, namely conductivity to alkalinity and together with temperature and pH to pCO$_2$, turbidity to suspended particulate matter (SPM) concentrations, and fDOM to dissolved organic carbon (DOC) concentrations (Zuijdgeest et al., 2016). Here, we expand on those correlations: covariation between sensor-measured turbidity and fDOM and particulate and dissolved organic carbon and nutrient concentrations showed that, with a certain error margin, it is possible to quantify the carbon, nitrogen, and phosphorus dynamics based on sensor deployment (Fig. 4.3, Appendix 1). Samples and sensor readings for these correlations were collected during sampling campaigns capturing low-water conditions in 2013 and falling-water conditions in 2015 and analyzed according to procedures published earlier (Zuijdgeest et al., 2016). More details regarding the laboratory analyses can be found in the Appendix. There are several critical points to be addressed before continuing analysis with these correlations. First, note that the fDOM concentrations were at low levels during the field campaigns used for calibration (maximum in the calibration set 23 QSU) compared with the complete record, that reached maximum values around 70 QSU (mean 42 QSU, min 7.6 QSU, max 72 QSU). Second, the DOP concentrations measured in the laboratory were close to or below the limit of quantification of our method (LOQ < 0.15 µM). These numbers should therefore be considered as estimates. Third, the correlations to turbidity appear to be somewhat skewed by one high-turbidity value, measured at Senanga during low water conditions. We have no indication that this is a measurement error. By keeping this sample in the
calibration series, POC and PP could be underestimated at turbidity values below 2.7, while PN could be overestimated at turbidities of more than 2.7 FNU, relative to those values obtained when the high-turbidity sample is excluded from the calibration. And fourth, we observed some high-turbidity events during the first months of the deployment. These events (>20 FNU, or >2x mean turbidity), were probably due to the following artifact and therefore removed from the record: the probe was deployed underneath a floating jetty, which acted as a harbor. Arrival of larger boats could stir up sediments, leading to artificial high-turbidity events. In summary, the sensor-derived concentrations should be assessed critically, but can provide valuable, high-resolution data from a remote area.

![Figure 4.3](image)

**Figure 4.3** Correlations between turbidity and particulate nitrogen and fDOM and dissolved nitrogen. The 95% confidence interval is shown in grey; equation and statistical parameters included in the figure.

**Error propagation**

In order to account for the uncertainty in the correlations between the sensor parameters and the biogeochemical species of interest, the 95% confidence intervals were calculated (Fig. 4.3). These confidence intervals were then also applied to the records of the sensor deployment. For values falling outside of the calibration range, the same confidence interval as the highest point in the calibration series was applied. Therefore, the error ranges at high turbidity and fDOM are probably optimistic.
Results

Floodplain dynamics

Particulate carbon and nutrient concentrations reached their maxima at the beginning of the year, during the rainy season and the beginning of the flooding phase (Fig. 4.4). They dropped by a factor of 3 at maximum flood levels between March and May. The dissolved organic matter concentrations peaked somewhat later, towards March, which was still well before peak flow, and decreased slowly during the rest of the flood period. The sensor correlations can be checked against discrete laboratory analyses on samples from field campaigns of different years (2012-2015, including data by Teodoru et al., 2015). These data are marked with colored symbols in Figure 4.4 and indicate that the seasonal trends appear robust between the years 2012-2015 with comparable rainy seasons.
Figure 4.4 Sensor-derived POC, PN, PP, DOC, DON, and DOP records at Senanga (with 95% confidence intervals in grey), compared to the values measured at the same location during field campaigns of different years (Table 4.2). Low water marked as orange squares, high water as blue squares, and falling water as green squares. Data from Teodoru et al. (2015) shown as red squares.

**Loads**

Particulate loads were lowest at the end of the dry season, and increased as the flooding season progressed (Fig. 4.5). During the flooding season, from December to March, larger variability was visible in the measured turbidity values, not all of which is captured in the current representation. Values remained high well past peak flow, and decreased again after June. The dissolved fluxes showed a steady increase in loads from December onwards, with peak loads around peak flow in April. Part of the discrepancy between sensor-derived loads and discrete field data from different years might be due to higher discharges during the period of sensor deployment.
Figure 4.5 Loads in tons of carbon, nitrogen, or phosphorus per day at Senanga as calculated from the sensor data, with their 95% confidence intervals, and calculated from the field campaigns of different years (Table 4.2). Low water shown as orange triangles, high water as blue triangles, and falling water as green triangles, with error bar reflecting standard deviation in discharge measurements.

These seasonal records were used to obtain the yearly loads leaving the floodplain. Because of the high-turbidity events at the end of the data series, which deviate strongly from the overall trend, the last three points were removed when extrapolating the remainder of the dry season. These yearly loads are presented in Table 4.3, and will be used to constrain the biogeochemical budgets of Lake Kariba (see Discussion). During the flooding season (discharge $> 1000$ m$^3$ s$^{-1}$, February 2 until July 13, Fig. 4.2), 56% of the yearly particulate and 85% of the dissolved loads was exported. The period of peak flow with a discharge of more than 2500 m$^3$ s$^{-1}$ contributed 28% of the particulate and 49% of the dissolved yearly loads. For carbon and nitrogen, the dissolved organic fraction contributed most to the
budget (DON:PN 2.5-3, DOC:POC ~5), while most phosphorus (approximately 97%) was transported as particulate material (Table 4.3). Our field observations were consistent with earlier studies (Zurbrügg et al., 2013; Zuijdgeest et al., 2015) indicating that inorganic nitrogen and phosphorus contributed negligible amounts to total nutrient loads.

Table 4.3  Estimated yearly loads (in 10³ tons) at Senanga based extrapolation of the sensor data, with 95% confidence intervals between brackets.

<table>
<thead>
<tr>
<th>POC</th>
<th>PN</th>
<th>PP</th>
<th>DOC</th>
<th>DON</th>
<th>DOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>2.3</td>
<td>2.1</td>
<td>200</td>
<td>14</td>
<td>0.16</td>
</tr>
<tr>
<td>(17-29)</td>
<td>(1.9-2.8)</td>
<td>(1.3-3.0)</td>
<td>(180–220)</td>
<td>(11–17)</td>
<td>(0.13–0.19)</td>
</tr>
</tbody>
</table>

Changes in element ratios

Both the floodplain and the reservoir altered the carbon-to-nitrogen and nitrogen-to-phosphorus ratios (Fig. 4.6), but the direction of the impact varied between seasons and locations. The POC-to-PN ratios remained fairly stable throughout the seasons and along the river, while the highest DOC:DON ratio was observed during falling-water conditions in the floodplain. The nitrogen-to-phosphorus ratios were most variable and generally highest during high water. The PN:PP ratio decreased along the floodplain during high water, while the reservoir altered the ratio in opposite direction. During low water, DOP concentrations were undetectable, so no ratios could be determined. Again, the floodplain and the reservoir changed the DON:DOP ratios in an opposite direction.
Figure 4.6 Particulate and dissolved carbon-to-nitrogen and nitrogen-to-phosphorus ratios upstream (up) and downstream (dn) of the Barotse Plains (in green) and Lake Kariba (in blue). Samples are separated into seasons: blue for high water (HW – 04/2013), orange for falling water (FW – 06/2015) and green for low water (LW – 10/2013). During low water conditions, no PP was measured downstream of the dam and DOP could not be detected at any of the four sampling locations.

### Seasonality of the reservoir outflow

Downstream of the floodplain, DOC showed very little variation between the various field campaigns, while POC and PN showed some variation. Variation between the seasons was highest for total phosphorus, and no particulate phosphorus was analyzed for the dry season, partially accounting for the large discrepancy. In light of the AFRIVAL project (KU Leuven, Belgium), a monitoring station was operated for almost two years near Chirundu (80km downstream of Kariba). Seasonal patterns were captured by regular sampling (every 2-4 weeks). Samples were analyzed for a suite of parameters, including POC, PN, DOC, and inorganic nutrients. While the POC:PN ratio remained extremely stable throughout the year (8.45±0.55), concentrations of the individual species varied. Inorganic nutrients were not distinctly higher downstream of the dam compared to upstream, and showed no clear seasonal patterns.
Discussion

Sensor-derived biogeochemistry

A recent UNEP report documents that Africa has only 0.02 measurement stations for water quality per 10’000 km$^2$. This density is two orders of magnitude lower than in Europe or North America (UNEP, 2016). Laboratory analyses based on water sampling will not close this gap in the near future. Proxy measurements by recording instruments using in-situ sensing techniques could therefore provide valuable information on processes and drivers affecting water quality in many tropical river basins. We have shown previously (Zuijdgeest et al., 2016) how sensor-derived biogeochemical data can provide high-resolution time-series of processes such as aquatic carbon turnover in remote areas. Keeping in mind the possibility for inter-annual variability, the good qualitative correspondence between discrete samples from different field campaigns and the sensor-derived seasonal patterns demonstrates again how the integration of hydrological and chemical records could fill the data voids on the global maps of riverine processes.

The particulate loads presented in this study show a slightly different pattern than those previously published for total suspended matter (Zuijdgeest et al., 2016), with more elevated organic matter concentrations during peak flow. This is caused by differences in the correlations and the absolute difference between highest and lowest concentrations. Therefore, at higher discharge around peak flow, we still see elevated concentrations in the carbon and nutrient concentrations, but not so much in the total suspended load. Also, it might appear strange that the 95% confidence intervals of PN (Fig. 4.5) are not completely mirrored around the estimated values: this is caused by the extrapolation at low PN concentrations. The change in uncertainty intervals in the loads around the measurement gap is due to larger discharge, therefore magnifying the variability.

The sensor records provided valuable insights into the dynamics of the floodplain and allowed constraining floodplain budgets. These continuous estimates of carbon and nutrient exports form the floodplain over an annual cycle will be used in a next step to derive elemental mass balances for the reservoir.
Lake Kariba biogeochemistry

**Budgets of carbon and nutrients**

A previous effort to constrain the carbon and nutrient budgets of Lake Kariba (Kunz et al., 2011a), was limited by large uncertainties in the annual inputs from the tributaries. The sensor-derived data have provided constraints on the loads in the upper Zambezi, i.e. the inflow to Lake Kariba, thereby reducing this uncertainty. Measurements from immediately downstream of the reservoir and at Chirundu (roughly 80km further downstream) further provided information on the biogeochemistry of the outflowing water. The concentrations have been converted to loads using the average turbine outflow and its standard deviation from 2013/2014, a value of $1356 \pm 116\, \text{m}^3\,\text{s}^{-1}$. In the previous budget, a single measurement was converted to yearly loads by using an averaged outflow.

Two different estimates of methane emissions from Lake Kariba are available (DelSontro et al., 2011; Teodoru et al., 2015). These differ by almost an order of magnitude, from 10 to $88 \cdot 10^3\,\text{tons per year}$. As the spatial coverage of DelSontro et al. (2011) was much larger and they captured several of the pathways of CH$_4$ release, it was therefore deemed more representative and their number ($88 \cdot 10^3\,\text{tons per year}, 45\,\text{mg C}\,\text{m}^{-2}\,\text{d}^{-1}$) will be used in our budget for Kariba (Table 4.3).

While the reservoir was a source of methane, it has been shown previously that Lake Kariba is a sink for atmospheric CO$_2$ (Teodoru et al., 2015), estimated at $141\,\text{mg C}\,\text{m}^{-2}\,\text{d}^{-1}$ ($276 \cdot 10^3\,\text{tons per year}$) based on chamber deployments. At the same time, these authors estimated the primary production rate from $^{13}$C-labeled incubations at $16.6\,\mu\text{mol C}\,\text{L}^{-1}\,\text{h}^{-1}$, which would imply an input of organic carbon of $47 \cdot 10^6\,\text{tons of carbon per year}$, assuming a photic zone of 5 m. These primary production rates are at least an order of magnitude larger than values we reported for the Barotse Plains based on the oxygen records from the sensor deployment, below $1\,\mu\text{mol O}_2\,\text{L}^{-1}\,\text{h}^{-1}$ (Zuijdgeest et al., 2016). For a river that is known as oligotrophic, the numbers reported by Teodoru et al. (2015) seem very high.
Considering that there is very little change in DIC loads upstream and downstream of the reservoir (276±24 and 271±23 \cdot 10^3 tons of carbon per year, respectively), these numbers create a large surplus of carbon in our system without CO$_2$ outgassing from the reservoir. Therefore, the net gas exchange has not been constrained by our budget, but is instead determined by balancing the other sources and sinks (Table 4.4). Similar to the problems with gas exchange for the carbon budget, the available estimates of denitrification and nitrogen fixation in Lake Kariba have a high degree of uncertainty as a consequence of extrapolation. The net balance between these two is determined by balancing the other sources and sinks (Table 4.4).

**Table 4.4** Figures for the carbon, nitrogen, and phosphorus budgets, all in 10$^3$ tons C, N, or P per year. Inorganic nutrient contributions are not included, due to low concentrations compared to the organic fractions (Zuijdgeest et al., 2015). Inflow values determined from sensor deployment, outflow from the field campaigns with average outflow from Kariba turbines (2013-2014). Sedimentation from Kunz et al. (2011a) and CH$_4$ outgassing from DelSontro et al. (2011).

<table>
<thead>
<tr>
<th></th>
<th>DOC</th>
<th>POC</th>
<th>Total carbon</th>
<th>TN</th>
<th>TP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inflow</td>
<td>200</td>
<td>22</td>
<td>220</td>
<td>16</td>
<td>2.5</td>
</tr>
<tr>
<td>Outflow</td>
<td>55</td>
<td>13</td>
<td>68</td>
<td>4.7</td>
<td>0.17 *</td>
</tr>
<tr>
<td></td>
<td>(50 – 60)</td>
<td>(12 – 14)</td>
<td>(62 – 74)</td>
<td>(4.3 – 5.1)</td>
<td>(0.15 – 0.18)</td>
</tr>
<tr>
<td>Sedimentation</td>
<td>120</td>
<td>120</td>
<td>12 (11-62)</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>CH$_4$ flux</td>
<td></td>
<td></td>
<td>88</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Based on our best estimates of the sources and sinks of carbon, nitrogen, and phosphorus in Lake Kariba, we have set up budgets for the reservoir (Fig. 7). We determined that Kariba is indeed a net annual sink for CO$_2$ (54·10$^3$ tons of carbon per year), though not as large as previously reported (Teodoru et al., 2015), suggesting a larger contribution by primary production. Such a larger organic carbon input from primary production could also account for the high sedimentation rate, which is distinctly higher than the input of POC from the Zambezi. In addition, sorption of DOC onto suspended material may also contribute to the organic matter settling in the reservoir.
For nitrogen, the balance is lacking a very small input of $0.7 \cdot 10^3$ tons of carbon per year. This is well within the uncertainty ranges, but also shows that denitrification and nitrogen fixation are more or less balanced. For phosphorus, an input more than half as large as the river inflow is lacking ($1.8 \cdot 10^3$ tons of carbon per year). Release of phosphorus from the sediments will probably contribute to the missing source. This process has previously been found to be a significant contribution to the budget in reservoirs (Gin et al., 2011). Nevertheless, the amount of phosphorus released is likely somewhat lower than reported here, as the outflow load is underestimated due to lack of dry-season PP measurements.

![Diagram of carbon, nitrogen, and phosphorus budgets for Lake Kariba](image)

*all in $10^3$ tonnes per year

**bold:** flux constrained, **italic:** closing the budget

**Figure 4.7** Carbon, nitrogen, and phosphorus budgets for Lake Kariba based on export data from upstream floodplain and published fluxes (Table 4.4). Bold numbers indicate that the flux is constrained (see Tables 4.3 and 4.4), italic numbers were determined by closing the budgets.

In several aspects these budgets expand on and differ from previous budgets (Kunz et al., 2011a). In general, we have been able to better constrain the in- and outflows from the reservoirs. Differences can be found in the carbon balance, where the previous budget did not account for air-water exchanges. For nitrogen, the sign and magnitude of the difference between nitrogen fixation and denitrification changed, with the system taking up slightly more atmospheric nitrogen than losing
it via denitrification. Because the budgets have been better constrained with inflow data, we show that some of the sedimentary phosphorus is actually released again into the water column.

**Element ratios**

Downstream of Kariba, we observed lower POC:PN ratios than upstream, with values decreasing to 8 during falling water conditions in June (Fig 4.6). This lower C:N ratio in the outflow can be linked to the export of algal biomass, with typical C:N ratios between 4 and 10. During the other two campaigns, smaller (HW, April) and no (LW, October) change in POC:PN ratio was observed. This variability in the autochthonous C:N signature can be linked to the strong seasonal cycle could observed in the water column of Lake Kariba (M. Kunz, unpublished results 2007-2009). Around July, the reservoir was overturning, and showed low concentrations of inorganic nutrients at all depths. Thermal stratification became more prominent until February, and weakened during the remainder of the wet season. In June, the highest inorganic nutrient concentrations of ammonium and soluble reactive phosphorus were observed. These data indicate favorable conditions for a phytoplankton bloom during falling water conditions. The PN:PP ratio was low and more or less constant during falling water, but increased during high water. During both high and falling water, the DON:DOP ratio decreased markedly in the reservoir. These combined observations suggest release of phosphorus from the particulate phase and the sediments. Little change was observed in the DOC:DON ratios and in general, their values were following the input signature quite closely.

**Particle retention**

For African reservoirs, it has been suggested that an average of 25 (Syvitski et al., 2005) to 42% (Vörösmarty et al., 2003) of the particulate load is being retained. For the Zambezi, the basin-wide trapping efficiency has been estimated between 80 and 100% (Vörösmarty et al., 2003). Our element budgets for Lake Kariba
document specific retention efficiencies for carbon and nutrients. For POC and PN, the outflow amounted to 52% of the inflowing loads (12.4·10^3 tons POC retained per year, 1.3 for PN). By contrast, 87% of the inflowing phosphorus load (2.2·10^3 tons PP per year) was retained behind Kariba dam. These numbers for carbon and phosphorus burial are very similar to the results published by Kunz et al. (2011a): they found 87% P retention (86-97%) and a burial efficiency, defined as the net sediment carbon accumulation relative to the settling flux in the water column, of 41% for carbon. P retention was described as reasonable because of the long hydraulic residence time and high sediment removal potential. The value for nitrogen retention from Kunz et al. (2011a) was much higher (74%) than reported here. However, our value still falls well within tropical removal efficiency values for nitrogen (0.04-70%; Harrison et al., 2009). Particle and phosphorus retention has also been shown for the Three Gorges Dam in China (Gong et al., 2006). As a global average, dams and reservoirs are estimated to retain more than 40% of the inflowing total phosphorus load (Maavara et al., 2015).

**Greenhouse-gas emissions**

The Lake Kariba surface waters were undersaturated during the campaigns documented by Teodoru et al. (2015). Undersaturation of CO_2 in reservoir surface waters, and hence uptake of CO_2 by the reservoir, has previously been described for the Tana river (Bouillon et al., 2009; Tamooh et al., 2013). The campaigns by Teodoru et al. (2015) missed, however, the “overturn season” during falling waters at the begin of the dry season, when CO_2-rich deep-water is brought to the surface and results in a temporal outgassing flux. In a limnological study that included depth profiling, the water column was found to be highly oversaturated with respect to CO_2 (350-1100%; Kunz et al., 2011a). These observations support the rather small net CO_2 uptake in Figure 7. In recent assessments, tropical lakes and reservoirs are often reported to be oversaturated with respect to carbon dioxide, with a median value of 1900ppm (Aufdenkampe et al., 2011). However, it appears that this tropical estimate is based to a large degree on studies from the Amazon basin. It has been shown previously (Borges et al., 2015a) that the Amazon system
differs markedly from large tropical river systems in Africa. Taken together, our assessment and the study of Teodoru et al. (2015) indicate that the CO$_2$ transfer between deep subtropical reservoirs and the atmosphere may seasonally change its sign resulting in a rather small overall exchange.

While our budget indicates a small overall CO$_2$ uptake by Lake Kariba, there is a flux of methane from the reservoir to the atmosphere. The water column was highly oversaturated with respect to CH$_4$ (>500%; DelSontro et al., 2011). The flux of methane from Kariba to the atmosphere is of comparable magnitude as fluxes determined for Brazilian reservoirs at similar latitudes (Rosa et al., 2004). In a large dataset of reservoirs emissions, 12% of the reservoirs was found to be a sink for CO$_2$ (Barros et al., 2011). The strength of those sinks was generally $< 500$ mg C m$^{-2}$ d$^{-1}$, which is more than an order of magnitude larger than our estimate for Kariba (27 mg C m$^{-2}$ d$^{-1}$). The methane emissions from Lake Kariba (45 mg m$^{-2}$ d$^{-1}$; DelSontro et al., 2011) are within range for reservoirs at comparable latitudes, though higher than expected based on reservoir age (Barros et al., 2011). Considering the global warming potential of methane (34 CO$_2$ equivalent, CO$_2$eq), the net emissions from Lake Kariba are roughly $3000 \cdot 10^3$ tons C as CO$_2$eq per year ($= 3$ Tg / 0.003 Pg CO$_2$eq-C per year). The value of yearly Kariba emissions derived in this study falls within the range of greenhouse-gas emissions from equatorial reservoirs compiled by (Demarty and Bastien) (2011).

For the entire Zambezi catchment, the combined flux of CO$_2$ and CH$_4$ to the atmosphere was estimated between 10.8 and 16.2 Tg CO$_2$eq per year (Borges et al., 2015b), using the methods of Aufdenkampe et al. (2011) and Raymond et al. (2013), respectively. Using this scenario, our estimated emissions from Kariba would contribute between 18 and 28% to the total emissions from the Zambezi catchment. Scaled by the surface area of the reservoirs in the Zambezi catchment, they would contribute 43% to riverine greenhouse gas emissions. Total annual greenhouse gas emissions from hydroelectric reservoirs have been estimated at 0.8 Pg CO$_2$eq per year (Deemer et al., 2016), to which Kariba would contribute about 0.4%.
Biogeochemical alterations by the Barotse Plains

Element ratios

In the upstream part of the Zambezi river, POC:PN ratios of suspended matter were generally around 10, which is indicative of soil inputs. Along the floodplain, the POC:PN ratio decreased during high water, while it increased during the other two seasons. The decrease during maximum inundation could result from aquatic production on the inundated floodplain, whereas inputs of floodplain and terrestrial vegetation (Zuijdgeest, 2017) during FW and LW would result in higher ratios. The DOC:DON ratios were stable, though different during high and low water, and decreased along the floodplain during falling water. The DON:DOP ratios increased during high and falling water, and no DOP could be detected during low water. Combined with the DOC:DON ratio, this strongly suggests a source of nitrogen-rich organic matter during falling water. Since the wet season DOC:DON did not suggest this input, it seems likely that the increase in DON:DOP was at that time caused by removal of DOP. At the same time, the PN:PP ratio decreased along the floodplain. It could thus be, that some DOP was either adsorbed onto particulate matter or incorporated into living biomass. PN:PP values during low and falling water were distinctly lower than during high water, and increased along the floodplain. Overall, we see seasonal differences in the biogeochemical functioning of the floodplain. Algal production on the floodplain during high water could be responsible for lowering the POC:PN ratio and lowering the DON:DOP ratio, while inputs of vegetation and nitrogen-rich dissolved organic matter dominate at periods of lower water levels.

During high water, both PN and PP were retained by the floodplain, but not in the same ratio: PN was retained more effectively than PP. During low and falling water levels, additional inputs of nitrogen-poor terrestrial vegetation could have decreased PN concentrations, leading to lower ratios. Considering that N:P ratios in both terrestrial and freshwater biomass (28±15 and 30.2±15.9, respectively; Elser et al., 2000) are more elevated than those observed in the Barotse Plains, it appears the system was N-limited year-round. Nitrogen limitation in tropical floodplains has previously been described for the Paraná river, likely caused by
high denitrification rates on the floodplain and release of iron-bound phosphorus (Villar et al., 1998). This leaves an open question about the magnitude of nitrogen fixation rates in such systems.

**Particle retention**

The Barotse Plains are releasing particles on a yearly cycle, along with particulate phosphorus (approximately 80 tons per year), as determined by extrapolation of mass balances based on field measurements. This is in contrast to several other tropical floodplains: sediment retention has been shown for floodplains in the Tana river (Omengo et al., 2016a), and in the Paraná river (Villar et al., 1998). At the same time, the Barotse Plains are retaining particulate carbon and nitrogen on a yearly cycle (approximately 1200 tons POC, 100 tons PN). This suggest erosion of mineral soils, with associated phosphorus. Erosion from the floodplain seems likely, as soils on the floodplain are generally poorly developed (arenosols, i.e., sandy soils with little profile development, soil map from FAO/UNESCO from 1992, as presented by Gerrits, 2005). The loss of organic carbon and nitrogen could be either as burial on the floodplain, or as (greenhouse) gas emissions.

**Greenhouse-gas emissions**

Emissions of greenhouse gasses in tropical African rivers have been linked with wetland coverage in the catchment (Borges et al., 2015b). Previously-reported high aquatic CO$_2$ and CH$_4$ concentrations downstream of the Barotse Plains (Teodoru et al., 2015) further suggested that floodplains are hotspots for emissions. Sensor-records showed large CO$_2$ oversaturation downstream of the floodplain during the flooding season (Zuijdegeest et al., 2016). Combining these sensor-derived CO$_2$ records with a gas transfer coefficient determined in the field (Teodoru et al., 2015), the average annual emissions from the river downstream of the Barotse Plains are estimated around 480 g m$^{-2}$ yr$^{-1}$. Emissions downstream of the floodplain during the onset of the flooding season (approx. 12,500 mg C m$^{-2}$ d$^{-1}$ in mid-February 2012, Teodoru et al., 2015) are an order of magnitude larger.
than yearly-averaged flux downstream of the floodplain (approx. 1300 mg C m\(^{-2}\) d\(^{-1}\)), highlighting the large seasonal variability. The annual emissions fall within the range for tropical wetlands (240 gC m\(^{-2}\) yr\(^{-1}\)) and large rivers (>100m width; 1600 gC m\(^{-2}\) yr\(^{-1}\)) as summarized by Aufdenkampe et al. (2011).

In the absence of more detailed data, the point emission from the river downstream of the Barotse Plains can be assumed representative for the entire floodplain (7,700 km\(^2\); Hughes and Hughes, 1992). With this simplified assumption, the annual CO\(_2\) emissions from the Barotse Plains river-floodplain system are roughly 3.7 Tg per year. By comparison, total emissions from the much larger floodplains of the central Amazonian River amount to 0.21 Pg yr\(^{-1}\) (Abril et al., 2014). Normalizing these emissions to the area, though, leads to higher emissions from the Zambezi than the Amazon, 480 tons km\(^{-2}\) yr\(^{-1}\) versus 120 tons km\(^{-2}\) yr\(^{-1}\), respectively. Based on the land cover in the two catchments (Table 4.5), it could be suggested that woodland and shrubland sustain higher aquatic CO\(_2\) emissions than floodplains surrounded by dense tropical forest.

**Table 4.5** Land cover characteristics of the Amazon and the Zambezi catchments, data for the Amazon from Borges et al. (2015a), for the Zambezi from Borges et al. (2015b).

<table>
<thead>
<tr>
<th>Land cover</th>
<th>Amazon</th>
<th>Zambezi</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dense forest (%)</td>
<td>83</td>
<td>20.4</td>
</tr>
<tr>
<td>Mosaic forest (%)</td>
<td>4</td>
<td>0.0</td>
</tr>
<tr>
<td>Woodland and shrubland (%)</td>
<td>4</td>
<td>54.6</td>
</tr>
<tr>
<td>Grassland (%)</td>
<td>5</td>
<td>8.7</td>
</tr>
<tr>
<td>Cropland/ bare soil (%)</td>
<td>4</td>
<td>13.4</td>
</tr>
</tbody>
</table>

The only measurement available for methane emissions downstream of the floodplain was made at the end of the dry season in 2013 (Teodoru et al., 2015). Although this number, at 100 mg C m\(^{-2}\) d\(^{-1}\), is distinctly lower than the yearly-averaged CO\(_2\) fluxes from the same location, it suggests that the CO\(_2\)-equivalent emissions from the floodplain could be even larger.
Implications

Dams and reservoirs alter the riverine biogeochemistry in distinct, and often different ways. In Table 4.6 we summarize some of the most distinct effects by Lake Kariba and the Barotse Plains on river biogeochemistry in the upper Zambezi basin. Although further comparative analyses across the basin and with other tropical systems are necessary, several observations can serve as a starting point for general assessment of the biogeochemical effects caused by disappearing tropical floodplains and the expansion of hydropower reservoirs in tropical river systems:

Wetlands with intense flood dynamics are mobilizing particles and reservoirs are trapping them. While the intense flooding of the Barotse plains mobilizes particles into the river system specifically at rising floods, the reservoir acts as an efficient particle trap. Particle input into the mangrove system of the Zambezi delta is now linked almost exclusively to the Shire River inflow. Damming the Shire will reduce the particle flux to this sensitive coastal system by two orders of magnitude.

Wetlands are producing an excess of terrestrial biomass that supports aquatic life over long river reaches, while reservoirs are trapping organic carbon and releasing easily degradable aquatic biomass. In a similar way, oligotrophic tropic wetlands merely transform nutrients into dissolved and particulate organic matter. Anoxic conditions can mobilize phosphorus and trigger nitrogen fixation, while reservoirs act as net traps for nutrients. Downstream nutrient emissions from floodplains also carry a strong seasonal signature (with maximum loads during peak flow conditions) while large dams provide a continuous flux to downstream river reaches.

It remains challenging to quantify the net effect on greenhouse gas emissions when a wetland area is transformed into a reservoir surface. The observations in the Zambezi basin indicate that the net uptake of CO\textsubscript{2} by storage of organic carbon in sediments ($120 \cdot 10^3$ tons C yr\textsuperscript{-1}) is more than offset by ebullition of methane gas with $3000 \cdot 10^3$ tons C in the form of CO\textsubscript{2} equivalents per year.
Table 4.6 Quick overview of the different ways in which the reservoir and the floodplain affect particle dynamics, carbon and nutrient turnover, and greenhouse-gas emissions.

<table>
<thead>
<tr>
<th>Process</th>
<th>Kariba Reservoir</th>
<th>Barotse Floodplain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle dynamics</td>
<td>Retention</td>
<td>Export</td>
</tr>
<tr>
<td>Carbon turnover</td>
<td>POC burial</td>
<td>POC and DOC emission</td>
</tr>
<tr>
<td>Nitrogen turnover</td>
<td>Balance of N-fixation and denitrification</td>
<td>Net N-fixation</td>
</tr>
<tr>
<td>Phosphorus turnover</td>
<td>P burial</td>
<td>PP and DOP export</td>
</tr>
<tr>
<td>Greenhouse-gas emissions</td>
<td>Uptake of CO2</td>
<td>Emission of CO2</td>
</tr>
<tr>
<td></td>
<td>Emission of CH4</td>
<td>Emission of CH4</td>
</tr>
</tbody>
</table>

Acknowledgements

The authors thank Simon Baumgartner, Christian Dinkel, Renata Fulcri, Ivo Indergand, Kristina Peterson, Severin Wiens, and Cristian Teodoru for help in the field. Laboratory analyses were supported by Patrick Kathriner, Stewart Bishop, and Madalina Jaggi. This work has built strongly on earlier work by Manuel Kunz, Roland Zurbrügg, Tonya DelSontro, and Cristian Teodoru. Comments from Steven Bouillon and Nathalie Dubois on an earlier version are much appreciated. Institutional support was provided by Imasiku Nyambe (University of Zambia and its Integrated Water Resource Management Center), the Zambia Wildlife Authority, the Zambezi River Authority, and the Zambia Electricity Supply Corporation. Funding for this study came from the Competence Center for Environment and Sustainability (CCES) of the ETH domain, the Swiss National Science Foundation (Grants No. 128707 and 157750) and Eawag.
Appendix

Appendix 4.1: Correlations between sensor measurements and carbon and phosphorus

Similar to the PN correlations shown in the manuscript, correlations between turbidity and particulate carbon and phosphorus and between fDOM and dissolved organic carbon and phosphorus were determined (Fig. S4.1, Table S4.1).

Particulate carbon and nitrogen concentrations were determined by analyzing suspended matter on GF/F filters using an elemental analyzer isotope ratio mass spectrometer (EA-IRMS; ThermoFinnigan FlashEA 1112 coupled to a DeltaV Advantage Continuous-Flow IRMS). Samples for dissolved organic carbon and nitrogen were acidified in the field and concentrations determined using a Shimadzu TOC-L analyzer. Particulate phosphorus was determined via photospectroscopy after digestion with persulfate of replicate GF/F filters containing suspended material. Dissolved organic phosphorus was determined as the difference between total dissolved phosphorus (determined after similar digestion as the particulate phosphorus) and phosphate concentrations, both determined via photospectroscopy.
Figure S4.1 Correlations between turbidity and fDOM versus particulate and dissolved carbon and phosphorus, respectively. 95% confidence intervals are shown in grey.

Table S4.1 Statistical parameters of the correlations between turbidity and the particulate phases, and fluorescent dissolved organic matter and the dissolved organic phase.

<table>
<thead>
<tr>
<th></th>
<th>POC</th>
<th>PP</th>
<th>DOC</th>
<th>DOP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation</td>
<td>6.32*turb + 23.9</td>
<td>0.30*turb+0.70</td>
<td>8.03*fDOM+78.3</td>
<td>0.0015*fDOM+0.06</td>
</tr>
<tr>
<td>p value</td>
<td>0.00291</td>
<td>0.00790</td>
<td>0.000296</td>
<td>0.0986</td>
</tr>
<tr>
<td>r value</td>
<td>0.712</td>
<td>0.656</td>
<td>0.843</td>
<td>0.551</td>
</tr>
</tbody>
</table>
Chapter 5

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

Alissa Zuijdgeest
Roland Zurbrügg
Nanina Blank
Renata Fulcri
David Senn
Bernhard Wehrli

Biogeosciences, 12, 7535–7547, 2015
Abstract

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

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

Carbon-to-nitrogen ratios of particulate organic matter showed that soil-derived material was dominant year-round in the Barotse Plains, whereas the Kafue Flats transported particulate organic matter that had been produced in the upstream reservoir during the wet season. Stable carbon isotopes suggested that inputs from the inundated floodplain to the particulate organic-matter pool were important during the wet season, whereas permanent vegetation contributed to the material transported during the dry season. This study revealed effects of dam construction
on organic-matter and nutrient dynamics on the downstream floodplain that only become visible after longer periods, and it highlights how floodplains act as large biogeochemical reactors that can behave distinctly differently from the entire catchment.
Introduction

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

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

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

The type of organic matter transported by tropical rivers covaries with discharge. Both the Tana River in Kenya (Tamooh et al., 2014) and the Sanaga River in Cameroon (Bird et al., 1998) transported mainly organic matter from the degradation of $C_4$ plants during the wet season, while dry-season runoff is characterized by organic matter originating from $C_3$ plants. Spencer et al. (2010) also showed that the properties of organic carbon transported by a tributary of the Congo River vary during different hydrographic phases, with highest dissolved organic carbon and lignin concentrations during peak flow. In the same river, the particulate organic carbon concentration increased when the discharge increased (Mariotti et al., 1991).

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

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

**Study sites**

At 1.4x10^6 km^2, the Zambezi River basin is the fourth largest in Africa, and the only major African river draining into the Indian Ocean. Due to its geographic location, the catchment experiences a pronounced wet season during the passage of the Intertropical Convergence zone (December-March) and a dry season (Apr-Nov) during the remainder of the year.

The Barotse Plains are a near-pristine floodplain area in the upstream part of the Zambezi River in the western part of Zambia (Fig. 5.1). The hydrography in the Barotse Plains clearly reflects the climatic conditions, with peak flow around April or May and low flow between July and November (Fig. 5.2a). The total inundatable area is estimated at around 7,700 km^2 (Hughes and Hughes, 1992). The Kafue Flats are located along the Kafue River, one of the largest tributaries of the Zambezi River. Upstream of the Flats, the Itezhi-Tezhi dam (ITT, completed in 1978) stores a significant part of the wet-season runoff in order to allow for a continuous operation of the power station at Kafue Gorge (dam completed in 1972) downstream of the Kafue Flats. Evaporation from the reservoir changes the water level by 780 mm year\(^1\), according to Beilfuss (2012). At 6,000 km^2, the maximum inundated area of the Kafue Flats is smaller than that of the Barotse Plains (Hughes and Hughes, 1992). The hydrography of the Kafue Flats has been significantly altered by the presence of the dams (Fig. 5.2b), but the annual discharge did not change. Over the last decades, peak flow has been reduced (approximately -50%) and base flow has increased (roughly +50%, Fig. 5.2b). In
consequence, timing and extent of inundation in the Kafue Flats have changed (Mumba and Thompson, 2005). The floodplain area has been reduced by 40% due to permanent inundation, a direct result of elevated base flow sustained by the dam operation.

![Map of the Zambezi catchment](image)

**Figure 5.1** Map of the Zambezi catchment, with floodplains (in green) and large dams (red arrows) marked. Inserts show sampling stations during the dry (circles) and wet season (stars) in the Barotse Plains and Kafue Flats. Sampling stations will be further presented in distance along the river (km).
Figure 5.2 River discharge (a) at Senanga, the downstream boundary of the Barotse Plains (1988-2006 average and standard deviation), and (b) at the outflow of Itezhi-Tezhi (ITT) dam, the upstream boundary of the Kafue Flats. Discharge for the Kafue Flats are means of pre-dam (1960-1971) and post-dam construction (Kafue Gorge dam: 1972-1977; ITT dam: 1978-2010) periods. Data from the Department of Water Affairs and Zambezi River Authority: permission for reprint first granted to Blaser (2013).

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

Sampling

Sampling of the main river channel at multiple locations along the floodplains (Fig. 5.1) was conducted during peak flow, hereafter called the wet season (April or May; Barotse Plains 2009, 2013; Kafue Flats 2008, 2009, 2010), and low flow, referred to as the dry season (October; Barotse Plains 2008, 2013; Kafue Flats 2008). Samples were collected from surface water in the middle of the well-mixed channel (50cm, Barotse Plains) or at mid-depth (Kafue Flats) using a peristaltic pump. The similarity of the results from different years (Zurbrügg et al., 2012; Zurbrügg et al., 2013) allowed the combination and averaging of the data sets in order to obtain generalized patterns for the two systems and seasons. Discharge in the main channel was measured using a RiverRay ADCP (acoustic Doppler current profiler; for Barotse Plains, dry season data from the Zambezi River Authority were used).

Laboratory analyses

Samples for dissolved nutrient concentrations were filtered through 0.45 µm filters. Dissolved inorganic nitrogen (DIN, limit of quantification, LOQ, of nitrogen analyses < 4 µM), phosphate (LOQ phosphorus analyses < 0.2 µM), and the sum of nitrate and nitrite were measured by chemiluminescence detection (Antek 9000). Ammonium was determined by standard colorimetric technique. Total dissolved nitrogen and total phosphorus (TDN and TDP) were determined by chemiluminescence detection (Antek 9000) following persulfate oxidation (Solórzano and Sharp, 1980; Bronk et al., 2000). Samples for particulate phosphorus concentrations during the wet season were collected onto 0.7 µm GF/F filters (Whatman) and measured using a sequential phosphorus extraction method (SEDEX, Ruttenberg, 1992 as modified by Slomp et al., 1996). Samples for dissolved organic carbon (DOC, precision < 10 µM) and dissolved inorganic carbon (DIC, precision < 10µM) were filtered through 0.7 µm GF/F filters (Whatman) and analyzed on a Shimadzu TOC-L (Barotse Plains) and on a Shimadzu 5050...
TOC analyzer (Kafue Flats, DOC only). DIC concentrations for the Kafue Flats were calculated from pH and alkalinity measurements (data not shown). Stable oxygen isotopes were determined on filtered water samples (0.45 µm nylon filters) using a Picaro L2120-I Cavity Ringdown Spectrometer (Barotse Plains, precision 0.05‰) or a MultiFlow preparation module connected to a continuous-flow IRMS (isotope ratio mass spectrometer; Isoprime, UK, precision 0.2‰; Kafue Flats) and calibrated against in-house standards ranging from 0 to -22.5‰

Riverine suspended matter was collected on pre-weighed GF/F filters (Whatman). After freeze-drying of samples, suspended matter concentrations were determined by weight difference. Particulate organic carbon and nitrogen and their stable isotopic compositions (POC, PN, δ¹³C and δ¹⁵N, respectively) were determined using an elemental analyzer-isotope ratio mass spectrometer (EA-IRMS; Thermo-Fischer MAT 253 or ThermoFinnigan FlashEA 1112 coupled to a DeltaV Advantage Continuous-Flow IRMS) and calibrated against in-house standards (δ¹³C: -15 to -30‰ VPDB, precision 0.1‰; δ¹⁵N: -1.1 to +32.7‰ air, precision 0.2‰).
Results

Hydrology and oxygen isotopes

During the wet season, the runoff in the main channel of both floodplains was characterized by a discharge minimum roughly in the middle of both systems (Fig. 5.3). Located around 100 km and 200-300 km downstream in the Barotse Plains and in the Kafue Flats, respectively, constrictions in the riverbed were present, which promoted flooding of the surrounding floodplain area (Zurbrügg et al., 2012). During the dry season, the discharge remained fairly constant in both systems with a gain due to tributaries along the Barotse Plain and a slight loss in the Kafue Flats. Note, however, that the peak discharge in the wet season was about 4 times higher in the Zambezi crossing the Barotse Plains compared to the dammed Kafue River (Fig. 5.2).

Figure 5.3 Discharge and stable oxygen isotope signals in the Barotse Plains and the Kafue Flats during wet and dry seasons. Discharge and $\delta^{18}$O data for the Kafue Flats have been published previously in Zurbrügg et al. (2012).
The intense river-floodplain exchange left a distinct $\delta^{18}O$ signal in both systems: the rivers lost water to the floodplain during the wet season. Downstream of the stretch where discharge in the river decreased, the $\delta^{18}O$ of the river water changed sharply towards heavier values (Fig. 5.3). The overall $^{18}O$ enrichment of the channel water between the upstream and downstream sampling locations was more pronounced in the Kafue Flats during the wet season. In the Barotse Plains, the $\delta^{18}O$ signal showed an overall shift from -2.0‰ in the upstream part to -0.9‰ at the downstream end. In the Kafue Flats a sharp increase towards heavier values was observed downstream of the channel constriction. To correct for different travel distances along the river stretches, the change in $\delta^{18}O$ per 100 km of river length was estimated: for the Barotse Plains this enrichment was +0.26‰ and for the Kafue +0.56‰ per 100 km. During the dry season, no significant increase in the isotopic signal of oxygen was observed in the Barotse Plains, while in the Kafue Flats enrichment occurred at +0.17‰ per 100 km.

Concentrations and loads

For a comprehensive comparison of the concentrations of carbon, nitrogen, and phosphorus species along the two floodplains during contrasting seasons, all measurements along the floodplain have been considered, irrespective of spatial trends (Fig. 5.4). The occurrence of large spatial variations along the floodplain, or differences between measurement methods between the different years, resulted in larger ranges.
Figure 5.4 Boxplots of the concentrations of dissolved and particulate carbon, nitrogen and phosphorus species along the Barotse Plains and the Kafue Flats during wet and dry seasons along the floodplain. The boxes represent the first and third quartiles, and the median. No measurements of particulate phosphorus were made on samples from the dry seasons. Carbon and nitrogen data of the Kafue Flats have been previously published in Zurbrügg et al. (2013).

The dissolved inorganic fraction dominated the total carbon concentration in both seasons and both systems (Fig. 5.4). Dissolved organic nitrogen (DON) was always the main nitrogen species. In the Barotse Plains particulate phosphorus (PP) was the dominant form during the wet season, while dissolved inorganic phosphorus (DIP) was generally the prevailing species during the dry season. Phosphorus concentrations were largely close to the detection limit in both systems, and were therefore excluded from the calculation of loads.

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

Loads were calculated from the discharge and concentration data for the respective species, as the water column was well mixed (see Appendix 2). Total carbon and nitrogen loads increased along the Barotse Plains during the wet season, mainly due to a larger contribution from the dissolved organic form (Fig. 5.5). The increase in total carbon load in the Kafue Flats during the wet season was mainly attributed to the dissolved inorganic fraction. The magnitude of the wet-season carbon loads leaving the floodplain area was comparable between the two systems (roughly 1500 t C d\textsuperscript{-1}, Fig. 5.5), while the nitrogen loads in the Barotse Plains were almost twice as high as those in the Kafue Flats (44 t N d\textsuperscript{-1} and 20 t N d\textsuperscript{-1}). During the dry season the loads decreased slightly.

Net export was determined as the difference between the load at the downstream end of the floodplain and the load at the upstream end of the floodplain (Table 5.1). During the wet season, the Barotse Plains were a sink for all particulate phases, while the Kafue Flats acted as a source (Table 5.1). Both systems were sources of DOC and DIC. Dissolved organic nitrogen was exported from both floodplains, but the Barotse Plains retained the small DIN flux, while the Kafue Flats were a minor source. During the dry season, the Barotse Plains acted as source of particulate matter. For the Kafue Flats this could not be determined due to a lack of POC and PN measurements in the downstream stretches of the river. DOC and DIC were retained by both systems. The Barotse Plains were a minor source of dissolved nitrogen, while the Kafue Flats retained both organic and inorganic nitrogen.
Figure 5.5 Dissolved and particulate carbon and nitrogen loads along the Barotse Plains and the Kafue Flats during wet and dry seasons. The loads of particulate carbon and nitrogen at the two most downstream locations in the Kafue Flats could not be determined for the dry season due to a lack of POC and PN measurements.

Table 5.1 Net export (in tons C per day and tons N per day), calculated as the difference between loads at the downstream and upstream ends of the respective floodplain, from the two floodplains during wet and dry seasons. Positive numbers indicate that the floodplain acted as a source (export), negative numbers indicate the floodplain acting as a sink (retention). POC and PN export from the Kafue Flats during the dry season could not be estimated due to a lack of measurements at downstream locations.

<table>
<thead>
<tr>
<th>System</th>
<th>Wet season</th>
<th>POC</th>
<th>DOC</th>
<th>DIC</th>
<th>PN</th>
<th>DON</th>
<th>DIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barotse</td>
<td></td>
<td>-38</td>
<td>170</td>
<td>270</td>
<td>-3.7</td>
<td>12</td>
<td>0.0</td>
</tr>
<tr>
<td>Plains</td>
<td>Dry season</td>
<td>14</td>
<td>-1.5</td>
<td>-78</td>
<td>1.6</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Kafue</td>
<td></td>
<td>6.5</td>
<td>160</td>
<td>640</td>
<td>0.6</td>
<td>11</td>
<td>0.1</td>
</tr>
<tr>
<td>Flats</td>
<td>Dry season</td>
<td>NA</td>
<td>-11</td>
<td>-89</td>
<td>NA</td>
<td>-0.8</td>
<td>-0.2</td>
</tr>
</tbody>
</table>
C:N ratios and isotopes

The C:N ratios of particulate organic matter (Fig. 5.6) remained fairly constant along the floodplain in the Barotse Plains and Kafue Flats during the wet season (10.8 ± 0.7 and 7.5 ± 0.7, respectively (statistically significant difference at 95% confidence intervals)). During the dry season the along-floodplain variability within each of the floodplains was larger (10.3 ± 1.5 and 10.3 ±1.8, respectively), but no significant difference was observed between the two systems. On average, particulate carbon was more depleted in $^{13}$C in the Kafue Flats than in the Barotse Plains during the wet season ($\delta^{13}$C = -28.5 ± 0.9 and -26.9 ± 1.1 ‰, respectively (statistically significant p<0.05)). During the dry-season, mean $\delta^{13}$C values were -28.5 ± 1.0‰ in the Barotse Plains and -26.5±1.9‰ in the Kafue Flats, again a significant difference. The organic matter in the Barotse Plains became more enriched in $^{13}$C during the wet season compared to the dry season, while in the Kafue Flats lower $\delta^{13}$C values were observed during the wet season than during the dry season (both significant, p < 0.05).

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

Paired analysis showed that there was no statistically significant (p <0.05) difference in particulate C:N ratios in the Barotse Plains between contrasting seasons, while there was a difference in dissolved C:N ratios and C-isotopic signals. In the Kafue Flats, there was a significant decrease in particulate C:N ratio from the dry to the wet season (as previously reported in Zurbrügg et al., 2013).
Figure 5.6 Carbon to nitrogen (C:N) ratios of particulate and dissolved organic matter as well as carbon isotopic signatures of particulate organic matter during wet (blue triangles) and dry (orange circles) seasons. The Kafue Flats data have been previously published in Zurbrügg et al. (2013).
Discussion

Hydrology and inundation dynamics

The discharge patterns (Fig. 5.3) showed how the bankfull capacity of the Zambezi and Kafue rivers varied along the floodplain stretch. In both systems water moved from the main channel onto the floodplain, at roughly 600 and 400 m³ s⁻¹ in the Barotse Plains and the Kafue Flats, respectively. Where the capacity of the channel increases again further downstream, water from the floodplains (and potential tributaries) returned to the main channel at higher rates. On the floodplain, flow velocities were extremely low (< 1 mm s⁻¹ on the Kafue Flats in May 2008, unpublished data), which led to prolonged residence times of the water on the floodplain, during which evaporation might occur, resulting in heavier δ¹⁸O signatures in floodplain water.

Using a mass balance approach based on oxygen isotopic data, Zurbrügg et al. (2012) calculated that >80% of the water in the Kafue Flats was on the floodplain for a certain amount of time during the wet season. Logistical constraints prevented the collection of similar remote floodplain samples in the Barotse Plains. Assuming a similar floodplain signal in the Barotse Plains as in the Kafue Flats, a first approximation was made to determine how much water in the Barotse Plains had been on the floodplain. This resulted in 50% of the water leaving the pristine floodplain area also having been outside the channel for a certain amount of time. This estimate shows that the interaction between river and floodplain was stronger in the Kafue Flats than in the Barotse Plains and reinforces the observation that a larger fraction of the river discharge in the Kafue Flats was forced onto the floodplain at the constriction location than in the Barotse Plains. In the published literature, high contributions of floodplain-derived water are also reported for the Tonle Sap Lake-floodplain system, where water from the Mekong contributed over 50% to the inflows of the lake and more than 80% of the outflows from the lake returned to the main river channel of the Mekong (Kummu et al., 2014). At peak flow in the Amazon, 97% of the river inflow occurred at overbank flow at the Cururi floodplain, and this water was on the floodplain for an average of 19 days, according to the modeling results by Rudorff et al. (2014).
During the dry season, the increasing discharge along the Barotse Plains is most likely caused by inflow of the Luanginga tributary. By contrast, the decreasing discharge in the Kafue Flats combined with a calculated 16% of the downstream discharge that had been on the floodplain for a certain amount of time (Zurbrügg et al., 2012) indicated that there was still exchange between the river channel and some permanently inundated areas in the downstream reaches of the Kafue Flats. From a regional perspective, the along-floodplain increase in the $\delta^{18}O$ signal in the Barotse Plains and Kafue Flats during the wet (flooding) season ($+0.21\%_\text{VSMOW}$ to $+0.56\%_\text{VSMOW}$ per 100 km) was considerably lower than the increase in the Okavango Delta during the dry (flooding) season ($+2.04\%_\text{VSMOW}$ per 100 km) and during wet season ($+0.74\%_\text{VSMOW}$ per 100 km; calculated from Akoko et al., 2013), indicating that there was significantly less extensive evaporation on the Zambezi catchment floodplains than in the inland Okavango delta.

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

During the wet season, the Barotse Plains were characterized by a net export of dissolved phases and retention of particulate material. Degradation processes or settling of particulate organic matter, either in the main channel or on the floodplain could result in apparent retention of POC and PN. The concurrent export of DOC, DIC, and DON could similarly be a result of degradation, or of the leaching of vegetation or soils. During the dry season, the patterns were reversed, indicative of inputs of organic matter from the Barotse Plains.

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

The observed net export of particulate organic matter may not have effects beyond the downstream reservoirs of Lake Kariba and Kafue Gorge (Fig. 5.1). Both impoundments will trap mobilized particles, and 70% and 90% of incoming total N and P are retained within Lake Kariba (Kunz et al., 2011a). Over the course of a year, the Barotse Plains were a sink for particulate phases, while both the Barotse Plains and the Kafue Flats were exporting large quantities of dissolved organic matter (Table 5.2). The export of dissolved organic matter, especially DOC, was 2-4 times higher than yields previously reported for the Zambezi catchment (Mayorga et al., 2010). The numbers are closer in magnitude to yields reported for the Amazon and Orinoco rivers, which both drain highly productive tropical rainforest (Lewis and Saunders, 1989; Beusen et al., 2005; Harrison et al., 2005a). Since the Zambezi mainly drains savanna ecosystems, catchment yields are a lot lower than from the other tropical rivers (Table 5.2). The negative yields of particulate matter show how floodplains can impact the riverine loads in trends opposite to those observed for the whole catchment. Additionally, the high dissolved organic matter yields further indicate that floodplains are intense biogeochemical reactors, which significantly affect riverine transport of organic matter from land to sea.
Table 5.2  Yields of carbon, nitrogen, and phosphorus in kilograms (C or N) per square kilometer per year from large river basins and floodplain yields from the Barotse Plains and Kafue Flats. Yields for this study are calculated from the maximum inundated areas mentioned in the “Study Sites” section, assuming 6 months of dry-season export and 6 months of wet-season export. POC and PN yields from the Kafue Flats during the dry season could not be estimated due to a lack of measurements at downstream locations, so no yearly yields were calculated.

<table>
<thead>
<tr>
<th>River</th>
<th>POC</th>
<th>DOC</th>
<th>PN</th>
<th>DON</th>
<th>DIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amazon</td>
<td>2900</td>
<td>5200</td>
<td>500</td>
<td>330</td>
<td>170</td>
</tr>
<tr>
<td>Congo</td>
<td>1400</td>
<td>3300</td>
<td>200</td>
<td>92</td>
<td>32</td>
</tr>
<tr>
<td>Orinoco</td>
<td>1500</td>
<td>5600</td>
<td>190</td>
<td>310</td>
<td>32</td>
</tr>
<tr>
<td>Oubangui</td>
<td>180</td>
<td>660</td>
<td>20</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>Zambezi</td>
<td>800</td>
<td>1000</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Barotse Plains</td>
<td>-570</td>
<td>4000</td>
<td>-50</td>
<td>300</td>
<td>-0.1</td>
</tr>
<tr>
<td>Kafue Flats</td>
<td>NA</td>
<td>4600</td>
<td>NA</td>
<td>300</td>
<td>-1.5</td>
</tr>
</tbody>
</table>

This study:


Sources of organic matter

Dissolved organic matter

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

The elevated C:N ratio of the dissolved organic matter was indicative of the
terrestrial origin of the organic material in both systems. The ITT reservoir did not have a pronounced impact on the dissolved phase (C:N around 23 during both seasons), which has previously been attributed to a mostly refractory dissolved organic-matter phase (Zurbrügg et al., 2013). The comparison with the Barotse Plains revealed a much larger variability in C:N of the dissolved matter, reaching dry-season values of 166 compared to the wet-season signatures around 18. While DOC concentrations were fairly similar during both seasons, the large decrease in DON concentrations from the wet to the dry season (Fig. 5.4) has resulted in this shift in dissolved C:N ratio.

The growth of seasonal vegetation on the inundated floodplain resulted in a large leaching potential of dissolved organic substances during the wet season, showing how processes on the floodplain affect the riverine biogeochemistry in this biogeochemical reactor. The increase in DOC and DON concentrations during the wet season in the Barotse Plains compared to the dry season also corresponds to the general observation that DOC export increases with runoff, caused by the shallowing of the flow paths through organic-rich upper soils (Aitkenhead-Peterson et al., 2003; Mulholland, 2003). Seasonal variability in DOC and DON concentrations has been previously shown in Hawaii (Wiegner et al., 2009) and Congo (Spencer et al., 2010). In Hawaii, flow paths are thought to change during changing hydrological conditions, and in Congo seasonal changes were considered indicative of different sources of dissolved organic matter, flow paths, and residence times. Runoff from inundated soils, such as found in the Zambezi River basin during the wet season, also tend to have higher DON concentrations (Aitkenhead-Peterson et al., 2003). This (potentially refractory) source of DON might be responsible for the high DON concentrations found in the Barotse Plains during the wet season. For the Kafue Flats, there was no significant seasonal change in DOC and DON concentrations between the wet and dry seasons. This might be due to the fact that an increase in DOC and DON concentration in the upstream catchment would be diluted and delayed by the presence of the Itezhi-Tezhi dam, showing after peak flow. With a residence time of 0.7 years, large fractions of organic carbon (±16%) and nutrient loads (50% N, 60% P) were trapped in the sediments of the reservoir (Kunz et al., 2011b). Monthly
measurements showed that the highest TOC concentrations occurred in the main channel in the floodplain area in May or June, after the peak flow (Wamulume et al., 2011). This could be a delayed effect of the increased concentrations at higher runoff during the wet season (November-March).

**Particulate organic matter**

The higher C:N ratio of the suspended matter in the Barotse Plains compared to the Kafue Flats indicates a year-round soil-derived source in the pristine part of the catchment. In contrast, C:N ratios found in the Kafue Flats during the wet season were indicative of aquatic production (Zurbrügg et al., 2013). This could be attributed to the presence of the ITT reservoir: both sediment trap data (Kunz et al., 2011b) and surface sediments from the reservoir (Supplementary information of Zurbrügg et al., 2013) showed a C:N ratio elevated from that observed in the Kafue Flats (12.1±0.6), similar to the numbers found for the suspended matter in the Barotse Plains. While degradation in the reservoir might also affect the C:N ratios, this typically leads to an increase. The observed difference between C:N ratios in the reservoir and in the river is therefore attributed to different sources. The presence of the dam significantly affected the chemical composition of the suspended matter, and while soil-derived suspended matter settled in the reservoir, mainly photosynthetically produced organic matter from the reservoir surface waters reached the Kafue Flats and eventually the Kafue-Zambezi confluence. The decrease in C:N ratio along the floodplain in the Kafue Flats during the dry season could be indicative of gradual organic-matter input from nitrogen-fixating vegetation. As a consequence of nutrient elimination in the ITT reservoir, widespread encroachment of N-fixing woody plants onto the floodplain has been observed (Blaser, 2013).

While the C:N ratio showed little variation throughout the year in the Barotse Plains, the stable C-isotopic signatures of the particulate matter further suggest different contributors to the POC in the river. During the wet season, the particulate organic matter in the Barotse Plains is $^{13}$C enriched compared to the dry season (-26.9 and -28.5‰, respectively). Organic-matter sources on the floodplain
(soils on average -18‰, abundant reeds between -12 and -27‰; unpublished data) had distinctly heavier δ13C signatures than the permanent vegetation in the area (average of six different tree species -28.3 ± 1.22 ‰; unpublished data). Shifts to isotopically heavier organic matter during the wet season, as observed in the Barotse Plains, have been described for the Tana River in Kenya (Tamooh et al., 2014), the Sanaga River in Cameroon (Bird et al., 1998), and the Congo River in central Africa (Mariotti et al., 1991). For all these tropical rivers, the source of the organic matter transported by the river changed with inundation. Connectivity of floodplains during high-water conditions resulted in enriched stable isotopic values in the riverine organic matter. During the dry season, inputs from permanent terrestrial vegetation resulted in more depleted δ13C signatures.

In contrast, the particulate organic matter in the Kafue Flats was more enriched during the dry season compared to the wet season (-26.5 and -28.5‰, respectively). The average dry-season δ13C value for the Kafue Flats should be interpreted with caution, since there was a clear spatial pattern: values became more depleted towards the edge of the floodplain. This spatial pattern has previously been attributed to floodplain-derived particulate organic matter, which would consist of phytoplankton and periphyton material in the permanently inundated area in the downstream reaches of this floodplain (Zurbrügg et al., 2013). In the upstream stretch of the floodplain that had more typical dry-season characteristics (i.e., no flooded areas), the dry-season value was heavier than the average reported earlier. Encroaching plant species have resulted in a vegetation pattern with C4 species occurring close to the river, and C3 species growing on the higher ground that is only seasonally flooded (Ellenbroek, 1987; Blaser, 2013). The inputs from these encroaching species can be considered to be terrestrial inputs of permanent vegetation, but as such resulted in a pattern contrasting with that observed in the Barotse Plains.

The difference in composition and origin between dissolved and particulate phases, i.e. DOM (dissolved organic matter) from terrestrial sources, and POM (particulate organic matter) more aquatically influenced, has previously been described for the Amazon (Hedges et al., 1986b; Aufdenkampe et al., 2007) and the Fly-Strickland system in Papua New Guinea (Alin et al., 2008). We showed that the
interaction of the river with its floodplain is responsible for the changes observed in organic-matter characteristics, and that floodplains should be considered as large biogeochemical reactors, which create specific environments that can differ from the processes occurring at the catchment level.

Figure 5.7 Summary of the organic-matter characteristics ($\delta^{13}$C, POC:PN, DOC:DON) and oxygen isotopic enrichment along the floodplain during the wet and dry season in the Barotse Plains and Kafue Flats. Proportional arrows indicate net export from the floodplain to the river (arrow towards the system) and removal rates of material from the river to the floodplain (arrow away from the system) of POM (POC+PN) and DOM (DOC+DON).
Conclusions

While the pristine Barotse Plains and dam-impacted Kafue Flats seem to have similar properties in terms of timing and dynamics of seasonal flooding, there are several marked differences between the two systems with respect to hydrology, carbon and nutrient dynamics, and the sources of the organic matter (Fig. 5.7). Based on an oxygen isotope mass balance, a larger fraction of water has spent time on the floodplain at the outflow of the Kafue Flats compared to the Barotse Plains. The two floodplains have significantly different concentrations of dissolved carbon and nutrient species during both wet and dry seasons. Over an annual cycle, the Barotse Plains retained particulate organic matter, and both floodplains exported more dissolved organic matter than previously reported for the Zambezi. This illustrates how large floodplain systems act as large biogeochemical reactors that behave distinctly differently from the rest of the catchment. Particulate organic carbon $\delta^{13}C$ values indicated a larger contribution of floodplain-derived organic matter in the Barotse Plains than in the Kafue Flats during the wet season, and the reverse situation during the dry season. However, the Kafue Flats have a reversed vegetation pattern as a consequence of woody encroachment towards the river, which was first observed after dam closure. Currently, permanent $C_4$ vegetation is found close to the river, whereas the seasonal growth has larger $C_3$ inputs; this is responsible for the seemingly contrasting patterns in particulate organic carbon $\delta^{13}C$ signatures. Both floodplains transported floodplain-derived material during the wet season, and inputs from permanent vegetation during the dry season.
Differences between the two systems can be attributed to the presence of the Itezhi-Tezhi reservoir upstream of the Kafue Flats, which altered the inputs to the particulate organic-matter pool in the Kafue Flats. Besides the effect of woody encroachment on the stable carbon isotopic signature, seasonal inputs of aquatic primary production in the upstream reservoir lowered the reactivity and POC:PN ratio in the Kafue Flats during the wet season. By contrast, soil material was transported during the dry season and year-round in the Barotse Plains. In summary, river-damming-induced vegetation changes in the floodplain towards more woody plants, and phytoplankton production added nitrogen-rich organic matter to the river system downstream.

Acknowledgements

The authors thank Wilma Blaser, Griffin Shanungu, Cristian Teodoru, Jason Wamulume, Mongu harbor personnel, and the Zambia Wildlife Authority for fieldwork assistance. Laboratory analyses were supported by Stewart Bishop, Madalina Jaggi, and Daniel Montluçon (all ETH Zürich); Kate Ashe, Chantal Freymond, Patrick Kathriner, Gijs Nobbe, Ruth Stierli, Stephan Suter, and Prosper Zigah (all Eawag); Moritz Lehmann, and Mark Rollog (both University of Basel). Comments from Tim Kalvelage (ETH Zürich) and our two reviewers (Lex Bouwman and Tim Jennerjahn) improved the manuscript. Institutional support was provided by Imasiku Nyambe (University of Zambia and its Integrated Water Resource Management Center), the Zambia Wildlife Authority, the Zambezi River Authority, and the Zambia Electricity Supply Corporation. 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.
Appendix

Appendix 5.1: Data

Table S5.1

<table>
<thead>
<tr>
<th>Station number</th>
<th>Distance along channel (km)</th>
<th>Month/Year sampled</th>
<th>Discharge (m$^3$/s)</th>
<th>δ18O (‰ VSMOW)</th>
<th>δ18O stdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP03</td>
<td>0</td>
<td>04/2013</td>
<td>1977</td>
<td>-1.80</td>
<td>0.10</td>
</tr>
<tr>
<td>BP05</td>
<td>14.4</td>
<td>04/2013</td>
<td></td>
<td>-1.92</td>
<td>0.03</td>
</tr>
<tr>
<td>BP06</td>
<td>32.8</td>
<td>04/2013</td>
<td></td>
<td>-2.04</td>
<td>0.07</td>
</tr>
<tr>
<td>BP07</td>
<td>48.6</td>
<td>04/2013</td>
<td>1957</td>
<td>-2.10</td>
<td>0.05</td>
</tr>
<tr>
<td>BP11</td>
<td>66.7</td>
<td>04/2013</td>
<td></td>
<td>-2.03</td>
<td>0.06</td>
</tr>
<tr>
<td>BP12</td>
<td>87.5</td>
<td>04/2013</td>
<td></td>
<td>-2.01</td>
<td>0.06</td>
</tr>
<tr>
<td>BP13</td>
<td>105.7</td>
<td>04/2013</td>
<td>1317</td>
<td>-1.95</td>
<td>0.04</td>
</tr>
<tr>
<td>BP16</td>
<td>129.1</td>
<td>04/2013</td>
<td></td>
<td>-1.31</td>
<td>0.04</td>
</tr>
<tr>
<td>BP17</td>
<td>150</td>
<td>04/2013</td>
<td></td>
<td>-1.37</td>
<td>0.03</td>
</tr>
<tr>
<td>BP01a</td>
<td>140</td>
<td>05/2009</td>
<td></td>
<td>-3.03</td>
<td></td>
</tr>
<tr>
<td>BP02a</td>
<td>143</td>
<td>05/2009</td>
<td></td>
<td>-3.56</td>
<td></td>
</tr>
<tr>
<td>BP03a</td>
<td>160</td>
<td>05/2009</td>
<td></td>
<td>-3.54</td>
<td></td>
</tr>
<tr>
<td>BP18</td>
<td>176.3</td>
<td>04/2013</td>
<td>1717</td>
<td>-1.66</td>
<td>0.06</td>
</tr>
<tr>
<td>BP04a</td>
<td>180</td>
<td>05/2009</td>
<td></td>
<td>-3.44</td>
<td></td>
</tr>
<tr>
<td>BP20</td>
<td>204.3</td>
<td>04/2013</td>
<td></td>
<td>-1.36</td>
<td>0.05</td>
</tr>
<tr>
<td>BP05a</td>
<td>200</td>
<td>05/2009</td>
<td></td>
<td>-3.25</td>
<td></td>
</tr>
<tr>
<td>BP06a</td>
<td>210</td>
<td>05/2009</td>
<td></td>
<td>-3.38</td>
<td></td>
</tr>
<tr>
<td>BP21</td>
<td>233</td>
<td>04/2013</td>
<td></td>
<td>-1.39</td>
<td>0.03</td>
</tr>
<tr>
<td>BP07a</td>
<td>240</td>
<td>05/2009</td>
<td></td>
<td>-3.43</td>
<td></td>
</tr>
<tr>
<td>BP23</td>
<td>251.1</td>
<td>04/2013</td>
<td>1740</td>
<td>-1.22</td>
<td>0.10</td>
</tr>
<tr>
<td>BP08a</td>
<td>240</td>
<td>05/2009</td>
<td></td>
<td>-3.43</td>
<td></td>
</tr>
<tr>
<td>BP24</td>
<td>278.3</td>
<td>04/2013</td>
<td></td>
<td>-1.19</td>
<td>0.05</td>
</tr>
<tr>
<td>BP09a</td>
<td>278.4</td>
<td>05/2009</td>
<td></td>
<td>-3.20</td>
<td></td>
</tr>
<tr>
<td>BP25</td>
<td>299.5</td>
<td>04/2013</td>
<td></td>
<td>-0.89</td>
<td>0.07</td>
</tr>
<tr>
<td>BP26</td>
<td>311.8</td>
<td>04/2013</td>
<td>2413</td>
<td>-0.99</td>
<td>0.05</td>
</tr>
<tr>
<td>Station number</td>
<td>Distance along channel (km)</td>
<td>Month/Year sampled</td>
<td>Discharge (m$^3$/s)</td>
<td>$δ^{18}$O (‰ VSMOW)</td>
<td>$δ^{13}$C (‰ VPDB)</td>
</tr>
<tr>
<td>---------------</td>
<td>-----------------------------</td>
<td>--------------------</td>
<td>---------------------</td>
<td>---------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>BP03</td>
<td>0</td>
<td>04/2013</td>
<td>1977</td>
<td>-1.80</td>
<td>-26.5</td>
</tr>
<tr>
<td>BP05</td>
<td>14.4</td>
<td>04/2013</td>
<td>-1.92</td>
<td>0.03</td>
<td>-26.2</td>
</tr>
<tr>
<td>BP06</td>
<td>32.8</td>
<td>04/2013</td>
<td>-2.04</td>
<td>0.07</td>
<td>-27.7</td>
</tr>
<tr>
<td>BP07</td>
<td>48.6</td>
<td>04/2013</td>
<td>1957</td>
<td>-2.10</td>
<td>-27.7</td>
</tr>
<tr>
<td>BP11</td>
<td>66.7</td>
<td>04/2013</td>
<td>-2.03</td>
<td>0.06</td>
<td>-27.4</td>
</tr>
<tr>
<td>BP12</td>
<td>87.5</td>
<td>04/2013</td>
<td>-2.01</td>
<td>0.06</td>
<td>-26.8</td>
</tr>
<tr>
<td>BP13</td>
<td>105.7</td>
<td>04/2013</td>
<td>1317</td>
<td>-1.95</td>
<td>-26.5</td>
</tr>
<tr>
<td>BP16</td>
<td>129.1</td>
<td>04/2013</td>
<td>-1.31</td>
<td>0.04</td>
<td>-25.7</td>
</tr>
<tr>
<td>BP17</td>
<td>150</td>
<td>04/2013</td>
<td>-1.37</td>
<td>0.03</td>
<td>-25.6</td>
</tr>
<tr>
<td>BP01a</td>
<td>140</td>
<td>05/2009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP02a</td>
<td>143</td>
<td>05/2009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP03a</td>
<td>160</td>
<td>05/2009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP04a</td>
<td>180</td>
<td>05/2009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP05a</td>
<td>200</td>
<td>05/2009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP06a</td>
<td>210</td>
<td>05/2009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP07a</td>
<td>240</td>
<td>05/2009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP08a</td>
<td>240</td>
<td>05/2009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP09a</td>
<td>278.4</td>
<td>05/2009</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP10a</td>
<td>299.5</td>
<td>04/2013</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP11a</td>
<td>311.8</td>
<td>04/2013</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Station number</td>
<td>Distance along channel (km)</td>
<td>Month/Year sampled</td>
<td>Discharge (m³/s)</td>
<td>δ18O (‰ VSMOW)</td>
<td>δ18O stdev</td>
</tr>
<tr>
<td>----------------</td>
<td>----------------------------</td>
<td>--------------------</td>
<td>------------------</td>
<td>-----------------</td>
<td>-------------</td>
</tr>
<tr>
<td>BP37</td>
<td>0</td>
<td>10/2013</td>
<td>203</td>
<td>-2.44</td>
<td>0.05</td>
</tr>
<tr>
<td>BP39</td>
<td>119.4</td>
<td>10/2013</td>
<td>227</td>
<td>-2.86</td>
<td>0.06</td>
</tr>
<tr>
<td>BP01a</td>
<td>140</td>
<td>10/2008</td>
<td></td>
<td>-2.71</td>
<td></td>
</tr>
<tr>
<td>BP02a</td>
<td>143</td>
<td>10/2008</td>
<td></td>
<td>-3.23</td>
<td></td>
</tr>
<tr>
<td>BP03a</td>
<td>160</td>
<td>10/2008</td>
<td></td>
<td>-3.06</td>
<td></td>
</tr>
<tr>
<td>BP04a</td>
<td>180</td>
<td>10/2008</td>
<td></td>
<td>-3.06</td>
<td></td>
</tr>
<tr>
<td>BP05a</td>
<td>200</td>
<td>10/2008</td>
<td></td>
<td>-3.21</td>
<td></td>
</tr>
<tr>
<td>BP06a</td>
<td>210</td>
<td>10/2008</td>
<td></td>
<td>-2.95</td>
<td></td>
</tr>
<tr>
<td>BP07a</td>
<td>240</td>
<td>10/2008</td>
<td></td>
<td>-3.14</td>
<td></td>
</tr>
<tr>
<td>BP08a</td>
<td>240</td>
<td>10/2008</td>
<td></td>
<td>-3.29</td>
<td></td>
</tr>
<tr>
<td>BP09a</td>
<td>278.4</td>
<td>10/2008</td>
<td></td>
<td>-2.87</td>
<td></td>
</tr>
<tr>
<td>BP38</td>
<td>299.5</td>
<td>10/2013</td>
<td>250</td>
<td>-2.50</td>
<td>0.08</td>
</tr>
<tr>
<td>Station number</td>
<td>Distance along channel (km)</td>
<td>Month/Year sampled</td>
<td>POC (µM)</td>
<td>DOC (µM)</td>
<td>DIC (µM)</td>
</tr>
<tr>
<td>---------------</td>
<td>----------------------------</td>
<td>-------------------</td>
<td>----------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>BP37</td>
<td>0</td>
<td>10/2013</td>
<td>31</td>
<td>134</td>
<td>1641</td>
</tr>
<tr>
<td>BP39</td>
<td>119.4</td>
<td>10/2013</td>
<td>55</td>
<td>1006</td>
<td>4.6</td>
</tr>
<tr>
<td>BP01a</td>
<td>140</td>
<td>10/2008</td>
<td>177</td>
<td>177</td>
<td>0.38</td>
</tr>
<tr>
<td>BP02a</td>
<td>143</td>
<td>10/2008</td>
<td>124</td>
<td>124</td>
<td>0.50</td>
</tr>
<tr>
<td>BP03a</td>
<td>160</td>
<td>10/2008</td>
<td>115</td>
<td>115</td>
<td>0.53</td>
</tr>
<tr>
<td>BP04a</td>
<td>180</td>
<td>10/2008</td>
<td>111</td>
<td>111</td>
<td>0.55</td>
</tr>
<tr>
<td>BP05a</td>
<td>200</td>
<td>10/2008</td>
<td>120</td>
<td>120</td>
<td>0.55</td>
</tr>
<tr>
<td>BP06a</td>
<td>210</td>
<td>10/2008</td>
<td>112</td>
<td>112</td>
<td>0.48</td>
</tr>
<tr>
<td>BP07a</td>
<td>240</td>
<td>10/2008</td>
<td>121</td>
<td>121</td>
<td>0.87</td>
</tr>
<tr>
<td>BP08a</td>
<td>240</td>
<td>10/2008</td>
<td>111</td>
<td>111</td>
<td>0.57</td>
</tr>
<tr>
<td>BP09a</td>
<td>278.4</td>
<td>10/2008</td>
<td>123</td>
<td>123</td>
<td>0.61</td>
</tr>
<tr>
<td>BP38</td>
<td>299.5</td>
<td>10/2013</td>
<td>81</td>
<td>103</td>
<td>1030</td>
</tr>
<tr>
<td>Station number</td>
<td>Wet season</td>
<td>Distance along floodplain (km)</td>
<td>Year sampled</td>
<td>Discharge ($m^3/s$)</td>
<td>$\delta^{18}O$ $(% VSMOW)$</td>
</tr>
<tr>
<td>----------------</td>
<td>------------</td>
<td>-------------------------------</td>
<td>--------------</td>
<td>---------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>KFS00</td>
<td>0</td>
<td>05/2009 and 05/2010</td>
<td>483</td>
<td>-4.89</td>
<td>0.05</td>
</tr>
<tr>
<td>KFS05</td>
<td>9.3</td>
<td>05/2009 and 05/2010</td>
<td>526</td>
<td>-4.89</td>
<td>0.03</td>
</tr>
<tr>
<td>KFS03</td>
<td>38.9</td>
<td>05/2009 and 05/2010</td>
<td>602</td>
<td>-4.87</td>
<td>0.06</td>
</tr>
<tr>
<td>KFS01</td>
<td>64.8</td>
<td>05/2009 and 05/2010</td>
<td>575</td>
<td>-4.77</td>
<td>0.04</td>
</tr>
<tr>
<td>KFS27</td>
<td>88.5</td>
<td>05/2009 and 05/2010</td>
<td>572</td>
<td>-4.41</td>
<td>0</td>
</tr>
<tr>
<td>KFS28</td>
<td>173.3</td>
<td>05/2009 and 05/2010</td>
<td>334</td>
<td>-4.36</td>
<td>0.07</td>
</tr>
<tr>
<td>KFS11</td>
<td>199.1</td>
<td>05/2009 and 05/2010</td>
<td>231</td>
<td>-4.18</td>
<td>0.06</td>
</tr>
<tr>
<td>KFS10</td>
<td>230.4</td>
<td>05/2009 and 05/2010</td>
<td>185</td>
<td>-4.05</td>
<td>0.02</td>
</tr>
<tr>
<td>KFS12</td>
<td>231</td>
<td>05/2009 and 05/2010</td>
<td>218</td>
<td>-3.68</td>
<td>0.09</td>
</tr>
<tr>
<td>KFS14</td>
<td>254.6</td>
<td>05/2009 and 05/2010</td>
<td>190</td>
<td>-3.45</td>
<td>0.07</td>
</tr>
<tr>
<td>KFS16</td>
<td>268.8</td>
<td>05/2009 and 05/2010</td>
<td>491</td>
<td>-2.80</td>
<td>0.01</td>
</tr>
<tr>
<td>KFS17</td>
<td>288.3</td>
<td>05/2009 and 05/2010</td>
<td>344</td>
<td>-2.47</td>
<td>0.01</td>
</tr>
<tr>
<td>KFS18</td>
<td>321.5</td>
<td>05/2009 and 05/2010</td>
<td>344</td>
<td>-2.47</td>
<td>0.01</td>
</tr>
<tr>
<td>KFS20</td>
<td>346.5</td>
<td>05/2009 and 05/2010</td>
<td>538</td>
<td>-2.93</td>
<td>0.02</td>
</tr>
<tr>
<td>KFS21</td>
<td>359</td>
<td>05/2009 and 05/2010</td>
<td>528</td>
<td>-2.74</td>
<td>0.04</td>
</tr>
<tr>
<td>KFS23</td>
<td>381.7</td>
<td>05/2009 and 05/2010</td>
<td>719</td>
<td>-2.66</td>
<td>0</td>
</tr>
<tr>
<td>KFS24</td>
<td>398.2</td>
<td>05/2009 and 05/2010</td>
<td>677</td>
<td>-2.58</td>
<td>0.19</td>
</tr>
<tr>
<td>KFS26</td>
<td>409.6</td>
<td>05/2009 and 05/2010</td>
<td>719</td>
<td>-2.66</td>
<td>0</td>
</tr>
<tr>
<td>Station number</td>
<td>Distance along floodplain (km)</td>
<td>Year sampled</td>
<td>Discharge (m³/s)</td>
<td>δ¹³C (‰ VSMOW)</td>
<td>δ¹⁸O (‰ VSMOW)</td>
</tr>
<tr>
<td>---------------</td>
<td>-------------------------------</td>
<td>--------------</td>
<td>-----------------</td>
<td>----------------</td>
<td>----------------</td>
</tr>
<tr>
<td>KFS00</td>
<td>0</td>
<td>05/2009 and 05/2010</td>
<td>483</td>
<td>-4.89</td>
<td>0.05</td>
</tr>
<tr>
<td>KFS05</td>
<td>9.3</td>
<td>05/2009 and 05/2010</td>
<td>1080</td>
<td>-4.89</td>
<td>0.03</td>
</tr>
<tr>
<td>KFS03</td>
<td>38.9</td>
<td>05/2009 and 05/2010</td>
<td>526</td>
<td>-4.87</td>
<td>0.06</td>
</tr>
<tr>
<td>KFS01</td>
<td>64.8</td>
<td>05/2009 and 05/2010</td>
<td>602</td>
<td>-4.88</td>
<td>0.02</td>
</tr>
<tr>
<td>KFS27</td>
<td>88.5</td>
<td>05/2009 and 05/2010</td>
<td>575</td>
<td>-4.77</td>
<td>0.04</td>
</tr>
<tr>
<td>KFS28</td>
<td>173.3</td>
<td>05/2009 and 05/2010</td>
<td>231</td>
<td>-4.18</td>
<td>0.06</td>
</tr>
<tr>
<td>KFS11</td>
<td>199.1</td>
<td>05/2009 and 05/2010</td>
<td>334</td>
<td>-4.36</td>
<td>0.07</td>
</tr>
<tr>
<td>KFS10</td>
<td>230.4</td>
<td>05/2009 and 05/2010</td>
<td>0.00</td>
<td>-4.41</td>
<td>0.00</td>
</tr>
<tr>
<td>KFS12</td>
<td>231</td>
<td>05/2009 and 05/2010</td>
<td>231</td>
<td>-2.80</td>
<td>0.01</td>
</tr>
<tr>
<td>KFS14</td>
<td>254.6</td>
<td>05/2009 and 05/2010</td>
<td>185</td>
<td>-2.47</td>
<td>23</td>
</tr>
<tr>
<td>KFS16</td>
<td>268.8</td>
<td>05/2009 and 05/2010</td>
<td>218</td>
<td>-2.93</td>
<td>0.19</td>
</tr>
<tr>
<td>KFS17</td>
<td>288.3</td>
<td>05/2009 and 05/2010</td>
<td>190</td>
<td>-2.74</td>
<td>0.04</td>
</tr>
<tr>
<td>KFS18</td>
<td>321.5</td>
<td>05/2009 and 05/2010</td>
<td>491</td>
<td>-2.66</td>
<td>0.00</td>
</tr>
<tr>
<td>KFS21</td>
<td>346.5</td>
<td>05/2009 and 05/2010</td>
<td>344</td>
<td>-2.47</td>
<td>23</td>
</tr>
<tr>
<td>KFS22</td>
<td>359</td>
<td>05/2009 and 05/2010</td>
<td>538</td>
<td>-2.93</td>
<td>0.02</td>
</tr>
<tr>
<td>KFS23</td>
<td>381.7</td>
<td>05/2009 and 05/2010</td>
<td>528</td>
<td>-2.74</td>
<td>0.04</td>
</tr>
</tbody>
</table>
# Table S5.4

<table>
<thead>
<tr>
<th>Kafue Flats</th>
<th>Distance along floodplain (km)</th>
<th>Year sampled</th>
<th>Discharge (m$^3$/s)</th>
<th>$\delta^{18}$O (‰ VSMOW)</th>
<th>$\delta^{18}$O stdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry season</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS00</td>
<td>0</td>
<td>10/2008</td>
<td>214</td>
<td>-3.59</td>
<td>0.19</td>
</tr>
<tr>
<td>KFS03</td>
<td>38.9</td>
<td>10/2008</td>
<td></td>
<td>-3.48</td>
<td>0.05</td>
</tr>
<tr>
<td>KFS01</td>
<td>64.8</td>
<td>10/2008</td>
<td>223</td>
<td>-3.36</td>
<td>0.02</td>
</tr>
<tr>
<td>KFS27</td>
<td>88.5</td>
<td>10/2008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS28</td>
<td>173.3</td>
<td>10/2008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS11</td>
<td>199.1</td>
<td>10/2008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS10</td>
<td>230.4</td>
<td>10/2008</td>
<td>170</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS12</td>
<td>231</td>
<td>10/2008</td>
<td>170</td>
<td>-3.08</td>
<td>0.25</td>
</tr>
<tr>
<td>KFS14</td>
<td>254.6</td>
<td>10/2008</td>
<td></td>
<td>-3.40</td>
<td>0.12</td>
</tr>
<tr>
<td>KFS15</td>
<td>254.7</td>
<td>10/2008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS16</td>
<td>268.8</td>
<td>10/2008</td>
<td></td>
<td>-3.26</td>
<td>0.24</td>
</tr>
<tr>
<td>KFS17</td>
<td>288.3</td>
<td>10/2008</td>
<td></td>
<td>-3.46</td>
<td>0.14</td>
</tr>
<tr>
<td>KFS18</td>
<td>321.5</td>
<td>10/2008</td>
<td></td>
<td>-3.14</td>
<td>0.13</td>
</tr>
<tr>
<td>KFS21</td>
<td>346.5</td>
<td>10/2008</td>
<td></td>
<td>-2.95</td>
<td>0.09</td>
</tr>
<tr>
<td>KFS20</td>
<td>348.1</td>
<td>10/2008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS22</td>
<td>359</td>
<td>10/2008</td>
<td></td>
<td>-2.92</td>
<td>0.11</td>
</tr>
<tr>
<td>KFS23</td>
<td>381.7</td>
<td>10/2008</td>
<td></td>
<td>-2.88</td>
<td></td>
</tr>
<tr>
<td>KFS24</td>
<td>398.2</td>
<td>10/2008</td>
<td>148</td>
<td>-2.64</td>
<td>0.11</td>
</tr>
<tr>
<td>KFS26</td>
<td>409.6</td>
<td>10/2008</td>
<td>148</td>
<td>-2.87</td>
<td>0.18</td>
</tr>
<tr>
<td>Station number</td>
<td>Distance (km)</td>
<td>Year sampled</td>
<td>Discharge (m$^3$/s)</td>
<td>δ$^{18}$O (‰ VSMOW)</td>
<td>δ$^{13}$C (‰ VPDB)</td>
</tr>
<tr>
<td>---------------</td>
<td>--------------</td>
<td>--------------</td>
<td>---------------------</td>
<td>---------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>KFS00</td>
<td>0</td>
<td>10/2008</td>
<td>214</td>
<td>-3.59</td>
<td>0.19</td>
</tr>
<tr>
<td>KFS03</td>
<td>38.9</td>
<td>10/2008</td>
<td>-3.48</td>
<td>0.05</td>
<td>-26.3</td>
</tr>
<tr>
<td>KFS01</td>
<td>64.8</td>
<td>10/2008</td>
<td>223</td>
<td>-3.36</td>
<td>0.02</td>
</tr>
<tr>
<td>KFS27</td>
<td>88.5</td>
<td>10/2008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS28</td>
<td>173.3</td>
<td>10/2008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS11</td>
<td>199.1</td>
<td>10/2008</td>
<td>74</td>
<td>-25.3</td>
<td></td>
</tr>
<tr>
<td>KFS10</td>
<td>230.4</td>
<td>10/2008</td>
<td>170</td>
<td>510</td>
<td>2300</td>
</tr>
<tr>
<td>KFS12</td>
<td>231</td>
<td>10/2008</td>
<td>170</td>
<td>-3.08</td>
<td>0.25</td>
</tr>
<tr>
<td>KFS14</td>
<td>254.6</td>
<td>10/2008</td>
<td>-3.40</td>
<td>0.12</td>
<td>-25.3</td>
</tr>
<tr>
<td>KFS15</td>
<td>254.7</td>
<td>10/2008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS16</td>
<td>268.8</td>
<td>10/2008</td>
<td>-3.26</td>
<td>0.24</td>
<td>0.41</td>
</tr>
<tr>
<td>KFS17</td>
<td>288.3</td>
<td>10/2008</td>
<td>-3.46</td>
<td>0.14</td>
<td>-25.3</td>
</tr>
<tr>
<td>KFS18</td>
<td>321.5</td>
<td>10/2008</td>
<td>-3.14</td>
<td>0.13</td>
<td>-27.3</td>
</tr>
<tr>
<td>KFS21</td>
<td>346.5</td>
<td>10/2008</td>
<td>-2.95</td>
<td>0.09</td>
<td>-29.0</td>
</tr>
<tr>
<td>KFS20</td>
<td>348.1</td>
<td>10/2008</td>
<td>759</td>
<td>3910</td>
<td>43.2</td>
</tr>
<tr>
<td>KFS22</td>
<td>359</td>
<td>10/2008</td>
<td>-2.92</td>
<td>0.11</td>
<td>0.44</td>
</tr>
<tr>
<td>KFS23</td>
<td>381.7</td>
<td>10/2008</td>
<td>-2.88</td>
<td>68</td>
<td>276</td>
</tr>
<tr>
<td>KFS24</td>
<td>398.2</td>
<td>10/2008</td>
<td>-2.64</td>
<td>0.11</td>
<td>0.42</td>
</tr>
<tr>
<td>KFS26</td>
<td>409.6</td>
<td>10/2008</td>
<td>-2.87</td>
<td>0.18</td>
<td>0.49</td>
</tr>
</tbody>
</table>
### Appendix 5.2: Channel heterogeneity

#### Table S5.5 Samples collected on the edge of the channel

<table>
<thead>
<tr>
<th>Barotse Plains</th>
<th>Distance along channel (km)</th>
<th>Month/Year sampled</th>
<th>Discharge (m³/s)</th>
<th>δ18O (% VSMOW)</th>
<th>δ18O stdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet season</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Station number</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BP03</td>
<td>0</td>
<td>04/2013</td>
<td>1977</td>
<td>-1.82</td>
<td>0.10</td>
</tr>
<tr>
<td>BP07</td>
<td>48.6</td>
<td>04/2013</td>
<td>1957</td>
<td>-1.82</td>
<td>0.05</td>
</tr>
<tr>
<td>BP13</td>
<td>105.7</td>
<td>04/2013</td>
<td>1317</td>
<td>-1.91</td>
<td>0.03</td>
</tr>
<tr>
<td>BP18</td>
<td>176.3</td>
<td>04/2013</td>
<td>1717</td>
<td>-1.31</td>
<td>0.11</td>
</tr>
<tr>
<td>BP23</td>
<td>251.1</td>
<td>04/2013</td>
<td>1740</td>
<td>-1.44</td>
<td>0.06</td>
</tr>
</tbody>
</table>

#### Table S5.6 Samples collected at different depths

<table>
<thead>
<tr>
<th>Kafue Flats</th>
<th>Water depth (m)</th>
<th>Month/Year sampled</th>
<th>Conductivity (µS/cm)</th>
<th>Dissolved oxygen (mg/L)</th>
<th>DOC (µM)</th>
<th>TDP (µM)</th>
<th>TDN (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet season</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS06</td>
<td>0.2</td>
<td>05/2008</td>
<td>170</td>
<td>7.66</td>
<td>1212</td>
<td>0.39</td>
<td>21.91</td>
</tr>
<tr>
<td>KFS06</td>
<td>0.8</td>
<td>05/2008</td>
<td>-</td>
<td>6.62</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS06</td>
<td>1.2</td>
<td>05/2008</td>
<td>170</td>
<td>6.60</td>
<td>1273</td>
<td>0.43</td>
<td>22.48</td>
</tr>
<tr>
<td>KFS07</td>
<td>0.2</td>
<td>05/2008</td>
<td>170</td>
<td>8.10</td>
<td>1084</td>
<td>0.36</td>
<td>22.52</td>
</tr>
<tr>
<td>KFS07</td>
<td>1.0</td>
<td>05/2008</td>
<td>170</td>
<td>7.79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS07</td>
<td>1.8</td>
<td>05/2008</td>
<td>170</td>
<td>7.53</td>
<td>1034</td>
<td>0.51</td>
<td>22.84</td>
</tr>
<tr>
<td>KFS07</td>
<td>2.0</td>
<td>05/2008</td>
<td>170</td>
<td>7.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS09</td>
<td>0.2</td>
<td>05/2008</td>
<td>7.66</td>
<td>170</td>
<td>1174</td>
<td>0.46</td>
<td>37.00</td>
</tr>
<tr>
<td>KFS09</td>
<td>1.0</td>
<td>05/2008</td>
<td>7.65</td>
<td>171</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KFS09</td>
<td>1.5</td>
<td>05/2008</td>
<td>7.62</td>
<td>170</td>
<td>1163</td>
<td>0.58</td>
<td>25.17</td>
</tr>
</tbody>
</table>
### Table S5.5

<table>
<thead>
<tr>
<th>Station number</th>
<th>Distance along channel (km)</th>
<th>Month/Year sampled</th>
<th>Discharge (m³/s)</th>
<th>$\delta^{18}O$ (‰ VSMOW)</th>
<th>$\delta^{18}O$ stdev</th>
<th>POC (µM)</th>
<th>DOC (µM)</th>
<th>DIC (µM)</th>
<th>PN (µM)</th>
<th>DON (µM)</th>
<th>DIN (µM)</th>
<th>PP (µM)</th>
<th>DOP (µM)</th>
<th>DIP (µM)</th>
<th>POC $\delta^{13}C$ (‰ VPDB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP03</td>
<td>0</td>
<td>04/2013</td>
<td>0</td>
<td>-1.82</td>
<td>0.10</td>
<td>34</td>
<td>175</td>
<td>160</td>
<td>2.8</td>
<td>10.4</td>
<td>0.00</td>
<td>0.13</td>
<td>0.22</td>
<td>0.05</td>
<td>-26.8</td>
</tr>
<tr>
<td>BP07</td>
<td>48.6</td>
<td>04/2013</td>
<td>0</td>
<td>-1.82</td>
<td>0.05</td>
<td>26</td>
<td>182</td>
<td>275</td>
<td>2.3</td>
<td>10.0</td>
<td>0.00</td>
<td>0.27</td>
<td>0.08</td>
<td>0.04</td>
<td>-27.6</td>
</tr>
<tr>
<td>BP13</td>
<td>105.7</td>
<td>04/2013</td>
<td>0</td>
<td>-1.91</td>
<td>0.03</td>
<td>25</td>
<td>183</td>
<td>420</td>
<td>2.4</td>
<td>9.7</td>
<td>1.53</td>
<td>0.13</td>
<td>0.08</td>
<td>0.02</td>
<td>-25.7</td>
</tr>
<tr>
<td>BP18</td>
<td>176.3</td>
<td>04/2013</td>
<td>0</td>
<td>-1.31</td>
<td>0.11</td>
<td>21</td>
<td>206</td>
<td>334</td>
<td>1.9</td>
<td>11.8</td>
<td>0.00</td>
<td>0.14</td>
<td>0.12</td>
<td>0.02</td>
<td>-26.1</td>
</tr>
<tr>
<td>BP23</td>
<td>251.1</td>
<td>04/2013</td>
<td>0</td>
<td>-1.44</td>
<td>0.06</td>
<td>15</td>
<td>230</td>
<td>387</td>
<td>1.5</td>
<td>12.9</td>
<td>0.00</td>
<td>0.10</td>
<td>0.10</td>
<td>0.02</td>
<td>-25.2</td>
</tr>
</tbody>
</table>
Chapter 6

Conclusions and outlook
The biogeochemistry of inland waters and their impact on global element budgets, specifically the carbon cycle, has been studied extensively, but much remains to be learned about systems in tropical and subtropical regions. With increasing anthropogenic stress on inland waters, it is important to understand the biogeochemical functioning of pristine systems and how these ecosystems might respond to anthropogenic pressures. This thesis has contributed to such knowledge, by investigating how river-floodplain processes in a tropical river affect the fluvial biogeochemistry and the composition of the riverine organic matter. The purpose of this chapter is to integrate the results from the individual chapters, link those to the questions set forth in the introduction, consider the implications of these results, and suggest avenues for future research.

**Seasonal patterns**

Particulate and dissolved phases behaved differently in the river-floodplain system of the Barotse Plains, with particulate loads peaking before peak flow and dissolved loads around peak flow (chapter 2). Particulate matter concentrations were high during low-water conditions, but particulate loads reached their maxima during flooding. At the same time as maximum particulate loads, dissolved concentrations peaked, but the maximum loads of dissolved phases were observed around peak flow.
Figure 6.1 Summary of the net export and retention of particulate organic matter (in orange) and dissolved organic matter (in green) at different points during the hydrograph, also in relation to the loads of suspended particulate matter (SPM, in orange) and dissolved organic carbon (DOC, in green) recorded at the downstream end of the floodplain.

Along with the seasonal changes in loads, the biogeochemical functioning of the floodplain also varies throughout the year. It was argued in chapter 5 that the Barotse Plains retain particulate organic matter during an annual cycle; expanding the data set with the data from the June 2015 campaign (see also chapter 5) results in somewhat smaller numbers. However, while particulate organic matter was retained, there was a net export of total suspended particles from the floodplain. Considering that the field campaigns did not capture the period with highest suspended loads (February/March; chapter 2), the estimated annual fluxes from the floodplain probably correspond to a lower boundary. Dissolved organic matter was also exported over an annual cycle, as captured by the field campaigns (chapter 4 and 5).
The balance between primary production and respiration in the river-floodplain system shifts throughout the year. The concept of the three flooding phases (chapter 2) describes a seasonal cycle of degradation during initial flooding, primary production during continued and maximum flooding, and more degradation during receding water levels. This is supported by the stable isotopic composition of the fatty acids (chapter 3). However, based on the seasonal export and retention of particulate and dissolved phases (chapter 5) it was suggested that there was degradation or particle settling during high water, while inputs of organic matter were dominating during low water and were probably derived from terrestrial vegetation (see section on the origin of riverine organic matter on the next page).

The role of hydrology

At different hydrological conditions, i.e., high, falling, and low water, the biogeochemistry of the floodplain was distinctly different. Oxygen isotopes in the river water showed an increase along the floodplain, indicating evaporation from the inundated floodplain. A mass balance approach showed that 50% of the downstream discharge had spent time on the floodplain. This highlights the movement of water between the river main stem and the floodplain (chapter 5).

Distinct hysteresis patterns were observed between biogeochemical parameters (oxygen, dissolved organic carbon, carbon dioxide, and suspended matter) and both discharge and travel time of the flood pulse over the floodplain (chapter 2). At longer travel times, more degradation of organic matter was occurring on the floodplain rather than in the river. As a result, the floodplain water became oxygen-depleted, and rich in dissolved organic carbon and carbon dioxide. The magnitude of greenhouse-gas emissions from the river-floodplain system was likely also closely linked to the characteristics of the flood pulse. Similar biogeochemical conditions were also observed in the river, due to mixing of the floodplain water into the main stem. These established relationships highlight and quantify how hydrological conditions exert influence on the river biogeochemistry.
Origin of riverine organic matter

Soil-derived organic matter was important for fluvial organic matter throughout the year (chapters 3 and 4), but the accompanying vegetation input varied with the seasons. A first approximation, based on the stable carbon isotopic signals (chapter 5), suggested inputs from the floodplain during high water, and input from permanent, terrestrial vegetation during low-water conditions. In chapter 2, different sources of organic matter were described during the three phases. In short, during low and rising water levels input from bare soil was thought to be dominant, whereas input from the floodplain was important during periods of inundation.

Downstream of the floodplain, the seasonal changes in riverine organic-matter composition can be clearly observed (Fig. 6.2). Low-water organic matter was characterized by depleted $\delta^{13}$C and lower radiocarbon content. The biomarkers exhibited low long-chained fatty acids and brGDGT concentrations, and highest alkane contributions. These qualities are indicative of input from a mixture of deeper mineral soils, with a degraded signature, and terrestrial vegetation. During high- and falling-water conditions, the organic matter stable carbon isotopic signature was more enriched than during low water, and the radiocarbon content indicated younger material. High-water organic carbon had large contributions of brGDGTs and fatty acids, but relatively low alkane abundance. When water levels receded, all biomarker abundances dropped markedly towards the end of the floodplain. During these times of inundation, the organic matter was derived from younger organic matter, and topsoil-associated organic matter.
Figure 6.2 Composition of the particulate organic matter downstream of the Barotse Plains during high water (HW, blue squares), falling water (FW, orange circles), and low water (LW, green triangles).

**Dam construction**

Before-and-after studies studying the impact of large hydropower projects on river biogeochemistry are very scarce. Comparison of similar floodplain systems, but with different degrees of anthropogenic impact, within a single catchment can provide some of the answers on how dam construction alters river biogeochemistry. By comparing the pristine Barotse Plains with the dam-impacted Kafue Flats, dam-induced changes in the origin of the organic matter became clear (chapter 5). Changes in flooding dynamics had allowed woody encroachment, resulting in contrasting patterns in the stable carbon isotopic signal. Additionally, the carbon-to-nitrogen ratios were altered due to aquatic production in the reservoir.

Such alterations in carbon-to-nitrogen ratios are also visible downstream of Lake Kariba, though also with a seasonal cycle (chapter 5). Furthermore, the studied reservoirs in the Zambezi catchment retain large quantities of organic carbon and nutrients, and alter the ratios in which nitrogen and phosphorus are available to downstream ecosystems.
Conclusions

1. What are the **seasonal patterns** of organic-matter cycling along a floodplain?

   The timing of maximum particulate and dissolved organic matter concentrations and loads in the river differed as a result of the functioning of the floodplain. During initial flooding, organic matter was degraded, followed by a phase of production on the floodplain during maximum flooding extent. With receding water levels, the system became heterotrophic once more.

2. What is the **role of hydrology** on river-floodplain biogeochemistry?

   A large fraction of the river discharge spent time on the floodplain during the flooding season. The retention of the flood pulse over the floodplain has been linked to biogeochemical characteristics, with more degradation of organic matter occurring on the floodplain at longer travel times.

3. Which are the **sources of riverine organic matter**, and how do their relative contributions change throughout the year?

   Throughout the year, soil-derived organic matter contributed to the fluvial particulate organic matter. During low water, this soil material derived from mineral soils and was supplemented by direct input from terrestrial vegetation. During periods of inundation, the sources of the riverine organic matter were topsoil and floodplain vegetation.

4. How does **dam construction** impact tropical fluvial biogeochemistry?

   The dams in the Zambezi catchment trap particles and organic matter and release easily degradable aquatic biomass, changing the quantity and signature of the downstream organic matter. In addition, altered flooding can favor changes in floodplain vegetation, further altering the signature of the organic matter.
Implications

In all aspects of this research, it has become extremely clear that the hydrological regime exerts large controls on the biogeochemical functioning of the river-floodplain system, for example the oxygen content in the river. Based on the sensor deployment, it was possible to quantify these controls to a certain extent. The results from the biomarker analyses and the comparison between the Barotse Plains and the Kafue Flats also highlighted how the biogeochemical functioning of the floodplain changed with different degrees of inundation.

As the hydrological cycle is strongly tied to climate, changes in precipitation and discharge have been observed and are to be expected for the Zambezi catchment. Over the past forty years, increased temperatures (+1.3°C since 1960, World Bank, 2016), a slight reduction in annual precipitation (-1.9mm/month compared to 1960, World Bank, 2016), increased inter-annual variability with more intense and widespread droughts, and a significant increase in heavy rainfall events have been observed in the Zambezi catchment (Beilfuss, 2012). Predictions on future rainfall trends for the Zambezi catchment are diverse and complex. Beilfuss (2012) worked under the assumptions that annual rainfall would decline 10-15%, based on the IPCC Fourth Assessment Report (IPCC, 2007), and that heavy rainfall events might change the seasonality in the Zambezi River basin. This changing seasonality in western Zambia would lead to more intense rainfall in March, but lower precipitation during the other months of the rainy season (Beck and Bernauer, 2011). Results from several global circulation models show altered seasonal and annual precipitation, though do not always agree on the direction of change (e.g., Stanzel and Kling, 2014; Schlosser and Strzepek, 2015; World Bank, 2016). For example, according to the csiro_mk3_6_0 model calculations, annual rainfall in the Zambezi catchment is expected to decrease under all representative concentration pathways (RCP’s, total anthropogenic radiative forcing in W m⁻²), while the ipsl_cm5a_mr model predicts more rainfall in all scenarios (World Bank, 2016).

In addition to changes in the hydrological cycle due to climate change, river flow is also not immune to anthropogenic alterations. Anthropogenic changes
that can be expected in the vicinity of the Barotse Plains include expansion of hydropower (Kabompo Gorge plans; Copperbelt Energy Corporation Plc, 2013) and development of irrigated agriculture. Agriculture can lead to loss of wetland area and functioning as a consequence of drainage, water storage, altered sediment balanced, eutrophication, and pollution (Galbraith et al., 2005).

While at this point it is difficult to predict how the travel time of a flood pulse over the Barotse Plains will be impacted by such changes in hydrology, travel time can definitely be expected to change. With the travel time, the biogeochemistry of the river-floodplain system would inadvertently also be affected. Changes in the biogeochemical composition of the river water would also occur as a consequence of prolonged retention time in an upstream reservoir (Friedl and Wüst, 2002; Zuijdegeest et al., 2015). Changes in inundation extent, both from natural and anthropogenic impacts, would change the functioning of the floodplain, as shown for the Kafue Flats (Blaser, 2013; Zuijdegeest et al., 2015). This has distinct impacts on the source and chemical composition of the organic matter, which currently show distinct seasonal differences. Organic-matter input from irrigated agriculture would further alter the signature of the organic matter transported downstream.

In summary, this thesis has provided several lines of argument that the biogeochemistry of tropical river-floodplain systems is likely to change, which may have global consequences for the carbon cycle.
Outlook: future research directions

While any research project is trying to answer certain questions, those answers typically only lead to more questions. For future research into the biogeochemical dynamics of tropical floodplains, I recommend the following directions. These suggestions focus on improving the understanding of the biogeochemical functioning of tropical river-floodplain systems. While expanding the current data set of the Barotse Plains with these proposals would be interesting, studying various tropical floodplains in the same systematic way would provide more generalized concepts of floodplains as biogeochemical reactors. Systems that could be considered are the floodplains of the Tana river (e.g., Omengo et al., 2016a) or in the Congo basin (e.g., Spencer et al., 2012; Hemingway et al., 2016).

**Hydrology:** for any future biogeochemical investigations, it would be very beneficial to better understand the flooding dynamics. To do so on the large scale, one could consider exploring optical satellite data such as MODIS to quantify the flooding extent (e.g., Meier et al., 2010), radar altimetry to determine the water levels (e.g., Michailovsky and Bauer-Gottwein, 2014), or even gravity field measurements to determine water storage on the floodplain (GRACE, e.g., Ahmed et al., 2014). Alternatively, though time-consuming, it would be interesting to perform discharge measurements at a higher spatial resolution, to investigate where the bankfull discharge decreases and hence the flood pulse is forced onto the floodplain.

This research has provided a hypothesis regarding the impact of water retention on the floodplain on riverine biogeochemistry, and specifically greenhouse gas emissions from the floodplain. Other tropical river-floodplain systems need to be studied in a similar fashion in order to test the hypothesis, such as the ones previously mentioned in the Tana or Congo catchments.

**Sampling strategy:** the long-term deployment of sensors has provided extremely valuable information on the seasonal dynamics of the river-floodplain system, and has shown that intense changes occur during the rainy season. While this can provide logistical challenges, sampling at high-resolution throughout the wet season upstream and downstream of any tropical floodplain would provide important information about the interactions between river, floodplain, and
vegetation. This would be specifically interesting combined with spatial data on flood extension and vegetation shifts. **Greenhouse-gas emissions:** The results from the sensor deployment showed high oversaturation of carbon dioxide throughout most of the flooding season, which likely results in large emissions. However, due to lack of the necessary environmental parameters (wind speed, flow velocity, etc.), estimating these would have led to large uncertainties. Expanding the before-mentioned intense sampling campaign with measurements of greenhouse-gas emissions, both from the river and the inundated floodplain, would contribute interesting results to efforts to constrain those emissions from inland waters. Besides chamber deployments, it would also be interesting to install an eddy covariance tower in the area and obtain area-integrated emissions. Considering that water on the floodplain is likely oxygen-depleted, not only carbon dioxide would be of interest, but also methane.

**Source-determination of organic matter:** The combination of methods used for this research has provided an integrated view of organic-matter dynamics and riverine biogeochemistry in the Barotse Plains. What is somewhat incomplete, is the analysis of the characteristics of end-member sources in the catchment. In future endeavors to disentangle different sources of riverine organic matter, more emphasis on identifying and analyzing the different potential sources of organic carbon would be beneficial. This could include collection of soil profiles and vegetation sampling, along with any sedimentary outcrops in the vicinity of the river.

The combination of bulk isotopes, plant waxes, and soil lipids has yielded valuable information. Expanding the analyses with analysis of lignin, and more extensive compound-specific isotope analysis could be a valuable addition to further disentangle different organic-matter sources throughout the seasons. Lignin proxies can provide further differentiation between leafy and woody vegetation, and another measure of (lignin-specific) degradation. Compound-specific isotope analysis of $^{13}$C could provide more detailed information about the plant sources. Isotopic measurements of hydrogen in plant waxes provides details about aridity and water stress, which in the case of the Barotse Plains could be linked to growing seasons of different vegetation types. Radiocarbon measurements on individual
homologues, both in suspended matter and soils, add detailed information about the retention of organic matter in the river-floodplain system. For all these compound-specific isotope analyses, larger quantities of material are needed. Filtering larger quantities of river water requires an adapted field program, or the use of in-situ pumps.

**Anthropogenic impact:** all suggestions above focus on the natural functioning of tropical floodplains, and how the river-floodplain interaction affects availability of carbon and nutrients for downstream ecosystems. However, with current and future plans for hydropower expansion in Africa, anthropogenic stress on tropical floodplains will increase. The comparison between the Barotse Plains and the Kafue Flats has elucidated marked difference in the composition and origin of the organic matter in a pristine and a dam-impacted tropical floodplain. Monitoring of floodplain dynamics before and after dam construction would further provide important understanding of the impacts of dams on floodplain functioning.
References


http://sdwebx.worldbank.org/climateportalb/home.cfm?page=country_profile&CCode=ZMB&ThisTab=ClimateFuture. [Accessed April 4, 2016].


Acknowledgements

This project would not have existed without Bernhard, who decided to give me a job based on a single interview. I am very grateful for the collaboration in shaping and executing this project, and your continued support. I always left your office inspired to continue working with the data or on a manuscript, and you helped me keep the bigger picture in mind. I also would like to thank Tim, for his immense knowledge on organic carbon, his support, critical eye, and editing pen. Thank you for welcoming me into the Biogeosciences group. I am grateful that Nathalie and Steven agreed to serve as external co-examiners of my thesis.

The various field trips during my PhD would not have been possible without help. So thank you Roland, Wilma, Griffin, Jason, and Chregu for introducing me to fieldwork in Zambia, and thank you Jasmin, Renata, Teo, Chregu, Simon, Krissy, Ivo, Severin, and Richard for accompanying me. During my numerous trips to Zambia, it was great to see Kawawa, Gerard and Graham, and prof. Nyambe again.

The laboratory facilities at ETH and Eawag have been a pleasure to work in, thanks to the support of Patrick, Daniel, Negar, Madalina, and Stewart. Sharing knowledge and experiences with Francien, Thomas, Tessa, Julia, and Clay made sure all the biomarker and radiocarbon work went off without a hitch.

I’ve learnt that I can’t really work in an empty office, so it was a good thing I’ve been able to share an office with Roland, Jasmin, Nuttakan, Tonya, Carole, Nina, Nathalie, Sébastien, Tim, Matthias, Rohini, Marie, Elisa, and Simon. Lunches before noon, ice cream runs in summer, feeding the fish, drinks on Thursday afternoon, it has been a pleasure. Thank you very much for your company!

Danke vielmal to the various students who went along to Zambia or worked with the sensors in Switzerland. Renata, Simon, Ivo, Severin, Thomas, and Hannah: thank you for your enthusiasm and your help in the lab and field. It may sometimes have been a challenge to balance my own work with your projects, but I’ve enjoyed working with you.

Maintaining your social life while you live abroad can be a challenge, dus dankjewel Mathilde, Bram, Nienke, Rein, Patrick, Nicole, Brenda dat jullie in Zürich langs gekomen zijn en dat we via Skype en WhatsApp contact gehouden
hebben. Ik kijk er naar uit om weer in de buurt te komen wonen! On the other end, there were a lot of people who have made life in Zürich a pleasure. Drinking tea, playing games, sports activities, … All would have been a lot less fun with Tessa, Krissy, Joep, Jenneke, Tim, Nathalie, Sebastian, and many more.

Moving away from family was harder on me than I thought. Lieve mam, dankjewel voor je eeuwige support and onze wekelijkse Skype-dates. Pap en Sandra, wat heerlijk dat jullie onderweg naar wintersport langs kwamen in Zürich. Yolande, Xander, en Colin: die Siblings-App was een briljante zet, en ik ben blij dat we zo op de hoogte blijven van elkaars leven. Nol en Laura, hartelijk bedankt voor alle berichtjes om te controleren hoe het er hier aan toe ging. Opa Leen en oma Iet, ik geniet er nog steeds van dat jullie allebei de moeite hebben genomen Skype te leren gebruiken toen Yolande en ik tegelijkertijd verhuisden.

And then last, but definitely not least, lieve Richard. Je was toch de aanleiding dat ik naar Zürich verhuisde, en hebt de afgelopen jaren enorm bijgedragen aan mijn geluk en gezondheid. Ik heb genoten van ons Zwitserland-avontuur, en kijk er naar uit om van Delft onze nieuwe thuisbasis te maken. Zonder jou was dit proefschrift er nooit gekomen.