Response to Reviewer 1

Dear dr. Bouwman,

Thank you for your efforts in reviewing our manuscript. Your comments from a modeler's perspective are much appreciated. Below you will find our responses to the issues you raised (paragraphs starting with >>), and the way we have incorporated your suggestions into the manuscript (in parentheses). The updated manuscript (track-changes Word document) and the updated supplementary material have been combined into one file, and added to this comment as a supplement.

Seasonal dynamics of carbon and nutrients from two contrasting tropical floodplain systems in the Zambezi river basin Authors: Zuijdgeest et al. This is an interesting study which compares the role of floodplains on biogeochemistry in two segments of the Zambezi river. The paper is well-structured, and presents results that could add much to our understanding of how floodplains and their soils and vegetation function in river biogeochemistry, how dams and reservoirs can impact this functioning. The way the authors have summarized their main results in Figure 7 is excellent. However, there are a few problems for me as a modeler to fully understand the discussion.

The first problem is in the sampling procedure. It is not clear to me how exactly was sampled: only one sample per season, or is the result presented an average of more that one sample? Also, years for different years are presented in one single Figure, e.g. Figure 3 180 data. Perhaps the authors could add a remark to justify this. If discharge is variable, the river loads will also vary, and perhaps the authors could add information on the variability of the discharge in Figure 2.

Along the floodplains, samples have been collected during various field campaigns on various locations along the floodplain (see Fig. 1 for details). If a system was visited more than once during a specific season (most noticeably the Kafue Flats during the wet seasons 2009 and 2010, with a preliminary study in 2008), the analyses for samples from the same location were averaged. This was justified by the similarity between results from the different years, as presented by Zurbrügg et al. (2012) and Zurbrügg et al. (2013). While this procedure has introduced additional variability in the absolute magnitude of the numbers presented, the trends were retained. In the manuscript a sentence has been added to section 3.1 ("The similarity of the results from different years (Zurbrügg et al., 2013;Zurbrügg et al., 2012) allowed combination and averaging of the data sets in order to obtain generalized patterns for the two systems and seasons.") and the standard deviations for the discharge measurements have been included in Fig. 3.

Additionally, it is possible to consider the variability in discharge for the data series presented in Fig. 2. While this might include a time component in its variability (global climate change, El Niño events), the updated figure includes the standard deviation over the 18-year period.

And what is the range shown in Figure 3? Is this the standard deviation calculated from all observations along the floodplain? Please provide this information.

We think you are referring to Fig. 4 rather than 3, as there is no standard deviation presented in Fig. 3. The range shown in Fig. 4 is indeed calculated from all observations along the floodplain during a specific season, and the boxes represent the first and third quartiles, and the median (which has been added to the figure caption). The information has been provided in the text as "For 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. 4). The occurrence of large spatial variations along the floodplain, or between the months sampled (see Supplementary Information) between the different years, resulted in larger ranges."

The second problem is in the terms used. In some cases it is wet/dry season (e.g. Table 1) and in other cases it is peak and base flow (title of Table 1). I suggest to use terms consistently (dry/wet season) as for example base flow may be confusing to people with a hydrology or other background.

This suggestion has been implemented, though the expression "peak flow" remains in use when considering the timing of processes, or when referring to results from literature.

The third problem is that it is not explained how river loads were calculated. Is this simple discharge times concentration? Is this justified, i.e. is the sample from the middle of the well-mixed channel representative of all water in the river? Also here perhaps a brief justification could be added, or at least a remark that this is a cause of uncertainty.

Loads were indeed calculated as discharge x concentration. We have found that there was little variation with depth and between the middle of the channel and close to the edge of the main channel. The latter we have measured during the 2013 campaign in the Barotse Plains, the former has been determined early in the project, during the initial Kafue Flats campaign in 2008. This information has been included in the Supplementary Material. In the manuscript, the paragraph introducing loads now starts with the following sentence "Loads were calculated from the discharge and concentration data for the respective species, as the water column was well mixed (see Supplementary Information for details)."

Finally, it is not clear what the term net export represents, and how this compares with the load. This is confusing because both terms are used within the same paragraph in section 5.2. The authors need to explain how net export (Table 1) was calculated. Can net export be deduced from Figure 5 from the difference between distance 0 and the endpoint?

The following explanation has been added in section 4.2: "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 1)." Parts of section 5.2 have been moved to section 4.2 to present these results in the results section rather than in the discussion, as suggested by the second reviewer.

Minor issues

Please check the references. I saw one missing reference (Melack et al., 2009).

This has been added.

The paper by Mayorga et al. (2005) is on the Amazon, so how can it have data for the Zambezi river.

This should have been Mayorga et al. (2010) and has now been corrected.

Instead of Yasin et al. (2010) please use the original publication where the observed river yield was taken from (probably Hall et al. 1977).

This has been changed.

I see some unclarities in section 4.3: line 12 "became enriched" and line 13 "lower". Compared to what, or is it enriched with increasing distance, or in time?

This sentence compared the wet season values to the previously mentioned dry season values, and has been changed to "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 δ^{13} C values were observed during the wet season than during the dry season (both significant, p < 0.05)".

Furthermore we would like to inform the reviewer about some more substantial revisions of the manuscript that have been made based on the comments of reviewer 2. The key issues addressed were:

- Updating the color coding for the figures, and replacing the exact numbers on export and removal rates in Fig. 7 with proportional arrows for particulate and dissolved organic matter;
- Moving and extending the description of Table 1 from section 5.2 to section 4.2;
- The discussion on hydrology (section 5.1) has been extended with a short section on the amount of water moved from the rivers to the floodplains;
- Section 5.2 has seen major revisions, to focus more on processes responsible for the export and retention observed;
- Section 5.3 has been re-arranged into two sections, separating dissolved and particulate organic matter into sections 5.3.1 and 5.3.2, respectively. Both the C:N ratios and the stable carbon isotopic signatures are combined to present a more integrated view of sources of particulate organic matter. Unlike in the initial manuscript, we now no longer distinguish

- between C₃ and C₄ vegetation, but rather between permanent and seasonal floodplain vegetation;
- Both the conclusion and the abstract have been shortened and more generalized.

References:

- Mayorga, E., Seitzinger, S. P., Harrison, J. A., Dumont, E., Beusen, A. H. W., Bouwman, A. F., Fekete, B. M., Kroeze, C., and Van Drecht, G.: Global Nutrient Export from WaterSheds 2 (NEWS 2): Model development and implementation, Environmental Modelling & Software, 25, 837-853, 10.1016/j.envsoft.2010.01.007, 2010.
- Zurbrügg, R., Wamulume, J., Kamanga, R., Wehrli, B., and Senn, D. B.: River-floodplain exchange and its effects on the fluvial oxygen regime in a large tropical river system (Kafue Flats, Zambia), Journal of Geophysical Research, 117, G03008, 10.1029/2011jg001853, 2012.
- Zurbrügg, R., Suter, S., Lehmann, M. F., Wehrli, B., and Senn, D. B.: Organic carbon and nitrogen export from a tropical dam-impacted floodplain system, Biogeosciences, 10, 23-38, 10.5194/bg-10-23-2013, 2013.

Response to Reviewer 2

Dear Dr. Jennerjahn,

Thank you for your efforts in reviewing our manuscript. Your detailed comments are much appreciated. Below you will find our responses to the issues you raised, and the way we have incorporated your suggestions into the manuscript (in "blue").

General comments:

The authors present an interesting study on river biogeochemistry from two Zambezi tributaries. Data and knowledge from African rivers are strongly underrepresented in the global data base and make this study a valuable addition. The study conducted in subbasins of the Zambezi River aims at assessing the effects of floodplains and dams on river biogeochemistry. Understanding of these processes in river catchments is important with regard to what ultimately reaches and affects the coastal ocean.

The paper is generally well structured and written. However, while the set of samples and analytical data appears to be robust and absolutely worthwhile publishing, the design of the study raises major concerns regarding the two major issues discussed: the effect of floodplains and dams. First, the authors collected data and samples from two stretches of the river passing through floodplains during dry and wet seasons. However, although the importance of the biogeochemical exchange between river and floodplain was stressed by the authors, samples were collected only in the middle of the river. While I agree with the authors that this exchange is important, I would also expect biogeochemical gradients from the river until the landward margin of the floodplain. The study design does not allow accounting for this. Having said this, the least the authors could do is try to find examples from the literature and discuss these.

For both systems, we did collect samples at the edges of the channel, and as far onto the floodplain as the dense vegetation would allow us. We found there was very little variability between the middle of the channel and the edge. This data is not presented because we only have these for the wet season in the Barotse Plains. Additionally, the dense reed vegetation, and sometimes-shallow water levels did not allow movement onto the floodplain by boat. Real channel to floodplain transects were therefore not feasible. This information has now been included in the Supplementary Information, and additional floodplain transects can be found in the supplementary material of Zurbrügg et al. (2013).

Second, the authors collected data from a floodplain stretch between two dams, but have no data/samples on the respective river portions upstream of the first (ITT) and downstream of the

second dam (KG) which makes it difficult to assess the dam effect, in particular with regard to quantification.

Data upstream of ITT has been collected and discussed by Manuel Kunz, some of which has been used in this manuscript as well. However, we were more interested in the floodplain processes that might have changed due to the presence of the dam, for which we did not need data from upstream of the reservoir. Downstream of the Kafue Gorge dam we did not collect samples, because there the Kafue River flows through a steep gorge without floodplains. It was therefore not considered part of our study.

Moreover, the discussion of the important issues often remains at the surface and is full of flaws, in particular when it comes to the use of C/N ratios and stable carbon isotopes. You will find detailed comments below. While the authors have a very good set of data and the issues discussed are highly relevant, the story is simply not yet there. Therefore, this paper cannot be recommended for publication in Biogeosciences in its present form. It will require major revisions to make it a robust study and valuable addition to the literature. However, I am convinced that the authors have the means to do so and would greatly appreciate to see this study published!

General comment regarding the reviewer's requests for more emphasis on the inferences from our study: our study is very descriptive in nature, and there is very little comparable information published for other tropical river-floodplain systems. Lacking process rates from our own work, and published context from comparable systems from the literature, we tried to focus on conclusions supported by the data.

Detail comments:

Abstract:

The abstract is rather long, ...

The abstract has been shortened from 449 to 380 words.

... in some places a bit confusing and ends with a little uninspired conclusions. I suggest to shorten the detail description of results and to put more effort on the inferences of the study. A final, clear take home message would be fine.

The abstract has been more generalized, with a clear take home message at the end.

P. 10546, l. 5: Why just "hydropower" dams? There are many multipurpose dams which affect river hydrology and biogeochemistry etc.

"Hydropower" has been removed; it can indeed be generalized here.

P. 10546, l. 11 ff.: These paragraphs are rather long and not really clear. In the first sentence you state that the "Barotse plains retain particles", but have "higher annual yields of POC and N: : :than

previously reported for the Zambezi: : ". This sounds a bit strange. It must not necessarily be a contradiction, but rephrasing could help make clear what is meant.

The abstract has been generalized, and shortened. This particular sentence has been incorporated in the new abstract in "Distinct seasonal differences have been observed in carbon and nutrient concentrations, loads, and export and retention behavior in both systems."

P. 10546, l. 23-27: There is a contradiction regarding organic matter (OM) sources. While you first stress the importance of aquatically produced OM during the wet season, you state in the following dominances of C3 vs. C4 vegetation. This does not match and raises a general issue with the use of C isotope composition. The relevance of autochthonous OM production is often neglected. For example, depending on the carbon source freshwater plankton can have the same d13Corg as C3 vegetation. Moreover, rivers do not only transport plant material, but rather larger portions of soil material. That, in turn, often has a d13Corg in between that of C3 and C4 plants.

Rephrasing has removed the mismatch of information. The concerns regarding the use of stable carbon isotopes have been addressed with additional data and arguments in the discussion section, and the abstract has been adjusted accordingly. "Carbon to nitrogen ratios showed that soil-derived material was dominant year round in the Barotse Plains, whereas the Kafue Flats transported aquatically produced particulate organic matter (produced in the upstream reservoir) during the wet season. Stable carbon isotopes suggested that inputs from the floodplains to the particulate organic matter pool varied throughout the year in both systems, in opposite patterns. In the Kafue Flats, encroachment of woody plants since the construction of the dams could be responsible for the altered pattern."

P. 10547, l. 7-11: So, what are the clear effects? Name them. The following two sentences are rather commonplaces. Be more specific regarding your results. It will make it more interesting for the reader.

The commonplace sentences have been removed, and the final paragraph has been tailored to fit more to our results. "This study revealed effects of dam construction on organic matter and nutrient dynamics on the downstream floodplain that only become visible after longer periods, highlighting the need for continued monitoring after dam construction."

Introduction:

The introduction generally looks good.

P. 10548, l. 22 ff.: The first sentence is simply wrong. The type of OM never depends on discharge alone, but mainly on the sources and processes in the catchment. The following examples are quite arbitrary and not representative. Here again, we have the problem with the use of C isotopes; reducing it to C3 and C4 plants is too simple and definitely wrong!

The first sentence has been rephrased to "... co-varies with discharge". The examples provided are of African rivers, which is the framework in which we wanted to present our results. For these

examples, the use of C isotopes is cited as discussed by the respective papers. In the discussion section, additional data and arguments have been included in response to your comments.

P. 10549, l. 3-13: I suppose this paragraph should state the research problem, but remains a bit undetermined. It would benefit from clearly pointing out the gap in knowledge that this study wants to close.

We feel confident that P10549 L6-7 states the gap: the impact of dam-induced changes in hydrographs on floodplain biogeochemistry has not been studied. We have removed P10549 L11-13, which in the previous version led to the gap becoming hidden in the middle of the paragraph.

P. 10549, l. 14-24: And following up on that, this paragraph can also be a bit shortened and focused on what was done for what purpose.

We feel that the objective and the approach become sufficiently clear in the following sentences "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:

P. 10550, l. 15-19: What is much more important here and later for budget calculations: was there a change in transported water volume before and after dam construction? Is the water only used for power generation or also for irrigation and/or drinking water?

In the description of the study sites, the following information has been added after L12 (P10550): "Evaporation from the reservoir changes the water level by 780 mm year-1, according to Beilfuss (2012)." Otherwise, there is no change in the transported water volume, only a change in timing and pattern (P10550, L15-18). In the Kafue Flats there is some irrigation occurring close to the downstream end of the floodplain, in the vicinity of Kafue Town. The drinking water withdrawal is after Kafue Town, i.e. outside of our sampling area. In the Barotse Plains no organized irrigation is extracted. Drinking water extraction from the river is minimal, as most drinking water in Zambia originates from groundwater.

Methods:

There is no information at all about data quality. Add information on accuracy/precision of analyses. This is important in order to assess the relevance of differences in numbers discussed later.

For our laboratory analyses, the precision of the measurements was lower than the standard deviation among all the samples, as presented in Fig. 4. Moreover, we feel that adding accuracy and precision numbers for these fairly standard analyses would be too much detail and make the methods section unreadable. Precision for the isotopic values has been added " $(\delta^{13}C: -15 \text{ to } -30\%_{VPDB}, \text{precision } 0.1\%; \delta^{15}N: -1.1 \text{ to } +32.7\%_{air}, \text{precision } 0.2\%)$."

Results:

In general, all results sections can be shortened. Quite often they contain repetitions, first describing general trends and then repeating them with numbers. I also don't like the style how the isotope data are described. Sometimes they are reported as "water O-isotopic signal", then a depletion of one isotope is mentioned in the same sentence with a simple delta notation. For reasons of clarity and to make it easier for the reader I suggest to use exclusively low or high delta values.

We wanted to avoid endless repeats of δ^{18} O, and were therefore using synonyms that are widely used and accepted. We have tried, however, to accommodate the comments of the reviewer by removing some of the synonyms and implement the suggestion.

P. 10552, l. 13-14: The distances displayed here do not match with the scale in the inset maps in figure 1. Correct this.

In the updated manuscript, for both systems the distances in the plots are distance along the river, within the floodplain. This has been updated in the figure axes, and in the caption of Fig. 1 ("Sampling stations will be further presented in distance along the river (km)."

P. 10552, l. 11-16: Why should river constrictions lead to a discharge minimum? One should expect higher velocities/discharge in such a case. The following sentences provide an explanation, but this phrasing is a bit unfortunate.

River constrictions in a valley or steep channel would indeed lead to higher velocities, but on the floodplains the water can leave the normal river bed, and spread laterally onto the floodplain. In the Kafue Flats, we observed a reduction of flow velocity, caused by the resistance of the adjacent reeds (slack flow effect). The section has been rephrased: "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. 3). Located around 100 km and 200-300 km downstream in the Barotse Plains and in the Kafue Flats, respectively, constrictions in the river bed were present, which promoted flooding of the surrounding floodplain area (Zurbrügg et al., 2012)."

- P. 10552, l. 19-20: What do you mean by "upstream Zambezi", the Barotse plains? Then say so. Rephrased: "...Zambezi crossing the Barotse Plains..."
- P. 10553, l. 16: What is meant by "organic nutrient species"? Carbon as such is not a nutrient. Changed to "organic carbon and nitrogen species".
- P. 10553, l. 23: Interesting to read about loads. But the reader does not get any information how and for which points/locations these loads were calculated. This information must be included.

The section on loads has been extended with the information on how the loads were calculated, and some of the descriptive sections that were previously in the discussion. This has resulted in the following paragraphs, replacing P10553 L23-28: "Loads were calculated from the discharge and concentration data for the respective species, as the water column was well mixed (see Supplementary

Information for details). Total carbon and nitrogen loads increased along the Barotse Plains during the wet season, mainly due to larger contribution by the dissolved organic form (Fig. 5). 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 is comparable between the two systems (roughly 1500 t C d-1, Fig. 5), while the nitrogen loads in the Barotse Plains were almost twice as high as those in the Kafue Flats (44 t N d-1 and 20 t N d-1) During the dry season the loads decrease 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 1). During the wet season, the Barotse Plains were a sink for all particulate phases, while the Kafue Flats acted as a source (Table 1). Both systems were sources of DOC and 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 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."

P. 10554, l. 15-19: The C/N ratio of 166 looks rather strange and results from only two measurements. Although you may find a statistically significant difference, I don't think that it has a real diagnostic value.

While this value does indeed only stem from 2 measurements, the measurement procedures are reliable, and both measurements resulted in a C:N ratio an order of magnitude larger than during the wet season as a consequence of very low DON values. As there is no indication that these are outliers, we prefer to document these values.

Discussion:

P. 10555: The whole discussion on the relevance of hydrology and inundation dynamics is absolutely not convincing. It is based on a mass balance approach with isotope data from another study for one of the flats and almost no data for the other flat. What is necessary for such a discussion is the volume of water moved and the period of inundation. From the discharge data and area of the floodplains the authors have, they should at least be able to calculate roughly the volume of water transported.

A new initial paragraph has been added to section 5.1: "The discharge patterns (Fig. 3) showed how the bankfull capacity of the Zambezi and Kafue Rivers varied along the floodplain stretch. In both systems water has moved from the main channel onto the floodplain, 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), which led to prolonged residence times of the water on the floodplain,

during which evaporation might occur, resulting in heavier $\delta^{18}O$ signatures in water that has spent time on the floodplain."

It has been stressed more thoroughly that the mass balance approach for the Barotse Plains is a first approximation (replacement of P1055,L5-7), and should be considered as such. "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 has spent time on the floodplain."

P. 10555, l. 20-21: What is meant here "with a floodplain contribution of 16%"? 16% of what coming from where? And following, what is meant by "there was still exchange between the river channel and some permanently inundated areas"? Could it be that lower discharge during the dry season is only related to evaporation? The paragraph then ends with a few examples from other areas/studies. But what is the inference with respect to own findings?

This has been rephrased: "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 having spent time on the floodplain (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."

The whole chapter "5.2 Export and retention behavior" is quite disappointing, because it simply repeats overall results and then speculates about the reasons for the observed behavior. It should be reduced drastically or needs a real discussion of the factors mentioned.

The results presented in this section have been moved to section 4.2 and the section has been rewritten to provide an argument about primary production and respiration occurring on the floodplain and in the river channel (5.2 Seasonality of C and N export and retention). The updated version of this section is as follows:

"During the wet season, the Barotse Plains were characterized by a net export of dissolved phases and retention of particulate matter. 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 leaching of vegetation or soils. During the dry season, the patterns were reversed, indicative of primary production on the 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 in the main channel, and degradation and leaching of soil and vegetation from the inundated floodplain (indicated by low oxygen concentrations of 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 might not have effects beyond the downstream reservoirs of Lake Kariba and Kafue Gorge, respectively (Fig. 1). Both impoundments will trap mobilized particles, and retain 70% and 90% of incoming total N and P within Lake Kariba (Kunz et al., 2011a). Nevertheless, on a catchment scale, mobilization of particulate organic matter from the inundated area of the river-floodplain systems resulted in specific POC and PON yields (net export per inundated area per year; Table 2) from the Barotse Plains, which were close to an order of magnitude higher than previously reported values for the entire Zambezi River (Beusen et al., 2005; Mayorga et al., 2010). Despite the behavior as a sink during the wet season, the normalization to inundated area has resulted in positive annual export from the floodplain. Also, DOC yields from the Barotse Plains were higher than previously estimated for the Zambezi, but comparable to those measured in the Amazon and Orinoco rivers (Table 2; Beusen et al. (2005); Harrison et al. (2005); Lewis and Saunders (1989)). Similarly, DON yields from the pristine floodplain were similar to values measured in the Amazon and Orinoco (Table 2). The Kafue Flats show negative DOC, DON, DIN yields, i.e. are retaining these species. These negative yields show how floodplains can impact the riverine loads in trends opposite to those observed for the whole catchment. Similarly, the high yields from the Barotse Plains underlined the dominant role of floodplains as biogeochemical reactors in riverine transport of organic matter from land to sea."

P. 10556, l. 14-17: What is the use of discussing concentrations in a chapter that deals with fluxes? This can be deleted.

The marked difference between DIC concentrations during different seasons in the Barotse Plains was responsible for the smaller difference in net export between the seasons compared to the Kafue Flats. This has been removed.

P. 10556, l. 19: ": : :Kafue flats were a minor source."? If I can believe table 1 the Kafue flats should be a minor sink for DIN (I read table 1 as follows: wet season 0.1 t N d-1, dry season -0.2 t N d-1; taken together a negative flux should mean retention; right?). It would be helpful to make clear in the legend of table 1 what positive and negative signs mean, i.e. export vs. retention.

We prefer discussing the seasonality, by separating the observations from the wet and dry season. This paragraph as a whole deals with the wet season, hence the statement that the Kafue Flats were a minor source (0.1 tN d⁻¹). The dry season is discussed in the next paragraph, starting on P10556-L24. An explanation of the calculation of the net export has been added in section 4.2: "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." Additionally, the caption of Table 1 has been updated: "Net export (in t C d⁻¹ and t N d⁻¹), 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 lack of measurements at downstream locations."

P. 10556, l. 19-23: This is hard to understand, the mixing of fluxes and loads and differences between numbers in table 1 and figure 5. I suppose the numbers are correct, but the way it is written up is confusing.

We feel confident that the source of the confusion has been removed now that the results part (relating to Fig. 5, including L19-23) has been moved to section 4.2.

P. 10556, l. 24-25: This is an interesting point, but as is nothing but speculation. It belongs to the issues mentioned above. If the reader should believe in the relevance of Aeolian input, there must be some facts and discussion underpinning it, not just a "most likely" without discussion.

& P. 10556, l. 27 ff.: Same issue: "DOC and DIC were retained by both systems, potentially converted: : "; just speculation. Provide arguments or delete this. The same holds true for the following statement on p. 10557, l. 3-6.

We've attempted to provide more arguments fur the observed patterns and feel confident that the updated version of the entire section (as mentioned above) has removed much of the speculation.

P. 10557, l. 7-10: This is an interesting point and relates to one of the major issues of the whole paper, the floodplain as a biogeochemical reactor. However, what comes is just a comparison to a few other systems and absolutely no discussion of the "biogeochemical reactor". So, what is happening there? What are the inferences for your own findings?

The inclusion of a more process-based explanation for the observed patterns strengthens the discussion of the biogeochemical reactor. In the updated section (see above), the seasonal inferences are now stated more clearly.

P. 10557, l. 19-21: If I can believe table 1 the Barotse Plains are a net sink for particulate matter. How shall we understand the statement that the "particulate matter mobilized in the floodplain will end up in the sediments of Lake Kariba"? Again, looking at table 1 you may have some mobilization during the dry season, but what would be important to discuss why you find large seasonal differences. You have very interesting findings, but do not discuss them.

The Barotse Plains are indeed a sink for particulate matter, but when considered as yearly yields per inundated area, the results (Table 2) show that it is actually a source, and we were referring to this material being trapped in Lake Kariba. I think some confusion has arisen from the use of terminology and the information presented in Tables 1 and 2. We've attempted to clarify this as need throughout the updated manuscript, and hope to have removed the source of the confusion.

P. 10557, l. 25-27: This is rather a commonplace. What I am missing are the inferences for the studied floodplains and what that could mean for the whole river catchment in terms of export vs. retention. What are the controls? How do they vary by season? Are the floodplains a sink or a source and is that different from other rivers?

The commonplace sentence has been somewhat altered and relocated to make it more specific to the Zambezi, with the paragraph now ending with: "These negative yields show how floodplains can impact the riverine loads in trends opposite to those observed for the whole catchment. Similarly, the high yields from the Barotse Plains underlined the dominant role of floodplains as biogeochemical reactors in riverine transport of organic matter from land to sea." It has been our goal to investigate the behavior of the floodplain during different seasons, and how this relates to the whole catchment (Table 2). The seasonal variability and its potential controls have been more extensively described in the updated manuscript (see updated section above). Comparison of our floodplains to other rivers is not very feasible, because very few comparable studies of tropical river-floodplain systems have been published, and comparing our results to temperate or arctic floodplains would introduce too many variables.

The style of discussion in the following chapters is rather annoying, every paragraph starts with a conclusion and then tries to bring some arguments for it. In a scientific paper own findings should be presented in context with other studies/areas/findings and discussed and then a conclusion can be drawn on own findings. This is something the authors should correct.

We feel it is important to stress the key message of a paragraph early on. This helps the reader navigate text. However, we have varied the style throughout the section.

P. 10558, chapter 5.3.1: This whole chapter does not discuss sources of dissolved organic matter as announced in the chapter heading "5.3 Sources of organic matter". It only once mentions runoff from inundated soils, the rest is seasonal variations without further source discussion.

We felt that this section did discuss the different sources of DOM during the contrasting seasons. However, it has been extended, following the adjustments in section 5.2. A paragraph has been added, that builds on the argument provided in section 5.2 "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, higher primary production 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 was contributing 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." Additionally, the paragraph on the DOC:DON ratio has been moved from section 5.3.2 (P10559, L8-18) to section 5.3.1.

P. 10558, l. 11: Do not use the term "can explain" (here and throughout the whole manuscript!). A person can explain something, but the "source of DON" cannot explain something.

This has been rephrased in the text.

Chapters 5.3.2 and 5.3.3 should be merged.

The two sections have been merged to a section called "Particulate organic matter".

As is they are parameter discussions, but not source discussions. The C/N ratio alone is not suitable for such a source discussion. It is affected by numerous factors, the initial difference between plankton and plants/soils is just one of them. Selective decomposition of OM increases the C/N ratio over time. Adsorption of inorganic nitrogen to fine-grained particulate matter (clays) leads to a low C/N ratio.

Visually, there is very little clay in the suspended particulate matter in both systems; especially in the Barotse Plains, the surroundings are mainly sandy (geological formation: Kalahari Sands).

The C/N range of terrestrial plants and soils is huge. Similarly, using the stable carbon isotope composition of OM alone to distinguish between sources is also of limited value. Also, just using it in terms of contributions of C3 and C4 plant material means ignoring all the other sources/factors that contribute to the d13Corg of a specific sample one considers. What you mainly find in river suspensions is not plant debris, but eroded soil (including plant debris and processed plant debris). The d13Corg of soil can be very different from the plant growing on it. Moreover, in the water you find micro- and macrophytes the d13Corg of which varies over a wide range. This can be very important in a river and in particular in floodplains. Of course, you can have a lot of microalgae (or not) depending on nutrients and turbidity etc. Moreover, I have myself observed macroalgae and water hyacinths in massive amounts in tropical rivers and reservoirs, all of them aquatic plants with a d13Corg that falls in the range between terrestrial C3 and C4 plants. All this is not mentioned in the discussion in this manuscript. And what is also mandatory for such a discussion is to have stable isotope data from the various OM sources you find in the area, not just literature data. Are there no stable isotope data available for the soils and terrestrial and aquatic plants from the area?

We have made no observations of macroalgae or water hyacinths. Initial results from a large effort of vegetation sampling in June 2015 in the Barotse Plains showed very little $\partial^{13}C$ values intermediate between C_3 and C_4 , further indicating that these water plants were of limited importance in our system. We do however have the following information about the various sources of organic matter for the Barotse Plains and the Kafue Flats (previously published in the supplementary material of Zurbrügg et al. (2013)):

- Soils: Barotse Plains -12.3 and -22.9‰, Kafue Flats -20.3±2.5 ‰
- Trees: on the Barotse Plains -28.3 ± 1.22 % (average of 6 different species)
- Most abundant reeds: Barotse Plains -25.9, -12.8, -27.3 ‰, Kafue Flats -13.3 and -25.5‰

From these numbers we perceive that any floodplain input, whether this was soil- or vegetation-derived, would result in heavier $\partial^{13}C$ values. We have restructured the two sections to focus on seasonal floodplain inputs in contrast to material from more permanent terrestrial vegetation.

Of course, if these data are not available, you have to use literature data, but these are often of limited value. Some interesting information from the area (resulting from other publications of the same group) is given (p. 10560, l. 11-13 and l. 19-26), but the own data are hardly discussed in the context of those observations. Take this up and develop the scenario which explains the observations made.

In the updated manuscript, the data mentioned above has been introduced, along with a more generalized argument on floodplain inputs. The new section includes both C:N and $\partial 13C$ data, and more of a scenario to explain the observations:

"The higher C:N ratio of the suspended matter in the Barotse Plains year-round indicates a 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: surface sediments from the reservoir showed an elevated C:N ratio (12.1±0.6, Supplementary information of Zurbrügg et al. (2013)), similar to the numbers found for the suspended matter in the Barotse Plains. Hence, the presence of the dam significantly affected the chemical composition of the suspended matter, and while soil-derived suspended matter settled in the reservoir, mainly photosynthetically produced 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 13C 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 δ 13C signatures than the permanent vegetation in the area (average of 6 different tree species -28.3 ± 1.22 ‰, unpublished data). Inputs from permanent vegetation were the dominant source of organic matter during the dry season, whereas inputs from the floodplain during the wet season led to more enriched values. 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). These studies clearly showed how the source of organic matter transported by tropical rivers is changing with inundation.

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 δ^{13} C value for the Kafue Flats should be interpreted with caution, since there is a clear spatial pattern: values become more depleted towards the end 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 more typical stretch of the floodplain however, the dry season value was even heavier. The encroaching species have resulted in a vegetation pattern with C_4 species occurring close to the river, and C_3 species growing on the higher grounds that are only seasonally flooded (Blaser, 2013;Ellenbroek, 1987). The inputs from these encroaching species can be considered as terrestrial inputs of permanent vegetation.

The difference in composition and origin between dissolved and particulate phases, i.e. DOM from terrestrial sources, POM more aquatic influence has previously been described for the Amazon (Aufdenkampe et al., 2007;Hedges et al., 1986) and the Fly-Strickland system in Papua New Guinea (Alin et al., 2008). We showed that the interaction of the river with its floodplain is responsible for the changes observed in organic matter characteristics, but that influence of aquatic production in the systems only originated from the reservoir. "

Chapter "6 Conclusions" is quite long and rather a summary with only a few conclusions. If it should stay like that, it should be called "Summary and conclusions". Moreover, in some places it is not clear and/or simply wrong.

The conclusion section has been shortened and more focused towards the conclusions of the study. *P. 10561, l. 14-15: What is meant by "yields"? Do you want to say that the Barotse Plains have a higher relative export per unit area and time? Then say so.*

The sentences relating to yields have been modified to express the net export rates from the floodplain, normalized to floodplain area.

P. 10561, l. 18-19: What is this? If I take a look at table 1 the Kafue Flats are doing exactly the opposite, with a small retention during the dry season and a high export during the wet season they seem to be a net sink for dissolved and particulate matter on an annual basis.

The reviewer refers to seasonal information from Table 1, while we were trying to convey the annual average as documented in Table 2. As mentioned previously in the discussion about section 5.2, we have taken steps to eliminate the confusion between information from Table 1 and 2.

P. 10561, l. 19-23: see my previous comment. This is one possibility or part of the explanation, but not the whole truth.

This part has been updated in accordance with the changes made in the discussion: "Particulate organic carbon δ^{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 reversed situation during the dry

season. The spatial distribution of C₃ and C₄ plants in the floodplains disrupts the signal of floodplain inputs during the wet season in the Kafue Flats."

P. 10561, l. 24 ff.: As mentioned before, this is just part of the story and therefore cannot remain as a conclusion.

While it is part of the story, we feel it is important to stress how changes in hydrology can have a secondary effect on longer time scales, that impacts the river-floodplain biogeochemistry. In the conclusions this has been included as the last sentence "This is a result of the presence of the dams that only became evident with time, and shows the importance for monitoring after dam construction."

P. 10562, l. 3-7: This is definitely wrong. The seasonal difference in C/N ratios is fairly small and it is absolutely in the range of aquatic plants. Of course, variations in soil OM contributions may play a role, but there may be other factors (see above).

The sentence may indeed be misleading. Sediments in the ITT reservoir have C:N ratios of 12, very much in the range of soils reported in the Kafue catchment (around 15; Zurbrügg et al. (2013)), whereas the water exiting the reservoir has a distinctly (and statistically significant) different signature of 8-10. A few sentences have been added after P10559, L7: "The decrease in C:N ratio along the floodplain in the Kafue Flats during the dry season could be indicative of organic matter input from nitrogen-fixating vegetation. As a consequence of nutrient elimination in the ITT reservoir, encroachment of N-fixing woody plants onto the floodplain has been observed (Blaser, 2013)."

P. 10562, l. 9-14: This is an interesting point, however, the reservoir effects were hardly discussed before and this seems to be rather a conclusion of the cited paper.

The reservoir effects have been extended in the discussion section, and the lines in the conclusion section have been merged into "Differences between the two systems that can be attributed to the presence of the Itezhi-Tezhi reservoir upstream of the Kafue Flats included a delay of the input of runoff-derived floodplain soil organic matter and...."

P. 10562, l. 15-16: No, it has not been shown. It has just been mentioned and was not really discussed. As such it is just an unjustified assertion. Nevertheless, I agree with the authors that this could be an important factor.

We are convinced that the improved line of evidence discussed in sections 5.2 and 5.3 now justifies conclusions along this line, and in the updated manuscript this sentence has been removed.

P. 10562, l. 17-19: No. The only difference one can see is in the seasonal discharge pattern and the change in the Kafue Flats before and after dam construction. However, the data presented in this study do not give any hint on specific transport or export pulses of dissolved and particulate matter besides the general dry vs. wet season differences.

We have shown that the timing of DOC and DON inputs to Kafue Flats deviate from an established process, which is visible in the Barotse Plains. Combining that observation with

previously published seasonal patterns has led to the conclusion that this must be an artifact of the presence of the dam. It has however been rephrased in the updated manuscript.

Tables:

Table 1: Clearly designating positive and negative signs to the terms "export" and "retention" (or similar) would help the reader to understand easily what is meant when the text refers to the numbers in the table.

The table caption has been updated to accommodate this.

Table 2: What is the use of this table? The numbers are to some extent mentioned in the text, but not really discussed. Why were (only) these rivers chosen and not others, for example, non-tropical rivers? Of course, it contains interesting information, but it is hardly used in the discussion. If it will remain as marginal as is now, it is sufficient to mention the numbers in the text and delete the table.

For comparison, we have chosen only large tropical rivers for which the relevant data was available, in order to place the values obtained for the floodplains into a broader perspective of similar systems. We feel that comparisons to other, non-tropical rivers and/or floodplains would require a comprehensive global review, which was well beyond the scope of our study. The comparisons between the various systems are presented in the text, and then the interested reader can refer to the table for the exact numbers.

Figures:

In general, I find the choice of colors and symbols a bit unfortunate, the differences are fairly small (e.g., black vs. dark blue) and they do not allow to distinguish easily.

The colors in the various figures have been modified, see below for details. In addition, Fig. 3 has been modified to dark blue and orange as well.

Figure 1: The distance scales in the floodplain insets do not match with distances mentioned in the text. What do the red symbols represent?

The red symbols represent the large dams in the catchment; a statement to this end has been added to the figure caption ("Map of the Zambezi catchment, with floodplains (in green) and large dams (red arrows) marked.").

Figure 4: I think, what you have there is not PON, but PN.

This has been corrected. The color scheme has been updated: particulate = dark blue, dissolved organic = orange, dissolved inorganic = light green.

Figure 5: Very hard to figure out what is what. Do not use grey scales, but color. In the case of nitrogen (figures e-h), does it mean there is no dissolved inorganic nitrogen?

The colors of this graph have been modified in the same fashion as figure 4. There was indeed very little DIN, with measurement values close to or below detection limits.

Figure 6: Symbols and color are too similar to distinguish easily. Be careful with the legend. What you show is the ratio of particulate organic carbon to particulate total nitrogen, but the ratio of dissolved organic carbon to dissolved organic nitrogen, right?

In order to better distinguish the two series, the square symbols have been replaced by triangles, and the colors have been altered (to dark blue and orange). The axes titles have been modified to POC:PN, DOC:DON, and $\partial^{13}C_{POC}$ ($\%_{VPDB}$).

Figure 7: I like the idea of having some kind of visual summary! However, as a reader I would prefer not to see the numbers again, but instead I would like to see the differences in the various sources/processes, e.g. export/retention, terrestrial/aquatic OM etc.

We consider that the expectations for a visual summary are a very personal matter, looking at the contrasting sentiments expressed by the two reviewers. To avoid repetition of the numbers, these have now been lumped together into POM and DOM, and the removal or export processes are represented with arrows proportional to the size of the flux.

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Zurbrügg, R., Wamulume, J., Kamanga, R., Wehrli, B., and Senn, D. B.: River-floodplain exchange and its effects on the fluvial oxygen regime in a large tropical river system (Kafue Flats, Zambia), Journal of Geophysical Research, 117, G03008, 10.1029/2011jg001853, 2012.

Zurbrügg, R., Suter, S., Lehmann, M. F., Wehrli, B., and Senn, D. B.: Organic carbon and nitrogen export from a tropical dam-impacted floodplain system, Biogeosciences, 10, 23-38, 10.5194/bg-10-23-2013, 2013.

1	Seasonal dynamics of carbon and nutrients from two
2	contrasting tropical floodplain systems in the Zambezi
3	River Basin
4	
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Abstract

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

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. Simultaneous retention of particulate carbon and nitrogen, and 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, respectively.

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 floodplain to the particulate organic matter pool varied throughout the year in both systems, in opposite patterns. In the Kafue Flats, encroachment of woody plants since the construction of the dams could be responsible for the altered pattern. Additionally, the timing of runoff-driven inputs during the wet season has been changed by the presence of the dams. This study revealed effects of dam construction on organic matter and nutrient dynamics on the downstream floodplain that only become visible after longer periods, highlighting the need for continued monitoring after dam construction.

Keywords: Zambezi, tropical floodplain, organic matter, nutrients, yields, dam, Barotse Plains, Kafue Flats

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1. Introduction

In current global budgets of organic matter and nutrients, large rivers (discharge > 400 km³ yr¹) 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., 2012;Alvarez-Cobelas et al., 2009). Global extrapolations based on the well-studied temperate and boreal systems are therefore prone to large errors because they neglect the distinct seasonal flooding of extensive tropical floodplain areas (Junk, 1999;Junk et al., 1989). Floodplain systems have been recognized for their potential to alter fluxes of particulate matter, organic carbon, and nutrients transported by rivers (McJannet et al., 2012;Fisher and Acreman, 2004).

During transport 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 (Barros et al., 2011;Bastviken et al., 2008;DelSontro et al., 2011), low oxygen concentrations and potentially toxic levels of reduced substances in the outflow from turbines (Kunz et al., 2013). In addition to the direct effects of hydropower reservoirs, energy demands often require flow regimes that deviate from the natural tropical situation, changing the hydrography in the downstream reaches of the river (Lu and Siew, 2006;Maingi and Marsh, 2002;Rood et al., 2005).

Floodplains make up a large fraction of all tropical wetlands (which cover about 2.5-3.5% of the Earth's surface), with areas of >10⁶ km² in South America and >10⁵ km² in Africa (Tockner and Stanford, 2002). Because of the large area, the periodic flooding and corresponding changing redox conditions, the high temperatures, and the intense rates of primary production (Junk and Piedade, 1993;Robertson et al., 1999;Ward and Stanford, 1995), the impact of tropical floodplains on riverine-transported organic matter and nutrients can be significant (Hamilton et al., 1997). River-floodplain exchange has been identified as a key process for the ecological and biogeochemical functioning in temperate (Hunsinger et al., 2010;Tockner et al., 2010) and tropical systems [e.g. Melack et al. (2009)]. Lateral exchange 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 <u>co-varies</u> 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 <u>from the degradation of C₄ plants</u> during the wet season, while dry season runoff is characterized by organic matter originating from C₃ plants. Spencer et al. (2010) also showed that the properties of organic carbon transported by a tributary of the Congo River vary during different hydrographic phases, with highest dissolved organic carbon and lignin concentrations during peak flow. In the same river, the particulate organic carbon concentration increased when the discharge increased (Mariotti et al., 1991).

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

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 damimpacted 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 (Zurbrügg et al., 2012;Wamulume et al., 2011;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.

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2. Study sites

<<Figure 1>>

At 1.4×10^6 km², 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 Inter Tropical Convergence zone (Dec-Mar) and a dry season (Apr-Nov) during the remainder of the year.

<<Figure 2>>

The Barotse Plains are a near-pristine floodplain area in the upstream part of the Zambezi River in the Western part of Zambia (Fig. 1). The hydrography in the Barotse Plains clearly reflects the climatic conditions, with peak flow around April/May and low flow between July and November (Fig. 2). The total inundatable area is estimated at around 7,700 km² (Hughes and Hughes, 1992). The Kafue Flats are located along the Kafue River, one of the largest tributary of the Zambezi River. Upstream of the Flats, the Itezhi-Tezhi dam (ITT, closed in 1978) stores a significant part of the wet-season runoff in order to allow for a continuous operation of the power station at Kafue Gorge (dam closed in 1972) downstream of the Kafue Flats. Evaporation from the reservoir changes the water level by 780 mm year¹, according to Beilfuss (2012). The maximum inundated area of the Kafue Flats is slightly smaller than of the Barotse Plains, at 6,000 km² (Hughes and Hughes, 1992). The hydrography of the Kafue Flats has been significantly altered by the presence of the dams (Fig. 2). Over the last decades, peak flow has been reduced (approximately -50%) and base flow has increased (roughly +50%, Fig. 2). 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.

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

3. Methods

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3.1 Sampling

Sampling of the main river channel at multiple locations along the floodplains (Fig. 1) was conducted during peak flow, hereafter called the wet season (April/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 in the middle of the well-mixed channel from surface water (50cm, Barotse Plains), or at mid-depth (Kafue Flats) using a peristaltic pump. The similarity of the results from different years (Zurbrügg et al., 2013; Zurbrügg et al., 2012) allowed 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 (for Barotse Plains dry season data from the Zambezi River Authority were used).

3.2 Laboratory analyses

Samples for dissolved nutrient concentrations were filtered through 0.45 µm filters. Dissolved inorganic nitrogen (DIN), phosphate, and the sum of nitrate and nitrite were measured by chemoluminescence detection (Antek 9000). Ammonium was determined by standard colorimetric technique. Total dissolved nitrogen and total phosphorus (TDN and TDP) were determined by chemoluminescence detection (Antek 9000) following persulphate oxidation (Solórzano and Sharp, 1980; Bronk et al., 2000). Samples for particulate phosphorus concentrations during the wet season were collected onto 0.7 µm GF/F filters (Whatman) and measured using a sequential phosphorus extraction method (SEDEX, Ruttenberg (1992) as modified by Slomp et al. (1996)). Samples for dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) were filtered through 0.7 µm GF/F filters (Whatman) and analyzed on a Shimadzu TOC-L (Barotse Plains) or on a Shimadzu 5050 TOC analyzer (Kafue Flats, DOC only). DIC concentrations for the Kafue Flats were calculated from pH and alkalinity measurements (data not shown). Stable oxygen isotopes were determined on filtered water samples (0.45 µm nylon filters) using a Picaro L2120-I Cavity Ringdown Spectrometer (Barotse Plains) or a MultiFlow preparation module connected to a continuous flow IRMS (Isoprime, UK; Kafue Flats) and calibrated against in-house standards ranging from 0 to -22.5\\[\text{WVSMOW}. 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, δ^{13} C and δ^{15} N, respectively) were determined using EA-IRMS (Thermo-Fischer MAT 253 or ThermoFinnigan FlashEA 1112 coupled to a DeltaV Advantage Continuous-Flow IRMS), and calibrated against in-house standards $(\delta^{13}\text{C: }-15 \text{ to } -30\%_{\text{VPDB}}$ precision 0.1%; $\delta^{15}\text{N: }-1.1 \text{ to } +32.7\%_{\text{air}}$ precision 0.2%).

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4. Results

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4.1 Hydrology and oxygen isotopes

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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. 3). Located around 100 km and 200-300 km downstream in the Barotse Plains and in the Kafue Flats, respectively, constrictions in the river bed were present, which promoted flooding of the surrounding floodplain area (Zurbrügg et al., 2012). During the dry season, the discharge remained rather constant in both systems with a gain due to tributaries along the Barotse Plain and a slight loss in the dry Kafue Flats. Notice, however, that the peak discharge in the wet season was about four times higher in the Zambezi crossing the Barotse Plains compared to the dammed Kafue River (Fig. 2).

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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 sharply turned towards heavier values (Fig. 3). The overall ^{18}O -enrichment of the channel water between the upstream and downstream sampling locations was more pronounced in 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 +0.36% and for the Kafue +0.56% per 100 km. During the dry season, no significant increase in isotopic signal of oxygen was observed in the Barotse Plains, while in the Kafue Flats enrichment occurred at +0.17% per 100 km.

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4.2 Concentrations and loads

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<<Figure 4>>

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For 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. 4). The occurrence of large spatial variations

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along the floodplain, or differences between measurement methods between the different years, resulted in larger ranges.

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The dissolved inorganic fraction dominated the total carbon concentration in both seasons and both systems (Fig. 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 detection limit in both systems, and were therefore excluded from the calculation of loads.

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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 are 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 are significant (hypothesis testing, p-values <0.05) for all species, except PP (wet season, p = 0.121) and DIP (dry season, p = 0.053).

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<<Figure 5>> <<Table 1>>

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Loads were calculated from the discharge and concentration data for the respective species, as the water column was well mixed (see Supplementary Information for details). Total carbon and nitrogen loads increased along the Barotse Plains during the wet season, mainly due to larger contribution by the dissolved organic form (Fig. 5). 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 is comparable between the two systems (roughly 1500 t C d⁻¹, Fig. 5), while the nitrogen loads in the Barotse Plains were almost twice as high as those in the Kafue Flats (44 t N d⁻¹ and 20 t N d⁻¹) During the dry season the loads decrease slightly.

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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 1). During the wet season, the Barotse Plains were a sink for all particulate phases, while the Kafue Flats acted as a source (Table 1). Both systems were sources of DOC and 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 lack of POC and PN measurements in the downstream stretches of the river.

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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.

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4.3 C:N ratios and isotopes

340 <<Figure 6>>

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The C:N ratios of particulate organic matter (Fig. 6) remained fairly constant along the floodplain in the Barotse Plains and Kafue Flats during the wet season (10.8 ± 0.7 and 7.5 ± 0.7 , respectively (statistically significant difference at 95% confidence intervals)). During the dry season the along-floodplain variability within each of the floodplains was larger (10.3 ± 1.5 and 10.3 ± 1.8 , respectively), but no significant difference was observed between the two systems. On average, particulate carbon was more depleted in 13 C in the Kafue Flats compared to the Barotse Plains during the wet season (8^{13} C = -28.5 ± 0.9 and -26.9 ± 1.1 ‰ respectively (statistically significant p<0.05)). During the dry season mean 8^{13} C values were $-28.5 \pm 1.0\%$ in the Barotse Plains and $-26.5\pm 1.9\%$ 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 8^{13} C values were observed during the wet season than during the dry season (both significant, p < 0.05).

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The C:N ratio of the dissolved organic phase was more variable: While the wet season values of 17.5 \pm 1.9 and 23.7 \pm 3.4 were <u>fairly</u> 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.

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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)).

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5. Discussion

5.1 Hydrology and inundation dynamics

The discharge patterns (Fig. 3) showed how the bankfull capacity of the Zambezi and Kafue Rivers varied along the floodplain stretch. In both systems water has moved from the main channel onto the floodplain, roughly 600 and 400 m³ s⁻¹ in the Barotse Plains and the Kafue Flats, respectively. Where

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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 ($\leq 1 \text{ mm s}^{-1}$ 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 $\delta^{18}O$ signatures in floodplain water.

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Using a mass balance approach based on oxygen isotopic data, Zurbrügg et al. (2012) calculated that >80% of the water in the Kafue Flats had spent time on the floodplain during the wet season. 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 has spent time on the floodplain. This resulted in 50% of the water leaving the pristine floodplain area having spent time outside the channel. This estimate shows that the interaction between river and floodplain was stronger in the Kafue Flats than in the Barotse Plains, 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, compared to 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 Curuai floodplain, and this water spent on average 19 days on the floodplain, according to the modeling results by Rudorff et al. (2014).

During the dry season, the increasing discharge along the Barotse Plains 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 having spent time on the floodplain (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. In a regional perspective, the along-floodplain increase in the δ^{18} O signal in the Barotse Plains and Kafue Flats during the wet (flooding) season (+0.21‰VSMOV to +0.56‰VSMOV per 100 km) was considerably lower than the increase in the Okavango delta during the dry (flooding) season (+2.04‰ per 100 km) and during wet season (+0.74‰VSMOV 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.

5.2 Seasonality of C and N export and retention.

<u>During</u> 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

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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 leaching of vegetation or soils. During the dry season, the patterns were reversed, indicative of inputs of organic matter from the Plains.

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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 of 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 potentially a minor contribution from sorption of dissolved organic phases onto particulate material.

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The observed net export of particulate organic matter might not have effects beyond the downstream reservoirs of Lake Kariba and Kafue Gorge, respectively (Fig. 1). Both impoundments will trap mobilized particles, and retain 70% and 90% of incoming total N and P within Lake Kariba (Kunz et al., 2011a). Nevertheless, on a catchment scale, mobilization of particulate organic matter from the inundated area of the river-floodplain systems resulted in specific POC and PON yields (net export per inundated area per year; Table 2) from the Barotse Plains, which were close to an order of magnitude higher than previously reported values for the entire Zambezi River (Beusen et al., 2005; Mayorga et al., 2010). Despite the behavior as a sink during the wet season, the normalization to inundated area has resulted in positive annual export from the floodplain. Also, DOC yields from the Barotse Plains were higher than previously estimated for the Zambezi, but comparable to those measured in the Amazon and Orinoco rivers (Table 2; Beusen et al. (2005); Harrison et al. (2005); Lewis and Saunders (1989)). Similarly, DON yields from the pristine floodplain were similar to values measured in the Amazon and Orinoco (Table 2). The Kafue Flats show negative DOC, DON, DIN yields, i.e. are retaining these species. These negative yields show how floodplains can impact the riverine loads in trends opposite to those observed for the whole catchment. Similarly, the high yields from the Barotse Plains underlined the dominant role of floodplains as biogeochemical reactors in riverine transport of organic matter from land to sea

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<<Table 2>>_

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5.3 Sources of organic matter

5.3.1 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, 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 was contributing 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 relatively pristine, as anthropogenic activities mainly add N in the form of DIN to aquatic systems (Berman and Bronk, 2003).

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The elevated C:N ratio of the dissolved organic matter was indicative of 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. 4) has resulted in this shift in dissolved C:N ratio.

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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 shallowing of the flow paths through organic-rich upper soils (Mulholland, 2003; Aitkenhead-Peterson et al., 2003). This seasonal variability in DOC and DON concentrations has been previously shown in Hawaii (Wiegner et al., 2009) and Congo (Spencer et al., 2010). Runoff from inundated soils, such as found in the Zambezi River Basin during the wet season, also tend to have higher DON concentrations (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/June, after the peak flow

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(Wamulume et al., 2011). This could be a delayed effect of the increased concentrations at higher runoff during the wet season (November-March).

5.3.2 Particulate organic matter

The higher C:N ratio of the suspended matter in the Barotse Plains year-round indicates a 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: surface sediments from the reservoir showed an elevated C:N ratio (12.1±0.6, Supplementary information of Zurbrügg et al. (2013)), similar to the numbers found for the suspended matter in the Barotse Plains. Hence, the presence of the dam significantly affected the chemical composition of the suspended matter, and while soil-derived suspended matter settled in the reservoir, mainly photosynthetically produced 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 δ^{13} C signatures than the permanent vegetation in the area (average of 6 different tree species -28.3 \pm 1.22 %, unpublished data). Inputs from permanent vegetation were the dominant source of organic matter during the dry season, whereas inputs from the floodplain during the wet season led to more enriched values. 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). These studies clearly showed how the source of organic matter transported by tropical rivers is changing with inundation.

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 δ^{13} C value for the Kafue Flats should be interpreted with caution, since there is a clear spatial pattern: values become more depleted towards the end of the floodplain. This spatial pattern has previously been attributed to

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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 more typical stretch of the floodplain however, the dry season value was even heavier. The encroaching species have resulted in a vegetation pattern with C_4 species occurring close to the river, and C3 species growing on the higher grounds that are only seasonally flooded (Blaser, 2013; Ellenbroek, 1987). The inputs from these encroaching species can be considered as terrestrial inputs of permanent vegetation.

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The difference in composition and origin between dissolved and particulate phases, i.e. DOM from terrestrial sources, POM more aquatic influence, has previously been described for the Amazon (Aufdenkampe et al., 2007; Hedges et al., 1986) and the Fly-Strickland system in Papua New Guinea (Alin et al., 2008). We showed that the interaction of the river with its floodplain is responsible for the changes observed in organic matter characteristics, but that influence of aquatic production in the systems only originated from the reservoir.

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Moved up [5]: The elevated C:N ratio of the dissolved organic matter compared to the particulate material was indicative of terrestrial origin of the organic material in both systems. While the particulate matter in the Kafue Flats was heavily influenced by the presence of the ITT reservoir, the reservoir did not have a pronounced impact on the dissolved phase (C:N around 23 during both seasons), which has previously been attributed to a mostly refractory dissolved organic mater phase (Zurbrügg et al., 2013). The comparison with the Barotse plains revealed a much larger variability in this undisturbed system with C:N of the dissolved matter reaching dry season values of 166 compared to the wet season signatures around 18. While DOC concentrations were fairly similar during both seasons, the large decrease in DON concentrations from the wet to the dry season (Fig. 4) has resulted in this shift in dissolved C:N ratio.

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Moved up [4]: The high contribution of DON to TDN further indicates that the Zambezi and Kafue Rivers are still relatively pristine, as anthropogenic activities mainly add N in the form of DIN to aquatic systems (Berman and Bronk, 2003).

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6. Conclusions

<< Figure 7 >>

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While the pristine Barotse Plains and dam-impacted Kafue Flats seem to have similar properties in terms of timing and dynamics of seasonal flooding, there are several marked differences between the two systems with respect to hydrology, carbon and nutrient dynamics, and sources of the organic matter (Fig. 7). Based on an oxygen isotope mass balance, a larger fraction of water has spent time on the floodplain at the outflow of the Kafue Flats compared to the Barotse Plains. The two floodplains have significantly different concentrations of dissolved carbon and nutrient species during both wet and dry seasons. Over an annual cycle, the Barotse Plains export more carbon and nutrients normalized to the floodplain area (yields) than previously reported for the Zambezi and other tropical rivers. The Kafue Flats are exhibiting negative yields, effectively retaining and accumulating organic matter and nutrients over a full hydrological cycle. Particulate organic carbon δ^{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 reversed situation during the dry season. The spatial distribution of C_3 and C_4 plants in the floodplains disrupts the signal of floodplain inputs during the wet season in the Kafue Flats.

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Differences between the two systems that can be attributed to the presence of the Itezhi-Tezhi reservoir upstream of the Kafue Flats, included a delay of the input of runoff-derived floodplain soil organic matter and altered inputs to the particulate organic matter pool in the Kafue Flats. The difference between sources of organic matter in the two floodplains partly also results from the presence of the Kafue River dams: since the dam construction, woody encroachment onto the Kafue Flats floodplain has increased, contributing to the wet-season signal of permanent vegetation. This is a result of the presence of the dams that only became evident with time, and shows the importance for monitoring after dam construction.

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Author contributions

A. L. Zuijdgeest, R. Zurbrügg, D. B. Senn, and B. Wehrli were responsible for the study design. A. L. Zuijdgeest, R. Zurbrügg, N. Blank, and R. Fulcri performed the fieldwork and the laboratory analyses. Data analysis was performed by A. L. Zuijdgeest, R. Zurbrügg, and D. B. Senn, and supported by N. Blank, R. Fulcri, and B. Wehrli. The manuscript was prepared by A. L. Zuijdgeest with contributions from all co-authors.

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Tables

Table 1. Net export (in t C d⁻¹ and t N d⁻¹), 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 lack of measurements at downstream locations.

System		POC	DOC	DIC	PN	DON	DIN
Barotse Plains	Wet season	-38	170	270	-3.7	12	0.0
	Dry season	14	-1.5	-78	1.6	0.0	0.0
Kafue Flats	Wet season	6.5	160	640	0.6	11	0.1
	Dry season	NA	-11	-89	NA	-0.8	-0.2

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Table 2. Yields of carbon, nitrogen and phosphorus in kg (C or N) km⁻² yr⁻¹ from large river basins and floodplain yields from the Barotse Plains and Kafue Flats. Yields for this study are calculated assuming 6 months of dry-season export, and 6 months of wet-season export. Inundation areas should be considered conservative estimates (see methods section for how inundation areas were estimated). Dry-season areas were estimated based on river length and width. POC and PN yields from the Kafue Flats during the dry season could not be estimated due to lack of measurements at downstream locations.

Sources: a Beusen et al. (2005), b Bouillon et al. (2014), c Esser and Kohlmaier (1991), d Harrison et al. (2005), e Lewis and Saunders (1989), Mayorga et al. (2010), g Hall et al. (1977).

River	POC	DOC	PN	DON	DIN
Amazon	2900 ^a	5200 ^d	500 ^a	330 ^d , 180 ^f	170 ^f
Congo	1400°, 400°	3300°, 1600°	200 ^a	92°, 58 ^f	32 ^f
Orinoco	1500 ^e	5600 ^d , 5200 ^e	190 ^e	310 ^d , 190 ^e , 170 ^f	
Oubangui	180-300 ^b	660-1500 ^b	20-29 ^b		
Zambezi	800 ^a	1000-2000 ^f	100 ^a	-	14 ^f , 100-300 ^g
This study:					
Barotse Plains	8000	3000	880	310	0
Kafue Flats	NA	-2700	NA	-200	-110

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Figures

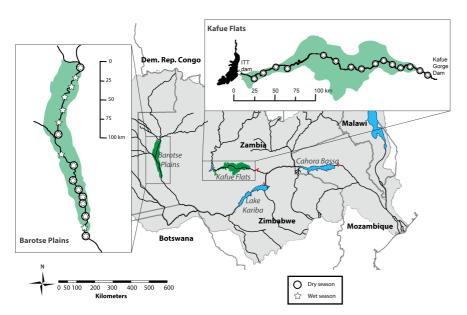


Figure 1. Map of the Zambezi catchment, with floodplains (in green) and large dams (red arrows) marked. Inserts show sampling stations during the dry (circles) and wet season (stars) in the Barotse Plains and Kafue Flats. Sampling stations will be further presented in distance along the river (km).

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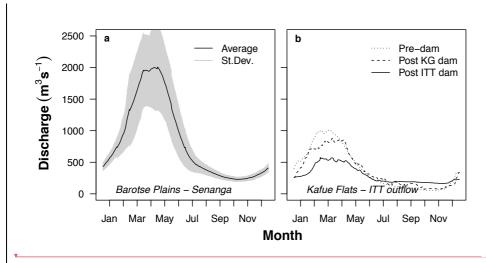
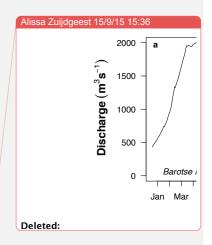


Figure 2. River discharge (a) at Senanga, the downstream boundary of the Barotse Plains (1988-2006 average and standard deviation) and (b) at the outflow of Itezhi-Tezhi (ITT) dam, the upstream boundary of the Kafue Flats. Discharge for the Kafue Flats are means of pre-dam (1960-1971), and post-dam construction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



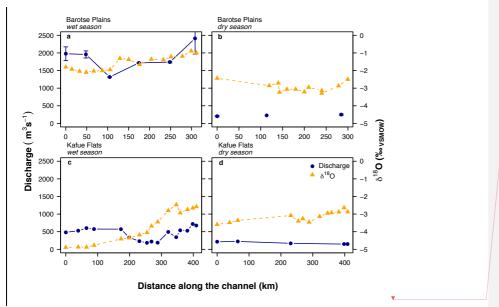
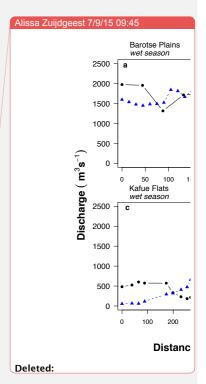


Figure 3. Discharge and stable oxygen isotope signals in the Barotse Plains and the Kafue Flats during wet and dry seasons. Discharge and $\delta^{18}O$ data for the Kafue Flats have been published previously in Zurbrügg et al. (2012).



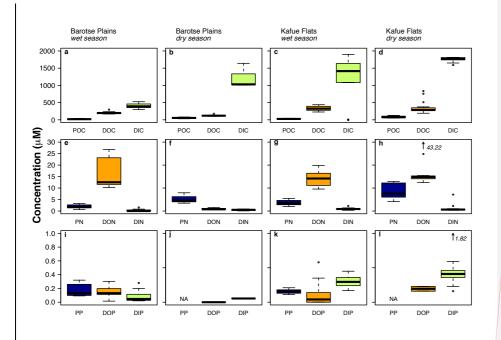
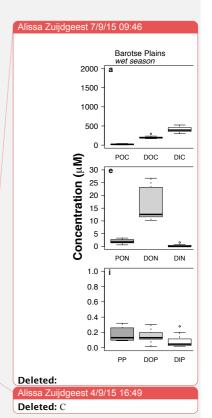


Figure 4. Boxplots of the concentrations of dissolved and particulate carbon, nitrogen and phosphorus species along the Barotse Plains and the Kafue Flats during wet and dry seasons along the floodplain. The boxes represent the first and third quartiles, and the median. No measurements of particulate 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).



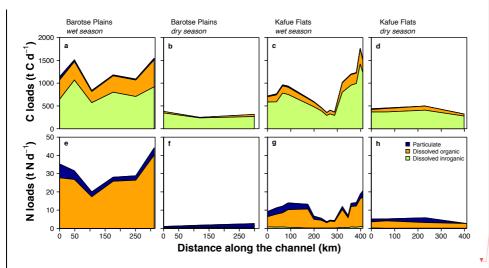
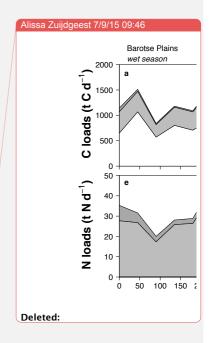


Figure 5. Dissolved and particulate carbon and nitrogen loads along the Barotse Plains and the Kafue Flats during wet and dry seasons. The loads of particulate carbon and nitrogen at the two most downstream locations in the Kafue Flats could not be determined for the dry season due to lack of POC and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



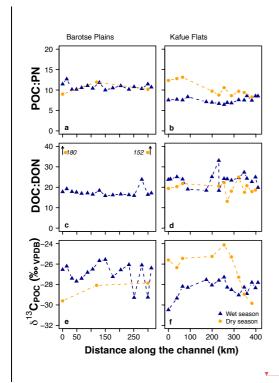
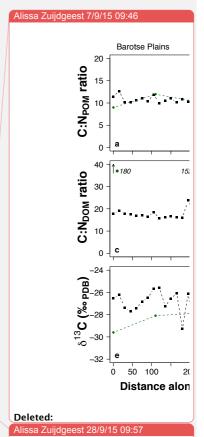


Figure 6. Carbon to nitrogen (C:N) ratios of particulate and dissolved organic matter as well as carbon isotopic signatures of particulate organic matter during wet (<u>blue triangles</u>) and dry (<u>orange</u> circles) seasons. The Kafue Flats data have been previously published in Zurbrügg et al.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



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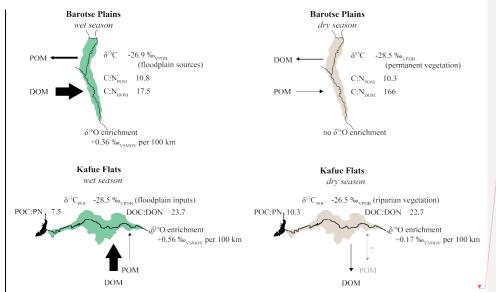
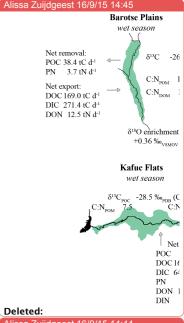


Figure 7. Summary of the organic matter characteristics (δ¹³C, POC:PN, DOC:DON), oxygen isotopic enrichment along the floodplain, and proportional arrows for net export and removal rates of POM (POC+PN) and DOM (DOC+DON) in the Barotse Plains and Kafue Flats during the wet and dry season.



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While the Barotse Plains retain particles during the wet season, annual yields of particulate organic carbon and nitrogen are higher than previously reported for the Zambezi and other tropical rivers. Enhanced wet-season runoff adds soil-derived dissolved organic carbon and nitrogen to the Zambezi River, with a corresponding increase in the Barotse Plains. Soil-derived organic matter dominates the particulate phase year-round in the Barotse Plains, and a varying influence of C₃- and C₄-plant vegetation can be observed throughout the year.

In contrast to the Barotse Plains, net export of particulate matter from the Kafue Flats has been observed during the wet season, but over an annual cycle, the Kafue Flats are effectively accumulating dissolved carbon and nutrients. In the Kafue Flats, the runoff-induced increase in dissolved organic carbon and nitrogen concentrations is delayed by the upstream dam operation. The dam reservoir also causes a shift in the source of the particulate organic matter – from soil-derived during the dry season to aquatically produced in the wet season – in the downstream Kafue Flats. Spatial zonation in vegetation and temporal flooding dynamics in the Kafue Flats result in mostly C₃-derived particulate organic matter during wet season, and a dominance of C₄-derived material during dry season. This pattern results from dam-induced changes in vegetation, as dam construction along the Kafue River has led to encroachment of woody plant species onto the Kafue Flats.

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

N d⁻¹ and 20 t N d⁻¹); here the upstream ITT reservoir removed most of the nitrogen (Kunz et al., 2011b).

During the dry season, the Barotse Plains acted as source of particulate matter, most likely caused by aeolian transport of dry floodplain soil material. For the Kafue Flats this could not be determined due to lack of POC and PN measurements in the downstream stretches of the river. DOC and DIC were retained by both systems, potentially converted to particulate phases by primary production. The Barotse Plains were a minor source of dissolved nitrogen, while the Kafue Flats retained both organic and inorganic nitrogen. The general decrease in C loads during the dry season in the Barotse Plains could probably be explained by the slightly higher discharge at the downstream end of the floodplain, due to lower concentrations flowing in from the Luanginga tributary (no data).

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

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5.3.3 Vegetation contributions

The stable C-isotopic signatures of the particulate matter further suggest different POC sources. During the wet season, the organic matter in the Barotse Plains is ¹³C enriched compared to the

Kafue Flats, indicating a C₄-plant-dominated source in the pristine system (δ^{13} C-C₃ approx. - 26‰_{VPDB}, vs. δ^{13} C-C₄ approx. -13‰_{VPDB}, as in

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). In contrast, during the dry season the situation is reversed, and the organic matter in the Kafue Flats shows higher C_4 contribution than in the Barotse Plains. The average dry season $\delta^{13}C$ value for the Kafue Flats should be treated with caution, since there is a clear spatial pattern: values become more depleted towards the end of the floodplain. This has previously been attributed to floodplain-derived particulate organic matter, which would consist of phytoplankton and periphyton material in the permanently inundated area in the downstream reaches of this floodplain (Zurbrügg et al., 2013).

Shifts to more C₄-derived organic matter during the wet season as observed in the Barotse Plains, have been described for the Tana River in Kenya (Tamooh et al., 2014), the Sanaga River in Cameroon (Bird et al., 1998), and the Congo River in Central Africa (Mariotti et al., 1991). These studies clearly showed how the source of organic matter is changing with inundation.

The contrasting trend in vegetation source in the Kafue Flats compared to other tropical rivers could be explained by the spatial distribution of C₃ and C₄ grasses: most of the C₄ species occur close to the river, while C₃ grasses and plants are found on the higher grounds that are only seasonally flooded (Blaser, 2013;Ellenbroek, 1987). This spatial variation could explain why the wet season organic matter in the Kafue Flats shows a higher contribution of C₃-derived organic matter, whereas during low water conditions only C₄ plants are inundated. Since the construction of the dams in the Kafue catchment, encroachment of woody plants onto the floodplain has been observed (Blaser, 2013). The encroaching species most likely contribute to the C₃ signal observed during the wet season. The regulation of water flow through the Kafue Flats has therefore had an indirect effect on the type of the particulate organic matter transported downstream by the river.

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In the Kafue Flats the C:N ratio of particulate organic matter shifts from a terrestrial to an aquatic signal during the wet season, due to a prolonged retention time in the reservoir (Zurbrügg et al., 2013). In contrast, the C:N ratio of the particulate organic matter in the Barotse Plains indicates that soil organic matter is the dominant source year-round. The concentrations of DOC and DON in the Kafue Flats do not change significantly between dry and wet season. Typically, increased precipitation and overland runoff result in higher concentrations of soil-derived organic matter.

However, based on previous year-round measurements (Wamulume et al., 2011), the increase in dissolved organic species is likely delayed by the reservoir, and occurs after peak flow. In the Barotse Plains on the other hand, increased export of DOC and DON during the wet season corresponds to the typical trends of increased export with increased precipitation and runoff.

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