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Carbon and nutrient fluxes from floodplains and reservoirs in the Zambezi basin

Alissa Zuijdgeest^{1,2,*}, Bernhard Wehrli^{1,2}

¹ ETH Zurich, Department of Environmental Systems Science, Universitätstrasse 16, CH-8092 Zürich, Switzerland

² Eawag, Swiss Federal Institute of Aquatic Science and Technology, Surface Waters – Research and Management, Seestrasse 79, CH-6047 Kastanienbaum, Switzerland

* present address: IHE Delft Institute for Water Education, Department of Water Science and Engineering, Westvest 7, 2611 AX Delft, the Netherlands

Corresponding author: a.zuijdgeest@un-ihe.org

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 reservoirs 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. To support such analyses, we propose a combination of specific sampling campaigns 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 ($120 \cdot 10^3$ t C per year) is offset by annual emissions of methane to the atmosphere with about $3000 \cdot 10^3$ t C-CO₂-equivalents. Therefore, building new dams will add permanent sinks of particles and nutrients to the land-ocean aquatic continuum, while draining riparian wetlands will disrupt their functions as temporal storage systems and source of terrestrial biomass for aquatic food chains.

Keywords: dam impacts, floodplain, Zambezi, carbon, nutrients, budgets

Highlights:

- Combination of discrete analyses and sensor deployments allows constraining mass balances of wetlands and reservoirs
- Biogeochemical alterations by floodplains and reservoirs differ in timing and direction
- Budgeting greenhouse gas emissions requires seasonal observations and catchment-scale approach

1. 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 lateral 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 another 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 larger 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 main stem 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 greenhouse gas 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 ; Kummur 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.

A recent report documents, however, that Africa has only 0.02 measurement stations for water quality per 10'000 km² (UNEP, 2016). This density is two orders of magnitude lower than in Europe or North America. 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. In the present study, we illustrate how high-resolution sensor data and conventional spot measurements can be combined in order to derive biogeochemical budgets for data-sparse regions.

In this context, our study follows one main objective. 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, a hydroelectric reservoir, on carbon and nutrient fluxes. In order to achieve this goal, we provide a synthesis of different studies conducted over the last years. The set of available data includes discrete chemical analyses of water and sediments and sensor deployments that cope with the significant seasonality of fluxes over large regional scales in remote areas. 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 compare the results with field studies from other tropical and subtropical sites.

2. Methods

2.1 Study sites

The Zambezi catchment in sub-Saharan Africa (Fig. 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; Zurbrugg et al., 2012; Zurbrugg 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 main stem 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 Itzhi-Tezhi reservoir in the Kafue tributary (Kunz et al., 2011b; Kunz et al., 2013). The remarkable size and hydrological characteristics of these major dams and wetlands in the Zambezi basin are outlined in Table 1.

FIG 1

Table 1 Physical characteristics of the large floodplains and reservoirs in the Zambezi catchment

System	Length (km)	Surface area (km ²)	Volume (km ³)
Barotse Plains	240 ^a	7700 ^a	
Kafue Flats	256 ^a	5660 ^a	
Lake Kariba	277 ^b	5364 ^b	156.5 ^b
Lake Cahora Bassa	250 ^c	2739 ^d	63 ^d

References: a) Hughes and Hughes (1992), b) Balon and Coche (1974), c) Davies (1986), d) Davies et al.

(2000)

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 drives the discharge patterns in the undisturbed parts of the catchment, upstream of the major hydropower dams. Accordingly, we scheduled three specific field campaigns in order to quantify concentrations and fluxes at low and high water levels and during receding floods (Fig. 2). During the 2013/2014 rainy season, this area exhibited flooding (discharge $> 1000 \text{ m}^3 \text{ s}^{-1}$) from February 2 until July 31, with peak flows (discharge $> 2500 \text{ m}^3 \text{ s}^{-1}$, 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. 2). Lake Kariba also exhibits annual flooding between November and May (Karengere and Kolding, 1995). During the subsequent dry period, deep convective mixing is generally triggered in July. Afterwards, thermal stratification re-establishes. The combination of strong seasonality of the discharge 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. While allocation of water quantity has been the subject of many studies and reports (Tilmant et al., 2012), awareness of water quality issues has been more limited.

FIG 2

2.2 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 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. For more details regarding sample collection and analysis, we refer to the relevant publications.

In short, 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 (Zuijdgheest et al., 2015).

Table 2 Data sources of measurements in the Zambezi catchment.

Location(s)	Sampling method	Parameters	Observation times	Ref
Barotse Plains, upstream of Kariba	Field sampling, water surface	POC, PN, PP, DOC,	04/2013 (HW)	a
		DON, DOP, SPM,	10/2013 (LW)	
		multi-probe	06/2015 (FW)	
	Sensor deployment (WTW EXO 2)	Temperature, conductivity, pH, dissolved O ₂ , fDOM, turbidity	Upstream 11/2013- 04/2014 Downstream 11/2013- 07/2014 (hiatus 03/2014)	b
Lake Kariba	Field sampling, sediment cores	POC, PN, PP	07/2007, 05/2008, 02/2009	c
	Field sampling	CH ₄ emissions	07/2007, 05/2008, 02/2009, 06/2009	d
Downstream of Kariba	Field sampling, water surface	POC, PN, PP, DOC, DON, DOP, SPM, multi-probe	04/2013 (HW) 10/2013 (LW) 06/2015 (FW)	#
Zambezi catchment	Field sampling	CO ₂ , CH ₄ emissions	02/2012, 02/2013, 10/2013	e

References: a) Zuijdgheest et al. (2015), b) Zuijdgheest et al. (2016); c) Kunz et al. (2011a); d) DelSontro et al. (2011); e) Teodoru et al. (2015); #) unpublished results, see methods above.

2.3 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 $p\text{CO}_2$, turbidity to suspended particulate matter (SPM) concentrations, and fDOM to dissolved organic carbon (DOC) concentrations (Zuijdgheest 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. 3, Appendix A). 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 (Zuijdgheest et al., 2016).

FIG 3

2.3.1 Method uncertainties

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. 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.

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 ($\text{LOQ} < 0.15 \mu\text{M}$). 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 $>2\times$ 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 spanning several months from a remote area.

2.4 Element budget analysis

2.4.1 Barotse Plains

Loads of carbon and nutrients per day were calculated from the sensor-derived concentrations and their confidence intervals (see below) combined with daily water level records from the Zambezi River Authority. 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.

2.4.2 Lake Kariba

The elemental budgets for Lake Kariba are constrained by the results from the Barotse Plains (as inflow), unpublished results from downstream of the reservoir, and literature values. 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 particulate concentrations of carbon and nitrogen varied, inorganic nutrients were not distinctly higher downstream of the dam compared to upstream, and showed no clear seasonal patterns. Because of differences in timing, and lack of accurate discharge data at Chirundu, the samples from the field campaigns have been used to constrain the outflow of Lake Kariba. 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 a previous budget (Kunz et al., 2011a), 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 $88 \cdot 10^3$ 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 ($88 \cdot 10^3$ tons per year, $45 \text{ mg C m}^{-2} \text{ d}^{-1}$) will be used in our budget for Kariba.

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 $141 \text{ mg C m}^{-2} \text{ d}^{-1}$ ($276 \cdot 10^3$ tons per year) based on chamber deployments. At the same time, these authors estimated the primary production rate from ^{13}C -labeled incubations at $16.6 \text{ } \mu\text{mol C L}^{-1} \text{ h}^{-1}$, which would imply an input of organic carbon of

$47 \cdot 10^6$ 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 $271 \pm 23 \cdot 10^3$ tons of carbon per year, respectively, estimated from Zuijdgeest et al. (2016)), these numbers create a large surplus of carbon in our system without CO_2 outgassing from the reservoir. 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 because reliable in-situ rates are lacking. Therefore, the net gas exchange of both carbon and nitrogen will not be constrained by our budgets, but is instead determined by balancing the other sources and sinks.

3. Results

3.1 Floodplain dynamics

Particulate carbon and nutrient concentrations at Senanga, downstream of the Barotse Plains, reached their maxima at the beginning of the year, during the rainy season and the beginning of the flooding phase (Fig. 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 and indicate robust seasonal trends between the years 2012-2015 with comparable rainy seasons.

FIG 4

Particulate loads were lowest at the end of the dry season, and increased as the flooding season progressed (Fig. 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.

FIG 5

From these seasonal records, we obtained the yearly loads leaving the floodplain (Table 3) which will be used to constrain and discuss the biogeochemical budgets of Lake Kariba. During the flooding season (discharge $> 1000 \text{ m}^3 \text{ s}^{-1}$, February 2 until July 13, Fig. 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 $2500 \text{ m}^3 \text{ s}^{-1}$ 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 (DOC:POC ~ 9 , DON:PN ~ 6), while most phosphorus (approximately 93%) was transported as particulate material (Table 3). Our field observations were consistent with earlier studies (Zurbrugg et al., 2013; Zuijdgeest et al., 2015) indicating that inorganic nitrogen and phosphorus contributed negligible amounts to total nutrient loads.

Table 3 Estimated yearly loads (in 10^3 tons) at Senanga based on extrapolation of the sensor data, with 95% confidence intervals between brackets.

POC	PN	PP	DOC	DON	DOP
22	2.3	2.1	200	14	0.16
(17-29)	(1.9-2.8)	(1.3-3.0)	(180 – 220)	(11 – 17)	(0.13 – 0.19)

The floodplain altered the carbon-to-nitrogen and nitrogen-to-phosphorus ratios of the riverine material (Fig. 6). During high water, both POC:PN and PN:PP ratios decreased along the floodplain, whereas these ratios increased during falling and low water conditions. The DOC:DON ratio varied throughout the year, with a distinct decrease along the floodplain during falling water and little change during high and low water. DON:DOP ratios increased markedly along the floodplain.

FIG 6

3.2 Lake Kariba biogeochemistry

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. These inflow loads were combined with unpublished results and literature values, leading to well-constrained budgets (Table 4). For carbon, atmospheric gas exchange was not constrained but determined by closing the budget. Similarly, the balance between denitrification and nitrogen fixation was used to balance the nitrogen budget.

Table 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).

	DOC	POC	TOC	TN	TP
Inflow	200 (180 – 220)	22 (17 – 29)	220 (200 – 250)	16 (13 – 20)	2.5 (2.0 – 3.0)
Outflow	55 (50 – 60)	13 (12 – 14)	68 (62 – 74)	4.7 (4.3 – 5.1)	0.17 * (0.15 – 0.18)
Sedimentation		120	120	12 (11-62)	4.1
CH_4 flux			88		

FIG 7

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 CO₂ ($54 \cdot 10^3$ tons of carbon per year). For nitrogen, the balance is lacking a very small input of $0.7 \cdot 10^3$ tons of nitrogen 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 phosphorus per year).

The POC:PN ratios of the riverine input to Lake Kariba remained fairly constant throughout the year, but the ratio in the outflow varied. The ratio decreased at times of high and falling water, with the largest difference observed during falling water, whereas no change was observed during low water. The PN:PP ratio increased during high water and decreased during falling water. The DOC:DON ratios showed little alteration downstream of the reservoir compared to upstream, though the value varied between seasons. DON:DOP ratios decreased downstream of the reservoir.

4. Discussion

4.1 Sensor-derived biogeochemistry

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. The difference comes from new correlations between sensor records and individual samples. 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. 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 from the floodplain over an annual cycle will be used in a next step to derive elemental mass balances for the reservoir.

4.2 Biogeochemical alterations by the Barotse Plains

4.2.1 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., 2016), 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 suggests erosion of mineral soils, with associated phosphorus. Erosion from the floodplain seems likely, as soils on the floodplain are generally poorly developed (arenosoils, 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.

4.2.2 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 falling and low water 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.

4.2.3 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 CO₂ and CH₄ concentrations downstream of the Barotse Plains (Teodoru et al., 2015) further suggested that floodplains are hotspots for emissions. Sensor-records showed large CO₂ oversaturation downstream of the floodplain during the flooding season (Zuijdgeest et al., 2016). Combining these sensor-derived CO₂ 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 km²; Hughes and Hughes, 1992). With this simplified assumption, the annual CO₂ 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 5), we suggest that woods- and shrubland sustain higher aquatic CO₂ emissions than floodplains surrounded by dense tropical forest.

Table 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)

	Amazon	Zambezi
Land cover	(Borges et al., 2015a)	(Borges et al., 2015b)
Dense forest (%)	83	20.4
Mosaic forest (%)	4	0.0

Woodland and shrubland (%)	4	54.6
Grassland (%)	5	8.7
Cropland/ bare soil (%)	4	13.4

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 $100 \text{ mg C m}^{-2} \text{ d}^{-1}$, 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.

4.3 Lake Kariba biogeochemistry

4.3.1 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 ($12.4 \cdot 10^3$ tons POC retained per year, 1.3 for PN). By contrast, 87% of the inflowing phosphorus load ($2.2 \cdot 10^3$ 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).

4.3.2 Budgets of carbon and nutrients

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.

Lake Kariba plays a smaller role as a carbon sink than 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.

Release of phosphorus from the sediments will probably balance 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.

4.3.3 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 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 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.

4.3.4 Greenhouse-gas emissions

The Lake Kariba surface waters were undersaturated during the campaigns documented by Teodoru et al. (2015). Undersaturation of CO₂ in reservoir surface waters, and hence uptake of CO₂ by the reservoir, has also been described for the Tana river (Bouillon et al., 2009; Tamooch 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 CO₂- rich deep-water is brought to the surface and results in a temporal outgassing flux. In a limnological study that included depth profiling, the deeper water column was found to be highly oversaturated with respect to CO₂ (350-1100%; Kunz et al., 2011a). These observations support the rather small net CO₂ 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 CO₂ 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 CO₂ 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 CH₄ (>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 CO₂ (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 CO₂ equivalent, CO₂eq), the net emissions from Lake Kariba are roughly 3000·10³ tons C as CO₂eq per year (= 3 Tg / 0.003 Pg CO₂eq-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 CO₂ and CH₄ to the atmosphere was estimated between 10.8 and 16.2 Tg CO₂eq 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 CO₂eq per year (Deemer et al., 2016), to which Kariba would contribute about 0.4%.

5. Summary

Dams and reservoirs alter the riverine biogeochemistry in distinct, and often different ways. In Table 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 a 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 CO₂ by storage of organic carbon in sediments ($120 \cdot 10^3$ tons C yr⁻¹) is more than offset by ebullition of methane gas with $3000 \cdot 10^3$ tons C in the form of CO₂equivalents per year.

Table 6 Overview of the different ways in which the reservoir and the floodplain affect particle dynamics, carbon and nutrient turnover, and greenhouse-gas emissions

Process	Barotse Floodplain	Kariba Reservoir
Particle dynamics	Export	Retention
Carbon turnover	POC and DOC emission	POC burial
Nitrogen turnover	Net N-fixation	Balance of N-fixation and denitrification
Phosphorus turnover	PP and DOP export	P burial
Greenhouse-gas emissions	Emission of CO ₂	Uptake of CO ₂
	Emission of CH ₄	Emission of CH ₄

6. Recommendations

As the number of large dams is increasing and the loss of riparian wetlands continues, biogeochemical research should address three important knowledge gaps. First, the extension and flooding dynamics of existing and lost riparian wetlands should be better mapped on a global scale. Such spatial analyses will help to derive better estimates for the hydrological and biogeochemical impact of transforming global river corridors. Second, comparative analyses of greenhouse gas emissions of riparian wetlands and dams in close proximity should improve our ability to calculate reliable carbon footprint of hydropower dams. Reconstructing natural emissions under pre-dam conditions is necessary for assessing the anthropogenic impact of dam construction on carbon budgets. Finally, water quality data for many large river systems in the global south remains poor. Improving the monitoring and analysis of river water quality in large parts of Africa should become a specific priority for scientists in river biogeochemistry and for river management. Sensor-derived data can help us to achieve this goal.

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Appendix A: Correlations between sensor measurements and carbon and phosphorus.

List of figure captions, and size preferences

Figure 1 Map of the Zambezi catchment, with largest floodplain systems shown in green and most important sampling locations as red circles

- 1.5 or 2 columns

Figure 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 $> 1000 \text{ m}^3 \text{ s}^{-1}$, peak flow (shaded area) as discharge $> 2500 \text{ m}^3 \text{ s}^{-1}$. 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).

- 1.5 or 2 columns

Figure 3 Correlations between turbidity and particulate nitrogen and fDOM and dissolved nitrogen. The 95% confidence interval is shown in grey; equation and statistical parameters are included in the figure.

- 1.5 or 2 columns. Could be made vertical to fit 1 column, if needed for formatting reasons.

Figure 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 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.

- 2 columns

Figure 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 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.

- 2 columns

Figure 6 Carbon, nitrogen, and phosphorus budgets for Lake Kariba based on export data from upstream floodplain and published fluxes (Table 4). Bold numbers indicate that the flux is constrained (see Tables 3 and 4), italic numbers were determined by closing the budgets.

- 1.5 columns

Figure 7 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.

- 2 columns

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

* all in 10^3 tonnes per year

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

Fig. 7

Graphical abstract