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

Supplementary information

1 Sampling of additional C and N pools in the Kafue Flats

1.1 Sampling, sample preparation, and analyses

In order to constrain the sources of dissolved organic matter (DOM) and particulate organic matter (POM), the stable isotopic composition of dry deposition, plants, periphyton, soils, and sediments from the Kafue Flats was analyzed. We also measured δ^{15}N-TDN from the water column of ITT reservoir (Station IT1 in Kunz et al., 2011). To measure N dry deposition, three acid-washed HDPE deposition traps, 600 cm^2 each, were installed at two locations in the dry floodplain in Lochinvar National Park (Figure 1c) and one trap on a float in the middle of the large adjacent lagoon (Figure 1). The land-based traps were installed at 2 m above ground and exposed for 5 to 11 days in May 2010. Deposited matter was dissolved in 2M HCl, and its δ^{15}N was measured as described the main article. Plant samples were taken from the first fully expanded leafs of C$_3$-grass *Phragmites australis* and C$_4$-grass *Vossia cuspidata*, two dominant species in the floodplain areas adjacent to the river channel (Ellenbroek, 1987). Plant, periphyton, soil, and sediment samples were collected along the main channel in October 2008. Plant material and soil was dried at 40°C, periphyton from submerged floodplain grasses and surface sediment samples were freeze-dried. All solid samples were homogenized and analyzed for C and N isotopic signature as described for POM in the main article.

1.2 Stable isotopes of floodplain and reservoir C and N pools

δ^{13}C and δ^{15}N of the measured floodplain and reservoir pools are presented in Table S1. The plant samples showed the typical C$_3$ and C$_4$ isotopic signatures for ^{13}C of -26‰ and -13‰, respectively (Martinelli et al., 1991; Smith and Epstein, 1971). The other floodplain pools were found to cluster around -20‰, sediment trap and sediments at ITT displayed a somewhat lower δ^{13}C. For δ^{15}N, dry deposition, periphyton, river sediments, reservoir sediments and sediment traps and averaged around 2‰. C$_3$-grass *Phragmites australis* had a δ^{15}N of ~4‰, and soils and the C$_4$-grass *Vossia cuspidata*, were close to 0‰.

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

	$\delta^{13}C$ (‰$_{VPDB}$)	$\delta^{15}N$ (‰$_{air}$)	C:N
	mean±SD	mean±SD	mean±SD
Kafue Flats floodplain			
Dry deposition	n.a.	2.3±0.2	n.a.
Vossia cuspidata (C_4)	-13.3±0.3	0.5±0.8	n.a.
Phragmites australis (C_3)	-25.5±0.4	3.9±0.6	n.a.
Periphyton[a]	-20.5±3.1	1.4±0.9	n.a.
Floodplain soil	-20.3±2.5	0.6±1.2	15.9±2.1
River sediment	-19.6±1.8	2.2±1.2	15.0±2.5
Itezhi-Tezhi reservoir			
Sediment traps[b]	-25.8±0.5[c]	2.5±1.5	9.7±0.5[c]
Sediments[d]	-23.8±3.5[c]	n.a.	12.1±0.6[c]
TDN[e]	n.a.	1.9±0.4	n.a.

[a] sampled from inundated stems of floodplain grasses.
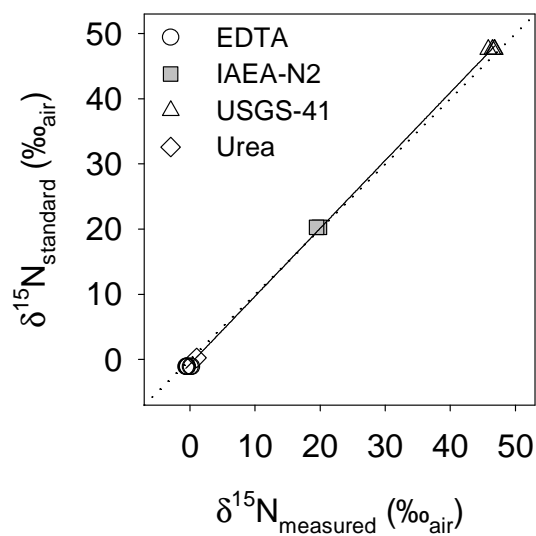[b] sampled from October 2008 to May 2009 at depths of 13 to 40 m behind the dam wall.
[c] data from Kunz et al. (2011)
[d] sampled in May 2008
[e] sampled in June 2009 behind ITT dam wall.

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

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

Figure S1. Calibration curve of a $\delta^{15}N$-TDN analysis run. EDTA, USGS-41and urea are organic N isotope standards, IAEA-N2 is a $(NH_4)_2SO_4$ isotope standard. The dotted line is the 1:1 line, the solid line represents the linear regression of $\delta^{15}N_{standard} = 1.043 \times \delta^{15}N_{measured} - 0.756$ ($R^2 = 0.9997$).

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

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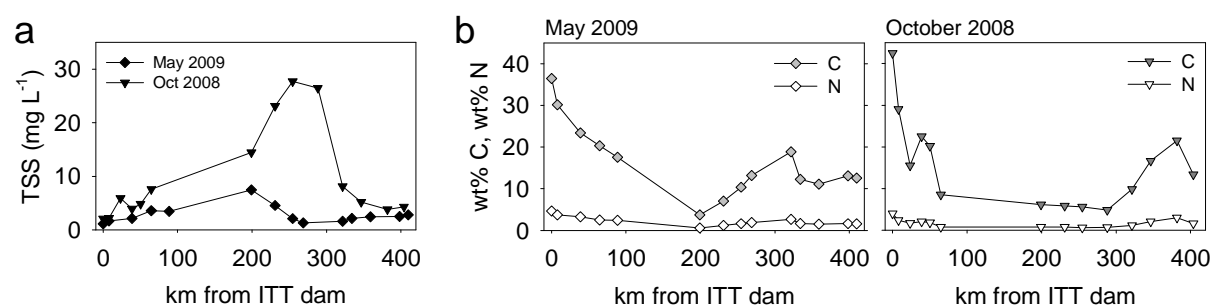
Figure S2: **(a)** TSS and **(b)** C and N content of the particles in the Kafur River for May 2009 and October 2008.

4 POC and PON monitoring over an annual cycle

During a monitoring campaign from June 2008 to May 2009, the concentrations and stable isotopic signatures of POC and PON were measured at five selected stations (0, 88, 231, 334, and 410 km) on a bimonthly basis (Wamulume et al., 2011). Concentrations of POC and PON and POC:PON showed an overall similar course like for the higher resolution October 2008 and May 2009 campaigns. δ^{13}C-POC showed higher temporal variation after the dam than along the river, but was fairly constant at -28.5±1.2‰ at the end of the floodplain (Figure S3d). Higher δ^{13}C-POC was associated with higher POC concentrations which might be indicative of a higher contribution of plant derived POM (Figure S3e). δ^{15}N-PON was in the range of other sampled N pools (Table S1) and did not vary systematically along the river.
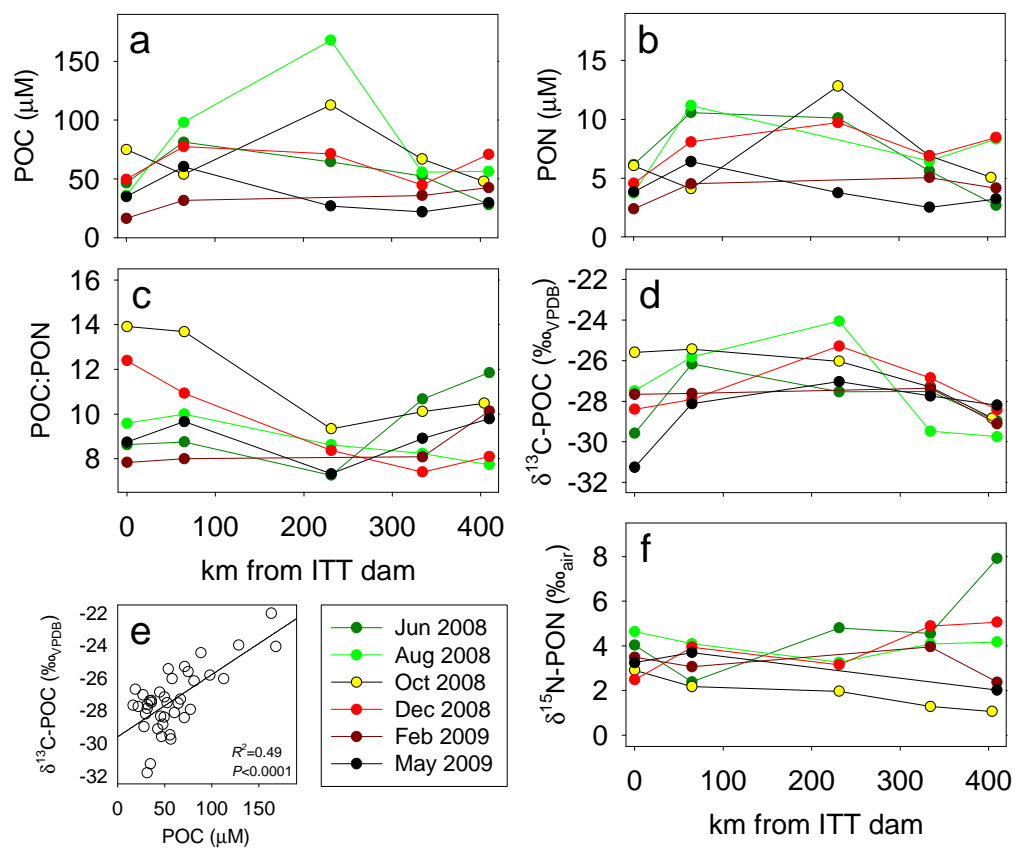
**Figure S3**. **(a)** POC and **(b)** PON concentrations, **(c)** POC:PON molar ratio, **(d)** δ^{13}C-POC, **(e)** correlation between concentration and δ^{13}C of POC, **(f)** δ^{15}N-PON at five stations along the Kafue River over an annual cycle, from June 2008 to May 2009. Data from October 2008 and May 2009 are reprinted for consistency.

5 PARAFAC modeling of excitation-emission matrices

5.1 PARAFAC model results

The comparison of different PARAFAC models with an increasing number of components resulted in a four-component model minimizing the sum of squared errors, relative to a three and five-component model (Figure S4). Higher component models were found inappropriate since they caused in discontinuities in the resulting components, indicated as sharp peaks in the 5-component line in Figure S2.
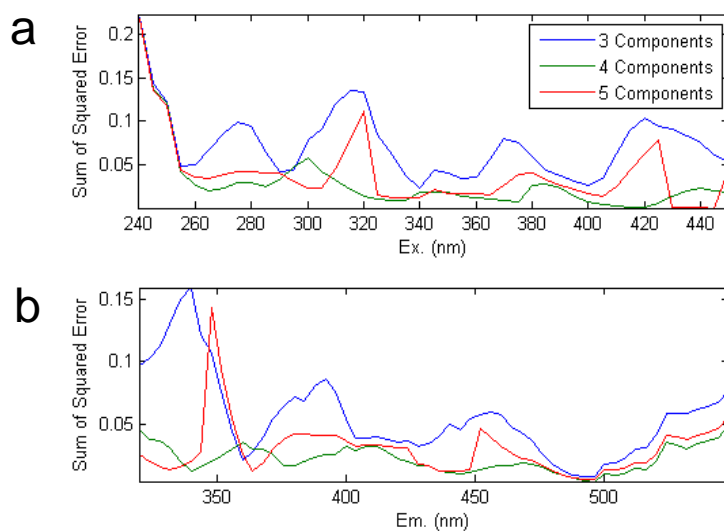
Figure S4. Sum of squared errors of 3-, 4-, and 5-component PARAFAC models for **(a)** excitation, and **(b)** emission wavelengths. Sharp peaks in the 5-component errors are caused by discontinuities in the components.

5.2 Identification of PARAFAC components

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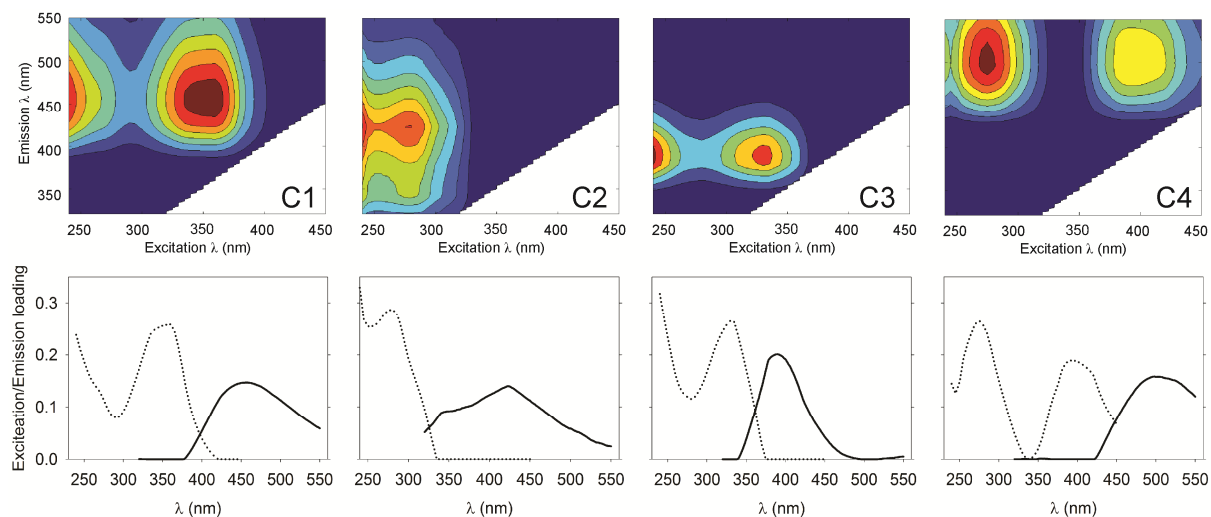

Figure S5. Components C1-C4 resulting from PARAFAC analysis. The upper panel shows the excitation-emission matrices (EEMs), the lower panel shows the excitation (dotted line) and emission (solid line) loadings of the components.

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

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

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

## 5.3 Fluorescence intensities (F_{max}) of PARAFAC components C1-C4
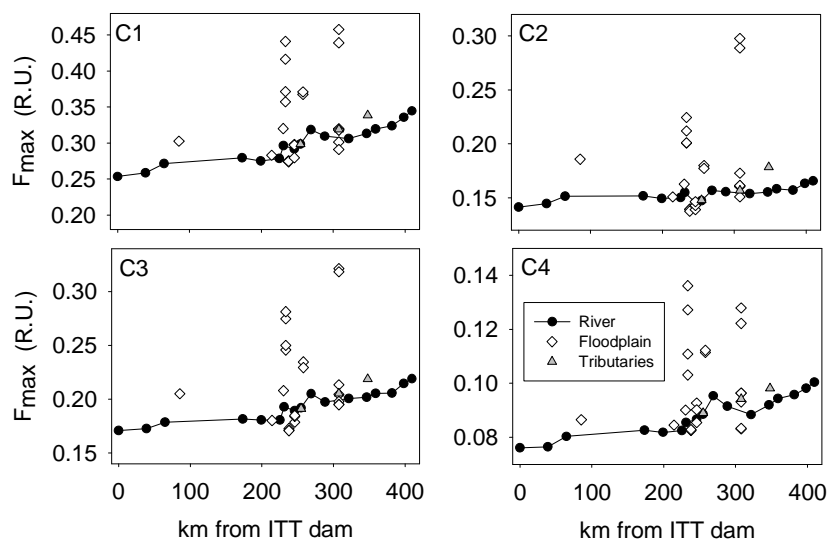
Figure S6. Fluorescence maxima (F_{max} in Raman units) for components C1-C4 along the river channel (black dots, solid line), for floodplain stations (empty diamonds) and tributaries (grey triangles).
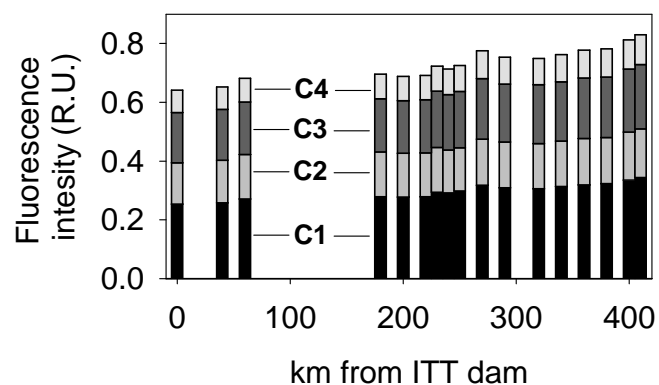
Figure S7. Contributions of components C1-C4 to the overall fluorescence (F_{max} in Raman units). C1 accounted for 40.7±0.6%, C2 for 20.9±0.8%, C3 for 26.4±0.2%, and C4 for 12.0±0.2% of the total fluorescence.

5.4 Ratios of component fluorescence relative to C3 along floodplain transects

Even though the component ratios for floodplain stations were overall statistically indifferent the river (ρ=0.097-0.872), some deviations from river stations were evident (Figure 9 in the main text). Floodplain transects T1-T5 (Figure 1) generally showed higher ratios for C1 and C4 when moving from river or shore towards the floodplain, while C2 ratio to C3 decreased.
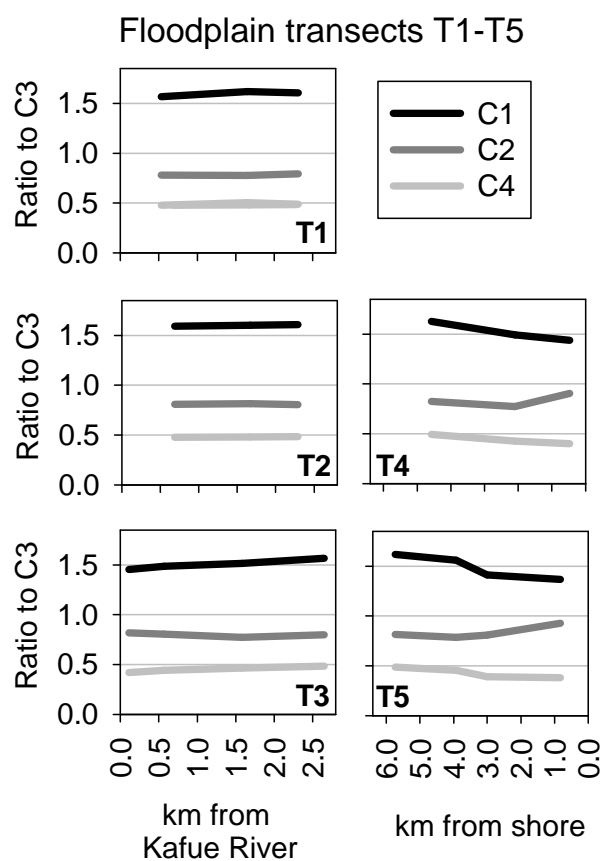
Figure S8. Ratios of the peak fluorescence F_{max} of C1, C2 and C4 relative to C3 ratios along floodplain transects T1-T5 (Figure 1c). Component C3 showed the highest correlation with DOC concentration (R^2=0.87). Note the reversed distance axis for different transects.

References

Coble, P. G.: Characterization of marine and terrestrial DOM in seawater using excitation emission matrix spectroscopy, Marine Chemistry, 51, 325-346, 1996.

Coble, P. G., Del Castillo, C. E., and Avril, B.: Distribution and optical properties of CDOM in the Arabian Sea during the 1995 Southwest Monsoon, Deep-Sea Research Part Ii-Topical Studies in Oceanography, 45, 2195-2223, 1998.

Cory, R. M., and McKnight, D. M.: Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter, Environmental Science & Technology, 39, 8142-8149, 10.1021/es0506962, 2005.

Ellenbroek, G. A.: Ecology and Productivity of an African Wetland System. Geobotany 9, Dr W. Junk, Dordrecht, 1987.

Ishii, S. K. L., and Boyer, T. H.: Behavior of Reoccurring PARAFAC Components in Fluorescent Dissolved Organic Matter in Natural and Engineered Systems: A Critical Review, Environmental Science & Technology, 46, 2006-2017, 10.1021/es2043504, 2012.

Jørgensen, L., Stedmon, C. A., Kragh, T., Markager, S., Middelboe, M., and Søndergaard, M.: Global trends in the fluorescence characteristics and distribution of marine dissolved organic matter, Marine Chemistry, 126, 139-148, 10.1016/j.marchem.2011.05.002, 2011.

Kunz, M. J., Wüest, A., Wehrli, B., Landert, J., and Senn, D. B.: Impact of a large tropical reservoir on riverine transport of sediment, carbon, and nutrients to downstream wetlands, Water Resources Research, 47, 16, 10.1029/2011WR010996, 2011.

Martinelli, L. A., Devol, A. H., Victoria, R. L., and Richey, J. E.: Stable carbon isotope variation in C3 and C4 plants along the Amazon River, Nature, 353, 57-59, 1991.

Smith, B. N., and Epstein, S.: Two categories of 13C/12C ratios for higher plants, Plant Physiology, 47, 380-384, 1971.

Stedmon, C. A., Markager, S., and Bro, R.: Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy, Marine Chemistry, 82, 239-254, 10.1016/s0304-4203(03)00072-0, 2003.

Stedmon, C. A., and Markager, S.: Resolving the variability in dissolved organic matter fluorescence in a temperate estuary and its catchment using PARAFAC analysis, Limnology and Oceanography, 50, 686-697, 2005.

Wamulume, J., Landert, J., Zurbrügg, R., Nyambe, I., Wehrli, B., and Senn, D. B.: Exploring the hydrology and biogeochemistry of the dam-impacted Kafue River and Kafue Flats (Zambia), Physics and Chemistry of the Earth, 36, 775-788, 10.1016/j.pce.2011.07.049, 2011.

Yamashita, Y., Jaffé, R., Maie, N., and Tanoue, E.: Assessing the dynamics of dissolved organic matter (DOM) in coastal environments by excitation emission matrix fluorescence and parallel factor analysis (EEM-PARAFAC), Limnology and Oceanography, 53, 1900-1908, 2008.