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Landscape Control on the Spatial and Temporal Variability of Chromophoric Dissolved Organic Matter and Dissolved Organic Carbon in Large African Rivers

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Abstract

The characteristics of colored dissolved organic matter (CDOM) as well as the concentrations and stable isotope composition ($\delta^{13}C$) of dissolved organic carbon (DOC) were characterized in several large rivers of Africa including the Congo, Niger, Zambezi, and Ogooué basins. We compared the spatial and temporal patterns of dissolved organic matter (DOM) quantity and quality along with various environmental gradients, including hydrology, river size, catchment vegetation, and connectivity to land. The optical proxies used include the absorption coefficient at 350 nm, the specific ultra-violet absorbance, and the spectral slope ratio (S_R = 275–295-nm slope divided by 350–400-nm slope). Our results show that land cover plays a primary role in controlling both DOC concentration and optical properties of DOM in tropical freshwaters. A higher cover of dense forest in the catchment leads to a higher quantity of highly aromatic DOM in the river network, whereas an increasing savannah cover results in lower DOC concentrations and less absorptive DOM. In addition to land cover, the watershed morphology (expressed by the average slope) exerts a strong control on DOC and CDOM in tropical rivers. Our results also show that the percentage of C3 and C4 vegetation cover is not an accurate predictor for DOM and CDOM quality in rivers due to the importance of the spatial distribution of land cover within the drainage network. The comparison of our results with previously published CDOM data in temperate and high-latitude rivers highlights that DOM in tropical freshwaters is generally more aromatic, and shows a higher capacity for absorbing sunlight irradiance.

Key words: Carbon cycle; Colored dissolved organic matter; Tropical rivers; Land cover; Landscape; Carbon isotopes.

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Introduction

The role of inland waters in the global carbon (C) cycle is now widely recognized to go beyond the downstream transport of C, but includes production, mineralization, storage, and emission of C to the atmosphere (Cole and others 2007; Battin and others 2008; Ward and others 2013; Abril and others 2014; Fasching and others 2014). A significant amount of terrestrial dissolved organic matter (DOM) is degraded in freshwaters through photochemical and biological mineralization and returns to the atmosphere as CO_2 (Cole and others 2007). However, the mechanisms underlying the relationship between DOM and CO_2 concentrations reported in temperate and boreal ecosystems (Sobek and others 2005; Lapierre and del Giorgio 2012), and more recently in African tropical inland waters (Borges and others 2015) are still debated (Lapierre and others 2013; Fasching and others 2014; Borges and others 2015). To date, most studies focusing on sources, composition, and fate of DOM and its link with CO_2 emissions have been conducted in temperate and high-latitude rivers due to their susceptibility to global climate change and anthropogenic activities (Wilson and Xenopoulos 2009; Stedmon and others 2011). Tropical rivers exhibit the highest riverine dissolved organic carbon (DOC) flux to the oceans (Meybeck 1993) but DOM cycling at the terrestrial–aquatic interface in these systems is poorly constrained with the exception of the Amazon River (Mayorga and others 2005; Pérez and others 2011; Remington and others 2011; Ward and others 2013).

The characterization of the chromophoric or colored fraction of DOM (CDOM) has been proposed as a powerful approach to study the composition, sources, and reactivity of DOM in aquatic ecosystems for numerous reasons. First, as the chemical composition of DOM determines its optical properties (Stedmon and Markager 2005), optical measurements allow us to trace DOM sources and processing in the river network (Jaffé and others 2008). Secondly, the measurement of the optical properties of DOM via in situ continuous measurement technologies can be used to assess DOC content, quality, and transport in freshwaters at high spatial or temporal resolution (for example, Downing and others 2009; Prairie and others 2010). Thirdly, remote sensing of CDOM by optical sensors on satellites is a powerful tool to study the distribution of terrestrial DOM in inland waters (for example, Massicotte and others 2013), and its fate in river plumes of major world rivers (for example, Salisbury and others 2011). Fourthly, recent studies have shown that terrestrial inputs of CDOM are a relevant component of the C cycle in inland waters by demonstrating a causal link between CDOM and riverine fluxes of CO_2 through photodegradation and microbial degradation processes (Lapierre and others 2013; Fasching and others 2014). Finally, CDOM measurements are an ideal tool for the study of DOM through extensive sampling programs (Jaffé and others 2008). Such studies have recently been performed in temperate (Spencer and others 2012) and Arctic rivers (Stedmon and others 2011), but to date no equivalent effort has been made for tropical rivers.

Land cover, in particular the areal extent of wetlands at the catchment scale, has been identified as a strong predictor for DOM concentration and composition in rivers (Eckhardt and Moore 1990; Frost and others 2006), suggesting that the role of riverine processes in altering the terrestrial DOC signal at the annual scale was minimal except in river systems with long surface water residence times (Hanley and others 2013). However, such analyses are mostly limited to temperate and boreal catchments and very few studies have assessed the effect of land cover and other catchment features on DOM in tropical rivers. However, the situation is likely to be different in tropical basins, as (1) wetlands of tropical landscapes, comprising swamps, marshes and seasonally or permanently inundated floodplains, consist of forest and/or savannah vegetation (Mayaux and others 2004) and (2) tropical rivers have been shown to exhibit contrasting DOC concentrations and CDOM properties depending on if they flow on forest-dominated or savannah-dominated basins (for example, Bouillon and others 2014; Mann and others 2014). Moreover, watershed morphology also influences riverine DOM concentration and composition by affecting, in part, the preferential hydrological connectivity between the vegetation unit fringing the river channel and receiving waters (Bird and Pousai 1997; Marwick and others 2014) and the residence time of the hydrological flow path in DOC-rich upper soil layers (Rasmussen and others 1989). In addition, catchments with similar land cover but contrasting soil properties can exhibit small scale differences in both the concentration and the chemical composition of stream DOM (McClain and others 1997). Thus, the dominant land cover within a catchment may be inadequate to predict DOM content and quality in rivers and more detailed studies are warranted to assess how the landscape morphology in term of size, shape, and

Table 1. Drainage Area, Discharge, Precipitation, and Dominant Soil Types of the Study Sites

Basin	Drainage area ($\times 10^6$ km^2)	Rank[1]	Discharge (km^3 yr^{-1})	Precipitation range (mm yr^{-1})	Dominants soil types[2]
Congo	3.7	1	1200	1400–2500	Ferralsols (50%), Arenosols (15%), Acrisols (10%), Gleysols (5%)
Niger	2.1	3	154	180–2100	Arenosols (25%), Leptosols (19%), Lixisols (13%), Plinthosols (14%)
Ogooué	0.2	14	150	1600–2200	Ferralsols (29%), Cambisols (29%), Plinthosols (14%), Arenosols (9%)
Zambezi	1.4	4	103	400–1500	Arenosols (26%), Leptosols (14%), Ferralsols (11%), Luvisols (11%)

[1]*Refers to the rank of the basin in terms of drainage area in the African continent.*
[2]*World Reference Base for Soil Resources (WRB) classification, from (Dewitte and others 2013).*

composition controls DOM concentration and composition in tropical ecosystems.

In this study, we aimed to assess how the various landscapes of major African basins affect DOC and CDOM patterns in rivers, and complements the need to explore the link between DOM and recent estimates of CO_2 emissions by African inland waters (Borges and others 2015). CDOM data were collected at biweekly frequency during a period between 1 and 2 years in several major tropical rivers of Africa, including the Congo, the Niger, the Zambezi as well as the Ogooué. In addition, our analysis integrates CDOM data obtained from several sampling campaigns aiming at describing spatial variability carried out during both wet and dry seasons in the Congo and the Zambezi. The dominant land cover of drainage basins ranged from typical rainforest (Ogooué River) to typical savannah (Niger River), with the Congo and Zambezi showing a mixture of both vegetation cover. Combined with data on the concentrations and the stable carbon isotope composition (δ^{13}C) of DOC, we used this large dataset to compare the spatial patterns of CDOM quality along a gradient of watershed morphology and vegetation cover. Finally, we compared this dataset with previously published CDOM data from temperate and Arctic rivers.

Material and Methods

Study Sites and Sampling Locations

The Congo, the Niger, the Zambezi and the Ogooué rivers are among the largest rivers of Africa, both in terms of drainage area and discharge (Table 1). The climatic conditions are highly variable between and within each basin: the Congo and the Ogooué drainage basins cross the Equator and have the highest precipitation level, whereas the Zambezi and the Niger basins, close to the Tropic of Capricorn and to the Tropic of Cancer, respectively, have a lower annual precipitation. Linked to precipitation patterns, the vegetation varies from typical tropical humid rainforest close to the Equator to grassland, woodland, shrubland, and desert area toward the Tropics (Figure 1). Consequently, the distribution of the different land cover classes is heterogeneous between large basins as well as within each of the drainage areas, especially for the Congo and the Zambezi Basins. One additional difference between the study sites arises from the soil types, being more heterogeneous in the Niger and in the Zambezi Basins compared to the Congo and the Ogooué Basins (Table 1; Supplementary Figure S1).

The Congo River was monitored at Kisangani (DR Congo, 0°31′N, 25°11′E). In the same area, water samples from the Tshopo River, a tributary draining a forest catchment, were also collected. Monitoring on the Niger River took place in Niamey (capital of Niger, 13°31′N, 2°06′E). The Zambezi River and its major tributary (the Kafue River) were monitored at Chirundu, about 100 km south of Lusaka (capital of Zambia, 15°25′S, 28°17′E). Both rivers were sampled upstream of their confluence and both rivers are influenced by the presence of dams further upstream (Teodoru and others 2015). The Ogooué River was monitored in Lambaréné (Gabon, 0°42′S, 10°14′E). Water samples were collected approximately biweekly for one to two years between 2011 and 2014 (Table 2), so that the sample collection encompassed the range of discharge conditions for each study site.

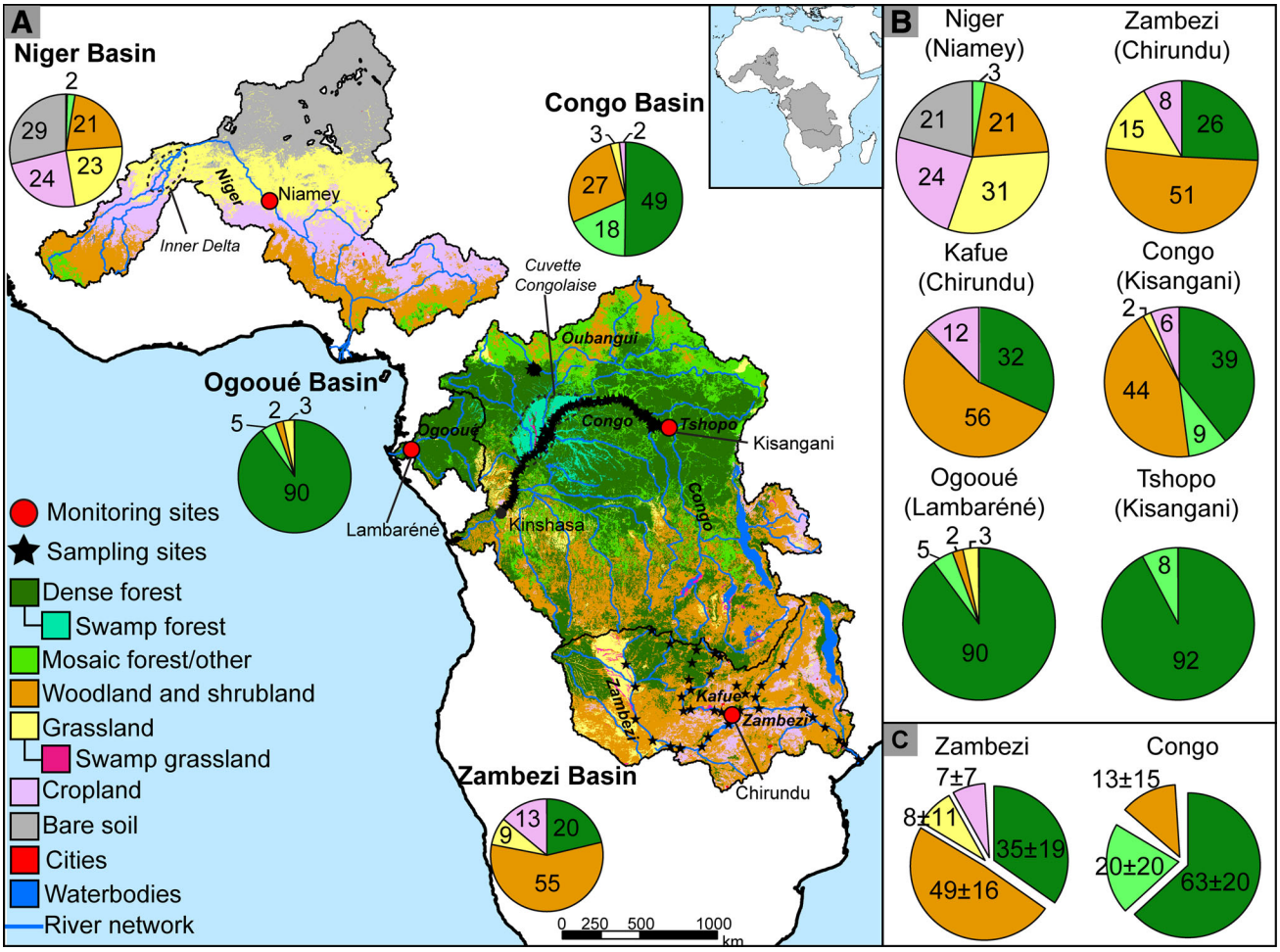


Figure 1. (**A**) Land cover map of study sites and sampling sites. *Red circles* indicate monitoring sites and *black stars* sites sampled during field campaigns. The pie charts show the fractional contribution (in %) of each land cover class for each drainage basin. (**B**) Fractional contribution (in %) of each land cover class in the catchment upstream of the sampling points for monitored rivers. (**C**) Mean and standard deviation of fractional contribution (in %) of each land cover class in the catchment upstream of the sampling points for samples collected during field campaigns. Land cover classes were defined from the Global Land Cover 2000 database (Mayaux and others 2004).

Additional CDOM data were obtained during field campaigns carried out during both dry and wet seasons along the Congo and the Zambezi rivers. A total of eight surveys were conducted in the Congo basin between 2010 and 2014 during which water samples were collected from the mainstem and from all tributaries encountered regardless of their size. Five of the campaigns were conducted from Kisangani to the confluence between the Congo and the Itimbiri tributary, located about 350 km downstream of Kisangani, during wet (November–December 2012, September 2013) and dry (May–June 2010, March 2014) periods (n = 103). Two extensive surveys were carried out during high waters (December 2013) and low waters (June 2014) along the 1700 km stretch from Kisangani to Kinshasa (n = 164). Two surveys (n = 16) were carried out in tributaries of the Oubangui catchment during dry (March 2011) and wet (November 2012) seasons mainly in the Lobaye province, Central African Republic (Bouillon and others 2014). The Zambezi River and its tributaries were sampled during wet (February–April 2012 and January–March 2013) and dry (October–November 2013) periods across the basin (n = 110) (Teodoru and others 2015). The dataset covers a wide range of geomorphological characteristics with respect to watershed morphology and land cover properties (Supplementary Figure S2).

Table 2. Sampling Period, Morphological Attributes, and Hydrological Fluctuations for Rivers Monitored

Rivers (station)	Sampling period	*n*	Drainage area ($\times 10^3$ km^2)	Mean slope (°)	Mean elevation (m)	Q_{max}/Q^1_{min}
Niger (Niamey)	03/04/11–17/03/13	50	675	0.28	336	26.2
Zambezi (Chirundu)	19/02/12–22/11/13	20	685	0.51	1049	1.6[2]
Kafue (Chirundu)	20/02/12–24/11/13	20	157	0.49	1122	3.2[2]
Congo (Kisangani)	10/12/12–29/05/14	47	972	0.96	1062	3.0
Tshopo (Kisangani)	10/12/12–29/05/14	47	58	0.41	581	n.d.
Ogooué (Lambaréné)	19/04/12–18/04/14	55	214	0.50	446	3.9

[1]*Ratio between maximal and minimal discharge during the sampling period.*
[2]*Sampling stations are located downstream of dams that regulate river discharge.*

DOC and CDOM Sampling and Analyses

Sampling was mainly performed from dugout canoes, and in a few cases from a bridge or from the river shore. Approximately, 2 l of water were collected 0.25 m below the water surface, kept away from direct sunshine, and filtered and conditioned within 2 h of sampling. Filtrations were performed successively on pre-combusted GF/F glass fiber filters (0.7 µm porosity), then on 0.2 µm polyethersulfone syringe filters. Samples for the measurement of DOC concentration and $\delta^{13}C_{DOC}$ signatures were stored in 40 ml glass vials with polytetrafluoroethylene (PTFE) coated septa with 50 µl H_3PO_4 (85%). Samples for CDOM analyses were stored in 20 ml amber glass vials with PTFE-coated septa but without H_3PO_4 addition. DOC samples were stored at ambient temperature, while CDOM samples were stored at 4°C. Samples for Fe were stored in high-density polyethylene 20 ml vials with 50 µl HNO_3 (85%).

DOC and $\delta^{13}C_{DOC}$ were analyzed with an Aurora1030 TOC analyzer (OI Analytical) coupled to a Delta V Advantage IRMS. Typical reproducibility observed in duplicate samples was in most cases less than ±5% for DOC, and ±0.2‰ for $\delta^{13}C_{DOC}$. Quantification and calibration was performed with an aqueous solution of IAEA-C6 and in-house sucrose standards. Fe was measured by inductively coupled plasma spectrometry (Agilent 7700x ICP-MS).

Absorbance was recorded on a Perkin-Elmer UV/Vis 650S spectrophotometer using a 1 cm quartz cuvette. Absorbance spectra were measured between 190 and 900 nm at 1 nm increment and instrument noise was assessed measuring Milli-Q water as blank. After subtracting the blank spectrum, the correction for scattering and index of refraction was performed according to Johannessen and Miller (2001), by fitting the absorption spectra to the data over the 200–700 nm range according to the following equation:

$$A_\lambda = A_0 e^{-S(\lambda-\lambda_0)} + K, \quad (1)$$

where A_λ and A_0 are the absorbance measured at defined wavelength λ and at reference wavelength λ_0 = 375 nm, respectively, S the spectral slope (nm^{-1}) that describes the approximate exponential decline in absorption with increasing wavelength and K a background offset. The fit was not used for any purpose other than to provide an offset value K that was then subtracted from the whole spectrum.

The specific ultra-violet absorbance ($SUVA_{254}$) was calculated as the UV absorbance at λ = 254 nm (A_{254}) normalized to the corresponding DOC concentration and was used as an indicator of the aromaticity of DOC with high values (>4 l mgC^{-1} m^{-1}) indicating the presence of more complex aromatic moieties and low values (<3 l mgC^{-1} m^{-1}) indicative the presence of mainly hydrophobic microbial-dominated compounds (Weishaar and others 2003). The natural UV absorbance of Fe at λ = 254 nm was estimated based on measured Fe concentrations (according to Weishaar and others (2003), a concentration of 0.02 mg l^{-1} of Fe produces an additive absorbance of 0.002 cm^{-1}) and was then subtracted from the UV absorbance measured. The corrected value of A_{254} was then used to calculate $SUVA_{254}$. These corrections are critical to avoid significant overestimation of $SUVA_{254}$ values, especially at low DOC/Fe ratios (Supplementary Figure S3).

Napierian absorption coefficients were calculated according to

$$a_\lambda = 2.303 \times A_\lambda / L, \quad (2)$$

where a_λ is the absorption coefficient (m^{-1}) at wavelength λ, A_λ the absorbance corrected at wavelength λ and L the path length of the optical cell in meters (0.01 m). The Napierian absorption

Table 3. DOC and CDOM Properties Measured at Monitored Rivers and During Campaigns

Basin	Monitoring/ campaigns	*n*	DOC (mg L^{-1})			$\delta^{13}C_{DOC}$ (‰)			a_{350} (m^{-1})			SUVA$_{254}$ (L mgC^{-1} m^{-1})			S_R		
			Mean ± SD	Min	Max	Mean ± SD	Min	Max	Mean ± SD	Min	Max	Mean ± SD	Min	Max	Mean ± SD	Min	Max
Congo	Congo River	47	5.1 ± 1.2	2.7	8.1	−27.6 ± 1.1	−29.9	−25.0	20.5 ± 5.1	9.3	34.7	4.7 ± 0.4	3.5	5.5	0.77 ± 0.02	0.73	0.83
	Tshopo River	47	3.7 ± 0.8	2.5	5.8	−29.8 ± 0.5	−30.4	−28.3	14.9 ± 3.7	8.1	23.3	4.7 ± 0.4	3.9	5.6	0.75 ± 0.04	0.70	0.84
	Campaigns	272	10.8 ± 10.3	1.3	67.8	−29.0 ± 1.1	−30.7	−25.2	42.5 ± 41.1	3.6	249.4	4.7 ± 0.6	2.6	5.9	0.77 ± 0.04	0.61	0.93
Ogooué	Ogooué River	55	5.1 ± 1.9	1.6	9.5	−29.6 ± 0.3	−30.4	−28.9	21.3 ± 8.1	7.4	40.8	5.0 ± 0.5	3.3	5.7	0.74 ± 0.03	0.62	0.82
Zambezi	Zambezi River	15	2.5 ± 0.6	2.1	3.4	−23.1 ± 0.3	−23.4	−22.5	1.7 ± 0.4	1.0	2.5	1.8 ± 0.5	1.2	3.1	1.12 ± 0.18	0.97	1.53
	Kafue River	17	4.3 ± 1.0	3.2	6.5	−22.8 ± 0.7	−24.0	−21.1	6.6 ± 2.9	1.5	12.7	2.8 ± 0.5	1.3	3.4	1.00 ± 0.06	0.90	1.10
	Campaigns	110	3.1 ± 1.0	1.3	5.9	−22.5 ± 1.4	−28.1	−19.6	6.3 ± 3.6	1.2	16.6	3.1 ± 0.7	1.4	5.1	0.98 ± 0.17	0.69	1.47
Niger	Niger River	32	2.4 ± 0.5	1.7	3.4	−23.7 ± 0.9	−25.9	−21.7	4.5 ± 1.8	2.5	10.1	2.7 ± 0.8	1.3	4.2	1.07 ± 0.19	0.82	1.49

coefficient at 350 nm (a_{350}) was chosen to assess CDOM content in order to facilitate comparison with other studies (Stedmon and others 2011; Spencer and others 2012). Spectral slopes for the intervals 275–295 and 350–400 nm were determined from the linear regression of the log-transformed *a* spectra versus wavelength. The slope ratio S_R, calculated as the ratio of $S_{275–295}$ to $S_{350–400}$, is related to the molecular weight distribution of DOM with values less than 1 indicative of enrichment in high molecular weight compounds and high values above 1 indicative of an high degree of low molecular weight compounds (Helms and others 2008).

Landscape Analysis

For each sampling site, we calculated the mean slope, mean elevation, and total drainage area of the contributing watershed in the geographic information system (GIS) software ArcGIS, using the subwatershed polygons defined by the HYDRO1K global hydrologic data set (U.S.G.S. 2000). The fractional land cover type of the contributing watershed was determined from the Global Land Cover (GLC) 2000 database of Africa (Mayaux and others 2004). For our study, the 27 sub-classes defined by the GLC database were aggregated in seven first level classes based on vegetation structural categories: dense forest, mosaic forest/other, woodlands and shrublands, grasslands, agricultural lands, bare soils, and others (Supplementary Table 1). In this study, we used *savannah* as a generic term including grassland, wooded savannah, and shrubland vegetation biomes. The soil types for each study sites were derived from the soil map of Africa at the continent scale produced by Dewitte and others (2013).

Results

DOC concentrations and a_{350} varied over a wide range among the study sites, from 1.26 to 67.8 mg l^{-1} and from 1.05 to 264.0 m^{-1}, respectively (Table 3; Supplementary Table 2). For large rivers (that is, at monitoring sites), highest mean DOC concentrations (>5 mg l^{-1}) were measured in the Congo and the Ogooué and lowest (<2.5 mg l^{-1}) in the Zambezi and the Niger. The seasonal variability in DOC concentration was less pronounced in the Zambezi, the Kafue, and the Niger compared to the other rivers, and was not correlated with the hydrological fluctuations indicated by the ratio of the seasonal maximum and minimum of freshwater discharge (Q_{max}/Q_{min}).

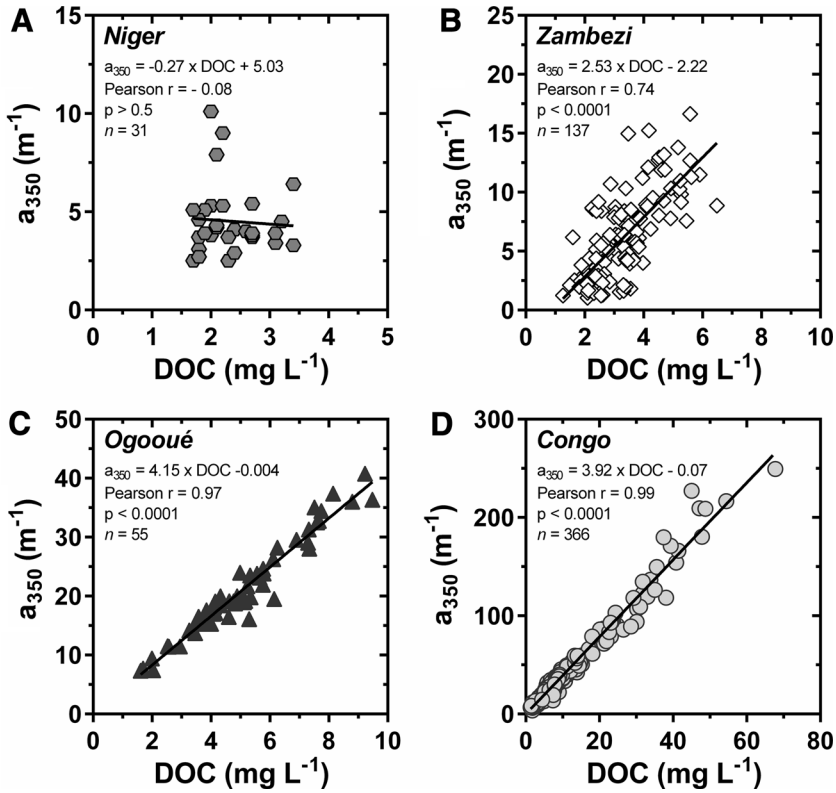


Figure 2. Relationships between a_{350} and DOC concentrations in (**A**) the Niger, (**B**) the Zambezi, (**C**) the Ogooué, and (**D**) the Congo basins.

Maximum DOC concentrations and highest variation were measured during campaigns carried out in the Congo basin, with a mean concentration of 10.8 ± 10.3 mg l^{-1} and values ranging from 1.3 to 67.8 mg l^{-1}. In contrast, the spatial variability in DOC concentrations was less pronounced in the Zambezi basin with a mean DOC concentration (3.1 ± 1.0 mg l^{-1}). In general, a_{350} values followed similar seasonal and spatial patterns across river basins as those of DOC. However, for an equivalent DOC concentration, a_{350} was about 50% lower in samples from the Zambezi and the Niger basin compared to those from the Congo and Ogooué. For example, while the Tshopo and Kafue rivers exhibited similar mean DOC concentrations (3.7 ± 0.8 and 4.3 ± 1.0 mg l^{-1}, respectively), a_{350} was much higher in the Tshopo River (14.9 ± 3.7 m^{-1}) than in the Kafue River (6.6 ± 2.9 m^{-1}). The correlations between a_{350} and DOC concentration were strong in the Congo and the Ogooué basins, weaker but still significant in the Zambezi basin, and not significant in the Niger basin (Figure 2). Overall, the slope of the relationship between a_{350} and DOC increased with increasing percentage of dense forest coverage (%DF), but this relationship levels off at %DF above 50% (Figure 3).

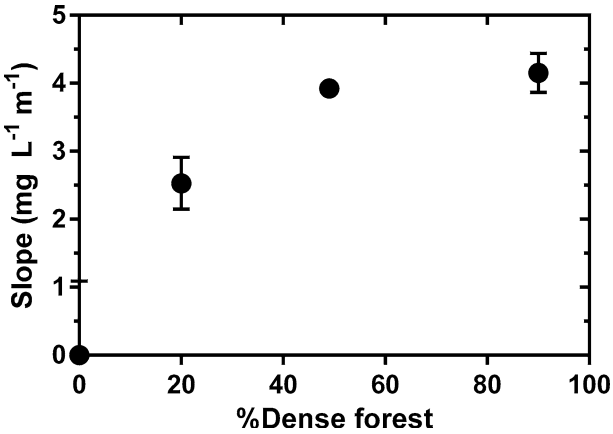


Figure 3. Correlation between the slope of the a_{350}/DOC relationship and the percentage of dense forest coverage at the basin scale. *Error bars* represent the 95% confidence intervals.

Based on DOC isotopic composition ($\delta^{13}C_{DOC}$) and optical properties of CDOM ($SUVA_{254}$ and S_R), the four studied basins can be grouped as follows: DOC-rich waters of the Congo and the Ogooué basins presented lower $\delta^{13}C_{DOC}$ signatures (averages from −29.8 ± 0.5 to −27.6 ± 1.1‰), higher aromaticity (mean $SUVA_{254} \geq 4.5$ l mgC^{-1} m^{-1}), and a higher contribution of high molecular weight

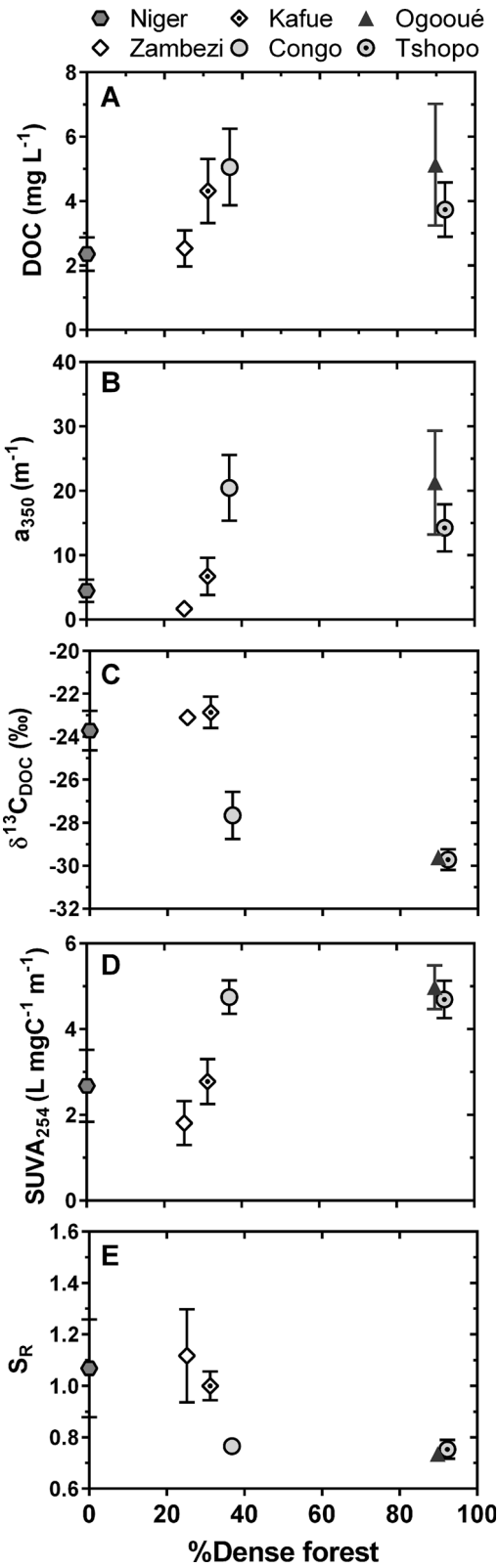


Figure 4. (**A**) DOC concentration, (**B**) a_{350}, (**C**) $\delta^{13}C_{DOC}$, (**D**) $SUVA_{254}$, and (**E**) S_R as a function of %DF at sampling points for large rivers.

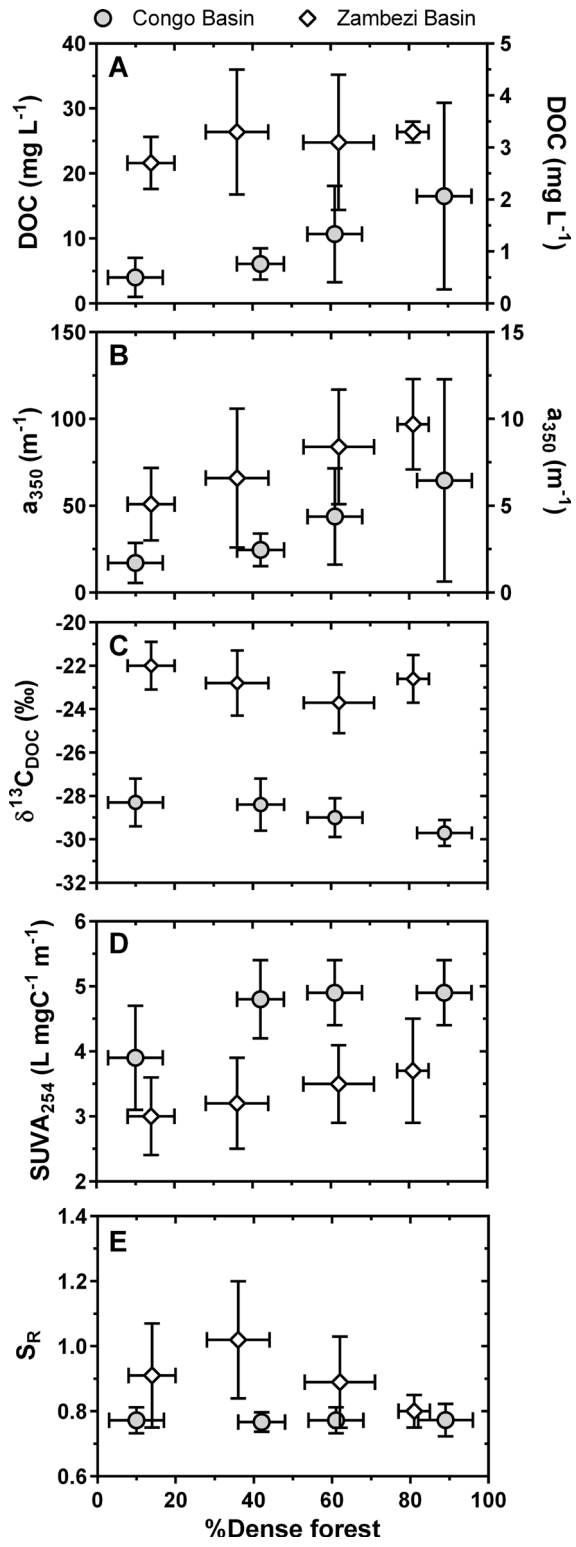
compounds (mean $S_R < 0.8$), while DOC-poorer waters of the Zambezi and the Niger basins were characterized by higher $\delta^{13}C_{DOC}$ signatures (averages from -23.7 ± 0.9 to -22.5 ± 1.4‰), lower aromaticity (mean $SUVA_{254} < 3.5$ l mgC^{-1} m^{-1}), and a higher degree of low molecular weight compounds (mean S_R closed to 1). Seasonal variations in CDOM properties were more marked in the Zambezi and the Niger basins compared to the Congo and the Ogooué basins. No clear correlations were found between $\delta^{13}C_{DOC}$ and CDOM properties and changes in hydrological flow (Q_{max}/Q_{min}).

The %DF in the catchment was chosen to explore potential links between land cover and riverine DOM due to the greatest range of variation compared to the other land classes (Supplementary Figure S2). When considering large African rivers sampled, no clear relationships appear between DOC properties and %DF (Figure 4A, C), or between CDOM properties and %DF (Figure 4B, D, E). Significant differences in riverine DOM can be observed in rivers draining typical savannah- or forest-landscapes (for example, the Niger versus the Ogooué and the Tshopo). However, river basins having heterogeneous land cover (for example, the Zambezi, the Kafue, and the Congo) exhibited contrasting DOC and CDOM patterns, with values close to rivers draining typical savannah- or forest-catchment.

Significant correlations between %DF and DOC/CDOM properties were observed within the Congo and the Zambezi basins (Figure 5). DOC concentrations and a_{350} (Figure 5A, B) were positively correlated with %DF in the Congo basin ($r = 0.43$ and 0.41, respectively, $P < 0.0001$, $n = 211$), whereas this was only the case for a_{350} in the Zambezi basin ($r = 0.38$, $P < 0.005$, $n = 84$). Similarly, $\delta^{13}C_{DOC}$ signatures (Figure 5C) decreased with increasing %DF in the Congo basin ($r = -0.54$, $P < 0.0001$, $n = 206$) but not in the Zambezi basin ($r = -0.18$, $P > 0.05$, $n = 80$). Regarding DOM composition, $SUVA_{254}$ values were positively linked to %DF in both basins ($r = 0.27$, $P = 0.0001$, $n = 197$ for the Congo and Pearson' $r = 0.33$, $P = 0.0025$, $n = 83$ in the Zambezi), whereas no relationship was observed between S_R and %DF ($P > 0.05$ in both basins).

Discussion

Data from this study provide evidence that the largest African basins strongly differ in their DOC and CDOM properties. We argue that this wide



variability results from several factors that interact in regulating DOC and CDOM in freshwaters, namely the land cover and the watershed morphology.

◂ **Figure 5.** (**A**) DOC concentration, (**B**) a_{350}, (**C**) $\delta^{13}C_{DOC}$, (**D**) $SUVA_{254}$, and (**E**) S_R as a function of the %DF at sampling point for tributaries and mainstem collected during campaigns. Data were bin-averaged for each 25% interval of dense forest cover and plotted against the mean %DF for these intervals. For (**A**) and (**B**), DOC concentrations and a_{350} are indicated on the *left axis* for the Congo basin and on the *right axis* for the Zambezi basin.

Effect of Land Cover on CDOM Released in the Fluvial Network

The effect of land cover can be assessed through the carbon isotopic composition of DOC by considering C_3 and C_4 vegetation as the dominant sources of DOM in these systems. In northern Australia, Bird and Pousai (1997) have shown that organic carbon in the surface soils of tropical forests (exclusively C_3) and tropical savannah (mixed C_3/C_4 woodlands and shrublands and exclusively C_4 grasslands) have contrasting isotopic signatures with values ranging from −29.4 to −27.2 ‰ and from of −26.6 to −14.4‰, respectively. Also, Kohn (2010) pointed to a decrease of the isotopic signature of C_3-plants with increasing mean annual precipitation, with values lower than −29‰ in environments receiving more than 2000 mm yr^{-1} of precipitation. The spatial distribution of $\delta^{13}C_{DOC}$ values in streams and rivers of the four studied basins appears to be in accordance with the spatial repartition of the dominant land cover. The high ratio between the concentration of particulate organic carbon (POC) and chlorophyll *a* (Chl *a*) measured in the Congo basin in this study (POC:Chl $a \sim 15000 \pm 45000$, $n = 223$, data not shown) also suggests that contribution to OM of in-stream phytoplankton production was negligible, as also reported in other African tropical rivers such as the Tana (Tamooh and others 2012). The low autochthonous contribution to the DOM pool in tropical rivers was already highlighted in basins of Madagascar (Marwick and others 2014) and in the Kafue Flats of the Zambezi basin (Zurbrügg and others 2013). Finally, even if phytoplankton DOC production has been shown in tropical lakes such as Lake Kivu, its rapid uptake by bacteria limits its accumulation and presence within the aquatic ecosystem (Morana and others 2014). For the above reasons, we assume that most the DOM is of allochthonous origin and that $\delta^{13}C_{DOC}$ values are representative of the relative inputs of DOM originating from C_3 and C_4 vegetation.

Clear distinctions emerge between C_3- and mixed C_3/C_4 dominated basins when DOC concentration and CDOM properties are plotted against

$\delta^{13}C_{DOC}$ (Figure 6). To assess the effect on soil variability on these patterns, we compared DOM properties in streams and rivers draining (1) similar land cover but different soil types and (2) different land covers but similar soil type (Supplementary Figure S4). In accordance with previous studies (for example, McClain and others 1997), we found that the soil type impacts the concentration and the chemical composition of stream DOM (Supplementary Figure S4A). However, these differences are relatively small and are obscured by the variations in stream DOM content and composition imposed by vegetation (Supplementary Figure S4B), suggesting a large-scale control of land cover on riverine DOM concentration and composition in tropical freshwaters.

Catchments dominated by C_3-biomass export greater quantities of DOC than those where C_4 biomass is more important (Figure 6A). The higher riverine DOC concentrations in forest areas compared to savannah areas have already been reported from the catchment to the continental scale in Africa (for example, Laraque and others 2009) as well in the Amazon Basin (Seyler and others 2004), and results from higher carbon standing stocks in tropical forest were compared to savannah ecosystems (Bird and Pousai 1997). However, although the lower values of riverine DOC concentration are not significantly different between forest and savannah biomes, lowest CDOM content were found in rivers receiving DOM from mixed C_3/C_4 savannah vegetation (Figure 6B). This result shows that DOM released from savannah soils is less optically active (that is, less absorptive) compared to DOM released from forest soils. The less absorptive character of DOM in savannah-dominated basins is reflected in the lower slope of the relationship between DOC and a_{350} in the Zambezi Basin (2.53) relative to the Congo (3.92) and the Ogooué (4.15) basins and by the fact that the slope of the relationship between DOC and a_{350} increases with the %DF across basins (Figure 3).

The repartition of $SUVA_{254}$ and S_R values along the $\delta^{13}C_{DOC}$ gradient shows that C_3- and mixed C_3/C_4-dominated basins strongly differ in their stream DOM composition (Figure 6C, D). This is not surprising given that the specific absorption coefficient of DOM is related to its chemical composition (Yacobi and others 2003). $SUVA_{254}$ and S_R can be used as proxies to trace the sources of DOM as well as the processes that regulate its fate in freshwaters. In general, highest DOC concentrations and CDOM load found in streams and rivers during high flow periods are linked with greatest aromaticity (high $SUVA_{254}$) and average molecular weight (low S_R) compared to base flow periods. Inversely, lower $SUVA_{254}$ and higher S_R values in streams can be expected during base flow periods when water originates from deeper mineral horizons of the soil profile (for example, Striegl and others 2005). Both sorption and biotic processes occurring during the transport of DOM produced in surface layers into underlying soil layers may affect its chemical composition, leading to a decrease in its aromaticity

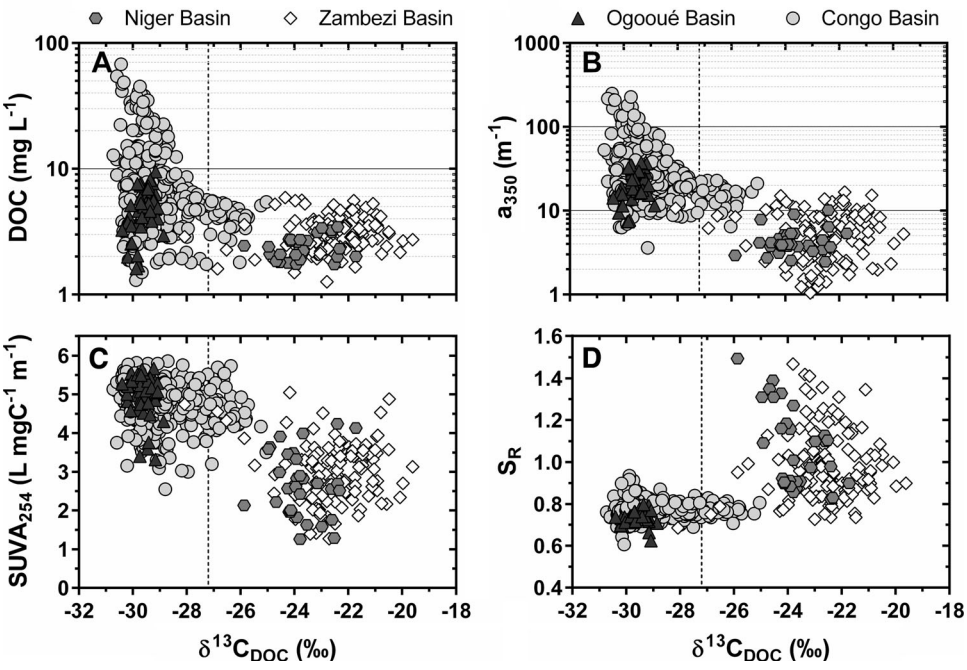


Figure 6. (**A**) DOC concentration, (**B**) a_{350}, (**C**) $SUVA_{254}$, and (**D**) S_R as a function of $\delta^{13}C_{DOC}$ values for all samples acquired in the Congo, the Ogooué, the Zambezi and the Niger basins. The *vertical dashed line* represents the upper $\delta^{13}C$ signature for organic carbon in the surface soils of exclusively C_3 tropical forests, according to Bird and Pousai (1997).

and molecular weight (Striegl and others 2005; Lambert and others 2013). The seasonal changes in the properties of CDOM, reported in a large variety of rivers ranging in size and hydroclimatic zones, are attributed to the seasonal shift in dominant source from modern plant material in organic-rich soil horizons during the high flow to older, more degraded soil OM originating from lower soil horizons during low flow conditions (Striegl and others 2005; Neff and others 2006; Raymond and others 2007; Stedmon and others 2011; Bouillon and others 2014).

The high $SUVA_{254}$ values concomitant with low $\delta^{13}C_{DOC}$ (Figure 6) indicate that C_3 biomass releases DOM with a greater proportion of aromatic and higher molecular weight compounds compared to C_4 biomass. Moreover, the narrow range of variability of these optical proxies compared to previous studies (see references above) suggests that changes in DOM sources were minimal despite significant seasonal hydrological variability, and that inputs of less degraded plant material continuously fuelled stream DOC. Keeping in mind that the data presented in Figure 2 include samples that cover the seasonal variability, the strong correlations between DOC and a_{350} observed in the Congo and the Ogooué basins support this assumption. In contrast, the large range of variation in $SUVA_{254}$ and S_R values observed for $\delta^{13}C_{DOC}$ greater than $-26‰$ suggest more pronounced changes in DOM sources across the hydrological year in savannah-dominated basins. Thus, the larger range in both $SUVA_{254}$ and S_R we observed in C_3/C_4 environments are indicative of different DOM source pools mobilized along the hydrological cycle, according to the two-source model described above. The contribution of several sources differing in their optical properties to stream CDOM export in savannah-dominated basins is supported by the relatively weaker correlation between DOC and a_{350} observed in the Zambezi basin (Figure 2).

Our results highlight that the variability in the optical properties of DOM transported in tropical river systems can be directly related to the different types of land cover. Similar observations have recently been reported at the regional scale in the northwestern part of the Congo basin (Mann and other 2014), and likely reflect inherent differences in the molecular composition of DOM derived from C_3 or C_4 biomass (or, in more general terms, between woody vegetation and grassland vegetation). DOM in forest floors or superficial soil horizons is known to be substantially more humic and aromatic, and contained a greater proportion of large and complex molecules compared to other land cover types (Qualls and others 1991; Aitkenhead-Peterson and others 2003). In addition, several studies have reported differences in the lability between C_4-compounds derived from grassland vegetation and C_3-compounds derived from woody vegetation both in soils (Bird and Pousai 1997; Wynn and Bird 2007) and aquatic ecosystems (Quay and others 1992; Mayorga and others 2005). For example, C_4-grasses fuel disproportionately the production of dissolved CO_2 in streams and rivers of the Amazon Basin (Mayorga and others 2005), indicating that grasslands may be intrinsically more biodegradable due to an enrichment in labile compounds in soil organic matter build up under grasses (see also Quay and others 1992; Wynn and Bird 2007). Consequently, soil OM (SOM) derived from grassland can be more efficiently processed by soil microorganisms, thus enhancing the incorporation of microbial inputs in the SOM pools and ultimately in the DOM pool. As microbial inputs have a low aromaticity (for example, Lambert and others 2013), this DOM pool would lead to lowering $SUVA_{254}$ and higher S_R values. In line with this hypothesis, Jaffé and others (2012), who studied the molecular complexity of DOM from small streams across climatic regions by detailed molecular characterization methods, showed that DOM derived from C_4-grassland was enriched in microbial inputs compared to other environments.

Watershed Morphology Effects on CDOM Released in the Fluvial Network

The correlations between %DF as estimated from GIS analysis and DOC or CDOM properties were not obvious across basins (Figure 4) and within a given basin (Figure 5). Although the large heterogeneity in terms of land cover, size, and morphological attributes of the sampling sites may also complicate the relationships between %DF and DOC/CDOM, the lack of significant correlations likely reflects the influence of additional features of the landscape on the loading and fate of DOM in tropical rivers.

The first proposed explanation concerns the spatial repartition of the land cover within the drainage basin. Marwick and others (2014) recently highlighted that $\delta^{13}C_{DOC}$ in C_4-dominated basins was biased toward the isotopic fingerprints of the C_3-enriched riparian fringe due to preferential hydrological connectivity with stream channel (see also Bird and Pousai 1997). The same likely occurs in the Zambezi basin, where $\delta^{13}C_{DOC}$ values were not correlated with %DF (Figure 5C). Indeed, the Zambezi River crosses numerous and extensive

floodplains characterized by substantial C_4 components that contribute to a great proportion of organic carbon export (for example, Zurbrügg and others 2013, Figure 1). By extension, we suggest that the difference in land cover between lowland and upland basins contribute to the discrepancies between GIS data and field measurements. For example, despite similar land cover partition at their sampling point (32 and 39% of %DF, respectively, Figure 1), the Kafue and the Congo rivers exhibited DOC and CDOM patterns matching those expected for rivers draining typical savannah- and forest-dominated catchments, respectively (Figure 4). However, while lowlands are covered by forest and the uplands by savannah in the Congo basin upstream of Kisangani, an opposite situation characterizes the Kafue catchment. Steeper slopes allow faster movement of water through the soils, which limits the residence time of hydrological flowpaths in the superficial layers of soils and thus reduces the amount of DOM reaching adjacent streams. Inversely, watersheds with low slopes have generally thicker organic horizons and longer residence times in soils, and are thus capable of supplying significant quantities of DOM (Rasmussen and others 1989). In line with this hypothesis, an altitude effect was observed in the Congo Basin for DOC and a_{350} with values decreasing with increasing the slope (Supplementary Figure S5). Our results highlight that the fractional distribution of C_3 and C_4 vegetation cover in tropical basins is not an accurate predictor for riverine DOM (and CDOM) quantity and quality. The spatial distribution of land cover types within the basin (along the riparian fringe and between lowlands and uplands) plays an integral role in controlling DOM in freshwaters, leading to discrepancies between GIS data and field measurements.

Additionally, photochemical and microbial degradation and the interaction between these two processes are known to strongly alter the optical properties of terrestrial DOM during its transport in freshwaters (for example, Spencer and others 2009; Fasching and others 2014). Measurements of pelagic respiration rates performed during field campaigns were 12.7 ± 5.8 and 14.5 ± 14.1 mmolC m^{-3} d^{-1} in the Congo and the Zambezi basins, respectively, which are close to the median value measured in African inland waters [~20 mmolC m^{-3} d^{-1}, Borges and others (2015)] and in the range of bacterial respiration rates reported in temperate and others tropical systems (Amado and others 2013). Microbial degradation of terrestrial DOM can efficiently consume aromatic compounds (for example, Ward and others 2013) and at the same time release new less aromatic compounds (Fasching and others 2014). Moreover, photochemical degradation has been shown to result in a preferential loss of CDOM compared to DOC due to the decay of photo-labile aromatic compounds (for example, Spencer and others 2009; Lapierre and del Giorgio 2014). This can lead to a quick alteration of DOM chemical composition and a significant shift in its optical properties at the first time of light exposure, as pointed by Spencer and others (2009) who irradiated DOM from the Congo River.

The water bodies that have extended water residence time, such as lakes, reservoirs or large floodplains, enhance the opportunities for these processes to decompose terrestrial DOC (Battin and others 2008). Thus, the low molecular weight and aromaticity of DOM in the Zambezi River at the outlet of the Kariba Reservoir (Figure 4) likely reflect photochemical and/or microbial degradation processes. Finally, increased solar radiation under open canopy conditions can also promote the loss of DOC exported downstream via photodegradation. For the Niger River at Niamey, the combination of (1) the slowdown of stream waters as the river enters the Inner Delta (Figure 1), (2) the lack of new inputs of terrestrial organic material by significant tributaries along the approximately 760 km stretch between the Inner Delta and Niamey, and (3) the total absence of shading along the same stretch may explain the lack of relationship between DOC and CDOM (Figure 2). Finally, the autochthonous production of uncolored DOM can impact the relationship between DOC and CDOM in lakes or estuarine systems (for example, Rochelle-Newall and others 2014). However, as discussed above, the autochthonous contribution to the DOM pool in our study sites is most probably low.

Tropical Rivers Versus Temperate and High-Latitude Rivers

To assess the variability of CDOM in streams and rivers along a climatic gradient, we compared our results with previous studies carried out in temperate (Spencer and others 2012), Arctic (Stedmon and others 2011; O'Donnell and others 2012; Spencer and others 2012), and other tropical systems (Yamashita and others 2010; Mann and others 2014) (data detailed in Supplementary Table 3). The comparison of the relationship between DOC and CDOM at the global scale highlights that while similar low slopes have been reported in all climatic biomes, maximum values tend to increase in the

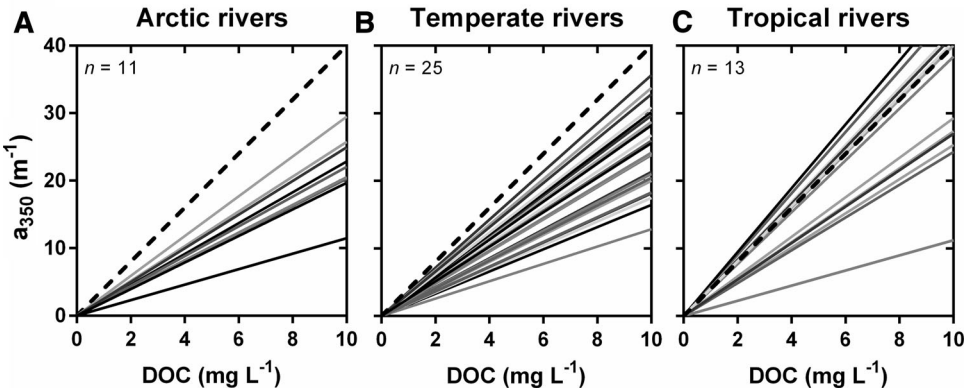


Figure 7. Relationships between CDOM (a_{350}) and DOC concentrations for published data in (**A**) Arctic rivers (Stedmon and others 2011; O'Donnell and others 2012; Spencer and others 2012), (**B**) temperate rivers (Spencer and others 2012), and (**C**) tropical rivers (Yamashita and others 2010; Mann and others 2014; this study). To simplify the comparison, the *y*-intercept was set to 0 and the relationship was plotted over the 0–10 mg L^{-1} [DOC] range. The *dashed line* represents the 4:1 slope. Data are detailed in Supplementary Table 3.

order Arctic < temperate < tropical rivers (Figure 7). The fact that the highest slope is found in tropical rivers can be related to the highly aromatic character of DOM in tropical ecosystems [Figure 8, see also Pérez and others (2011)], especially in tropical rainforest dominated basins (Table 3). The good correlation between the slope of the DOC/a_{350} relationship and $SUVA_{254}$ is not surprising, as $SUVA_{254}$ is by definition the specific absorption coefficient of DOM measured at 254 nm. In other words, higher $SUVA_{254}$ values are associated with a higher ability of DOM to absorb sunlight, supporting previous studies that show that aromatic molecules are key components of CDOM (for example, Spencer and others 2009).

The strong colored character of DOM can have strong potential implications for the reactivity of DOM and CO_2 emissions in tropical rainforest ecosystems. Indeed, recent studies have shown that fresh aromatic compounds can be extensively respired by microorganisms (Ward and others 2013; Fasching and others 2014; Lapierre and del Giorgio 2014) and that the photochemical susceptibility of CDOM is directly correlated with its initial aromatic nature (Lapierre and others 2013; Lapierre and del Giorgio 2014). For these reasons, recent studies have concluded that surface water CO_2 concentrations should increase as a function of CDOM (Lapierre and others 2013; Fasching and others 2014). However, a recent data compilation of CO_2 and respiration measurements in Sub-Saharan African inland waters, including the studied basin here, showed that less than 20% of CO_2 emissions were attributed to in-stream degradation of OM (Borges and others 2015). The fact that CO_2 river concentrations were correlated to above-ground terrestrial vegetation biomass, both within and across basins, lead these authors to conclude that the CO_2 oversaturation in rivers was to a large extent explained by lateral inputs of CO_2 from wetlands and groundwaters, and that an overall positive relationship between CO_2 and DOC concentrations is not necessarily causal. In absence of data on direct CO_2 production from photodegradation of CDOM, this contribution to CO_2 fluxes was not envisaged although it is unlikely that it could account for greater than 80% of CO_2 emissions that cannot be accounted by in-stream respiration. Indeed, in the Amazon black-waters (Rio Negro) photodegradation represents only a small part (<10%) of the total DOC mineralization (Amaral and others 2013), and explains less than 1% of its CO_2 emission (Remington and others 2011). Yet, we acknowledge that this pathway of CO_2 production needs to be further quantified in highly humic rivers such as the Congo.

It is possible that photodegradation of terrestrial CDOM in tropical rainforest ecosystems can be limited by shading of the dense canopy and light absorption by CDOM itself and that microbial degradation is limited by the low nutrient status (data not shown). This also could explain the strong relationship between DOC and CDOM in the Congo basin (Figure 2), where sampling encompassed both spatial and temporal dimensions. Degradation of terrestrially derived CDOM could, therefore, mainly be localized in areas of lowest canopy density with rivers or at sea in rivers

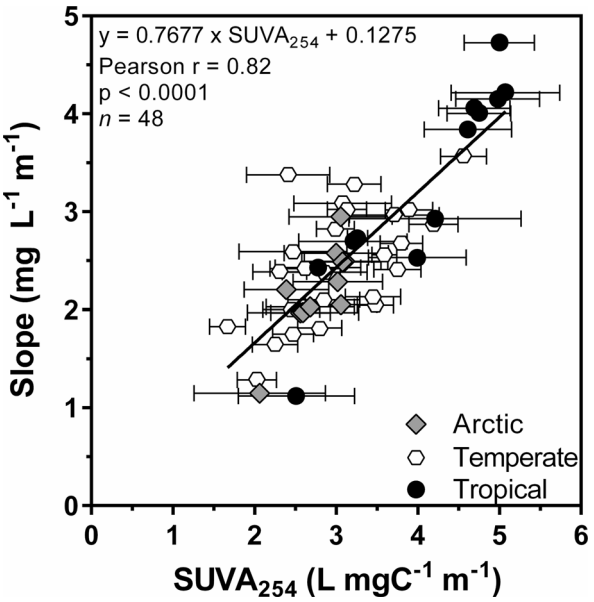


Figure 8. Correlation between the slope of the a_{350}/DOC relationship and mean $SUVA_{254}$ for stream waters at the global scale, including Arctic (Stedmon and others 2011; O'Donnell and others 2012; Spencer and others 2012), temperate (Spencer and others 2012), and tropical rivers (Yamashita and others 2010; Mann and others 2014; this study).

plumes. Further studies addressing biological and photochemical degradation rates at large scales are needed to better estimate the relative contribution of CO_2 emissions resulting from terrestrial inputs to those resulting from in-stream metabolism, especially in tropical rivers.

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