Contrasting silicon isotope signatures in rivers from the Congo Basin and the specific behaviour of organic-rich waters

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[1] We investigate the dissolved δ^{30}Si of the Congo River, the world's second largest riverine source of Si to the ocean. Small tributaries rich in dissolved organic carbon running through wetlands ("Black Rivers") exhibit the lowest δ^{30}Si ever measured in running surface waters (+0.02 ± 0.15‰), whilst the main branch and largest tributaries have higher values (+0.98 ± 0.13‰), well within the average of what has been measured so far. Our data suggest that the contribution of Black Rivers to the total discharge of the basin is 22 ± 10% and that δ^{30}Si is mostly controlled by weathering intensity rather than fluxes. We propose both a mass and Si-isotopic balance model, which suggest that the distribution of Si in the particulate and/or dissolved components in Congo rivers results mainly from mixing between two types of weathering regimes: one where clays are formed and remain stable, and one where they are dissolved under the action of organic matter. **Citation:** Cardinal, D., J. Gaillardet, H. J. Hughes, S. Opfergelt, and L. André (2010), Contrasting silicon isotope signatures in rivers from the Congo Basin and the specific behaviour of organic-rich waters, *Geophys. Res. Lett.*, *37*, L12403, doi:10.1029/2010GL043413.

1. Introduction

[2] It remains unclear how climate, the carbon cycle and vegetation interact with the silicon biogeochemical cycle. Silicate weathering mobilises and redistributes Si into secondary mineral phases, phytoliths in plants and soils, and dissolved and particulate Si in rivers and groundwaters. The Congo River is the second largest river and supplier of dissolved Si to the ocean [*Gaillardet et al.*, 1999] and is a valuable case-study since its basin remains largely pristine [*Meybeck*, 2003]. Most of the Congo river drains a low-lying relief area (elevation about 400 m) centered on the Equator and bordered by relief areas rarely above 2000 m. Vegetation is dominated by rain forest around the Equator and savannahs in the Northern and Southern part of the Basin, while the central part is characterized by inundated rainforest and swampy areas (Figure 1). Most of the basin is covered by lateritic formations, consisting mainly of ferralitic soils (93%) and recent brown soils and podzols zones in the swampy zone [*Négrel et al.*, 1993]. Previous studies have underlined that despite intense weathering, low weathering rates characterized the Congo Basin. A transport-limited regime of denudation dominates, which is in a dynamic steady state between soil production and destruction [*Gaillardet et al.*, 1995]. The contrast between the geochemical and weathering characteristics of the "Black rivers" (rich in dissolved organic carbon which run trough wetlands) compared to the other tributaries was also highlighted. While several studies used Si isotopes (δ^{30}Si) to trace weathering processes on small watersheds [e.g., *Ziegler et al.*, 2005a, 2005b; *Georg et al.*, 2006, 2007a; *Opfergelt et al.*, 2008], here we report riverine δ^{30}Si values of the Congo River and its main tributaries, which represents the first large scale study in a tropical pristine watershed using this tracer.

2. Material and Methods

[3] Sampling on the main branch of the Oubangui and Congo rivers and their tributaries was performed in November 1989 (except for Alima river sampled in November 1988) along a 1100-km long transect from Bangui to Brazzaville (hereafter referred to as the main branch (Figure 1)). Water samples were filtered through 0.2 μm cellulose acetate membranes to remove suspended matter and stored in Polypropylene bottles at 4°C until δ^{30}Si analysis in 2006. Some were acidified with concentrated nitric acid. Re-analysis of Si contents by spectrophotometry was performed in 2006 and the results (Table S1 of the auxiliary material) are in agreement, within ±4%, with the original data [*Dupré et al.*, 1996].[5] This provides evidence for the good conservation of Si in these samples. Similarly, no obvious and systematic differences in δ^{30}Si were observed between acidified and non acidified samples (Table S1). Si isotopes have been measured by MC-ICP-MS as δ^{29}Si relative to NBS28 standard [*Cardinal et al.*, 2003]. Data are presented as δ^{30}Si after application of the equilibrium mass fractionation conversion factor (δ^{29}Si = 0.5178 × δ^{30}Si) which has been verified to be valid on river samples [*Georg et al.*, 2006, 2007a]. Reproducibility and precision of the complete chemical and analytical steps is ±0.08 ‰ on δ^{29}Si (±2 standard deviations, σ_{SD}) similar to other current analytical capabilities [*Reynolds et al.*, 2007]. Data for 8 of the 19 new δ^{30}Si measurements presented have been fully replicated with similar reproducibility. No further replication was possible due to the limited volume of sample material. Accuracy has been further checked by an inter-laboratory comparison and on a daily basis by analyses of secondary reference materials (Table S1). Trace and major elements concentrations are available for some samples [*Négrel et al.*, 1993; *Gaillardet*

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[5]Auxiliary materials are available in the HTML. doi:10.1029/2010GL043413.

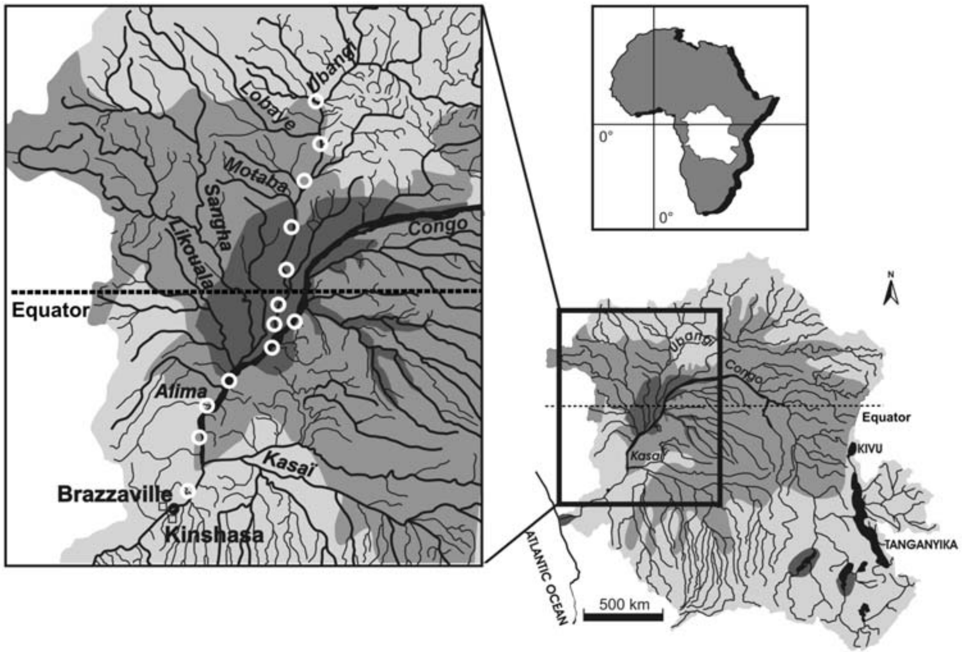

Figure 1. Congo watershed, sampling location and simplified vegetation map. Dark grey: swamps. Medium grey: rain forests. Light grey: wooded grassland and savanna. White circles identify the locations of samples. Frame: Oubangui-Congo transect where a higher resolution of the hydrologic network is displayed around the sampling area. Map adapted from *Nkounkou and Probst* [1987].

et al., 1995; *Dupré et al.*, 1996] whilst the others were analysed on a HR-ICP-MS Element 2 in 2007. This dataset (pH, suspended matter, Si, Al, Ca, Na and Mg contents) is provided in Table S1 along with the new dissolved δ^{30}Si values.

3. Results

[4] The δ^{30}Si values from the main branch are relatively uniform (+1.01 ± 0.12‰; $\pm 1\sigma_{SD}$) but significant variations are observed: The δ^{30}Si values decrease from +1.22‰ at Bangui to +0.83‰ before increasing after the confluence with the Congo River and then decreasing again slightly (Figure 2). All tributaries are isotopically lighter than the main river at their confluence with it, and the mixing of tributaries with the main river results in lower δ^{30}Si values of the main branch. Three rivers (Motaba, Likouala and Alima) exhibit very low δ^{30}Si values (average of +0.02 ± 0.15‰). These are the most ^{30}Si-depleted signatures measured so far in running surface waters (with the exception of one Icelandic river [*Georg et al.*, 2006]). These three rivers are located in the central depression of the Congo Basin and belong to the "Black River" group characterised by low pH, low suspended material and a high content of coloured

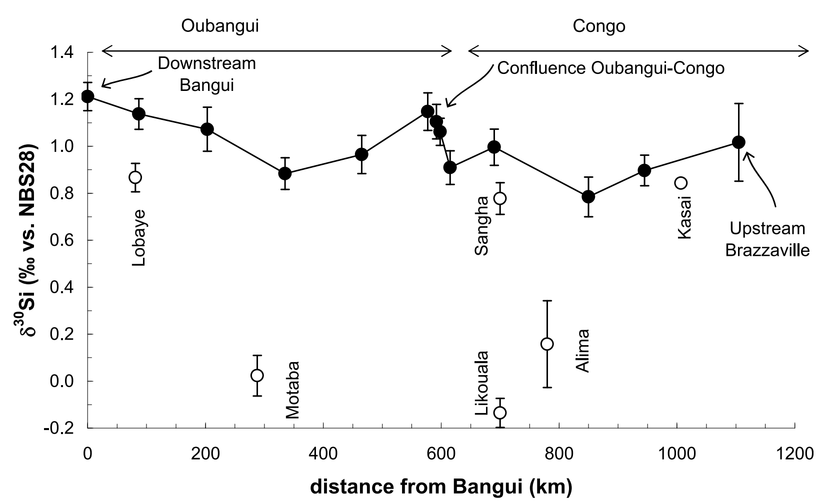

Figure 2. Dissolved δ^{30}Si along the transect Bangui to Brazzaville. Filled circles: Oubangui-Congo main branch. Open circles: Tributaries. Error bars are $\pm 1\sigma_{SD}$ of replicates or ±1 standard error of analysis (cf. Table S1).

dissolved organic carbon derived from wetlands [*Gaillardet et al.*, 1995; *Viers et al.*, 1997].

[5] The average δ^{30}Si value for the main branch of the Oubangui-Congo river is higher than the two values (+0.4 and +0.8 ‰) previously reported for the Congo River [*De La Rocha et al.*, 2000]. The δ^{30}Si values of most rivers published so far (+0.8 ± 0.3‰, n = 8 [*De La Rocha et al.*, 2000]; +0.84 ± 0.2‰, n = 40 [*Georg et al.*, 2006]; +0.63 ± 0.38‰, n = 25 [*Georg et al.*, 2007a]) are lower than the average of the main branch waters presented here (+1.01 ± 0.12‰, n = 13). Only tributaries to Lake Tanganyika (+1.61 ± 0.5‰, n = 8 [*Alleman et al.*, 2005] and Changjiang (Yangtze) River (+2.1 ± 0.7‰, n = 17 [*Ding et al.*, 2004])), display higher δ^{30}Si. In the case of the Yangtze River, the heavy composition was attributed to intensive rice cultivation which was removing Si as phytoliths.

4. Discussion

4.1. Contribution of Black Rivers to the Congo Water Flow

[6] Mass and isotopic budgets detailed in Text S1, based on river water discharges [*Dupré et al.*, 1996], suggest that additional, unsampled black water should reach the Oubangui-Congo main branch and could explain the decrease of its δ^{30}Si value, in accordance with the ubiquitous presence of swamps in this region (Figure 1). δ^{30}Si data suggest that Black Rivers supply 9.5 ± 4.2 km^3/s to the Congo along the 250 km-long section between the Congo-Oubangui confluence and downstream Alima-Congo confluence, constituting 22 ± 10% of total river discharge at Brazzaville (Text S1). This highlights the importance of wetlands in the hydrological cycle of the central depression of the Congo Basin.

4.2. Fractionation of Si Isotopes During Large Scale Weathering Process

[7] The Congo River δ^{30}Si data allows the large-scale nature of weathering to be described because the primary source of Si in rivers is bedrock weathering. The Congo shield is essentially composed of Precambrian crystalline magmatic and metamorphic rocks with a small proportion of carbonate and evaporite rocks [*Négrel et al.*, 1993]. The central low-lying relief area is made up of alluvial deposits and clastic sedimentary rocks [*Giresse*, 2005]. δ^{30}Si values reported in crustal rocks indicate a δ^{30}Si range between the mantle-derived protoliths (~−0.35‰ [*Georg et al.*, 2007b]) and the crustal derived components (~0‰ [*Ding et al.*, 1996; *André et al.* 2006]). Silicon isotopes are then fractionated during the formation of secondary products by chemical and biological processes, with a systematic preferential incorporation of light isotopes into precipitated phases, either in clays, phytoliths, diatoms, or during adsorption onto oxides (cf. overview in Text S2). These processes likely explain the higher δ^{30}Si values measured in soil waters [*Ziegler et al.*, 2005a, 2005b] as well as those measured in rivers [e.g., *Georg et al.*, 2006]. Black Rivers of the Congo Basin have unusually low δ^{30}Si, while the main branch of the Congo-Oubangui is ~1‰ heavier.

[8] To identify which of the above processes have led to these two contrasting δ^{30}Si values, we discuss the results in relation with other water geochemical parameters. δ^{30}Si data of Congo Basin Rivers are inversely correlated with Al:Si and positively correlated with (Ca+Mg):Al ratios and suspended matter content (Figure 3). These relations suggest mixing processes between water pools which have interacted differently with bedrock [*Georg et al.*, 2006]. The two end-members are (*i*) Black Rivers with high Al:Si ratios, low δ^{30}Si (0‰), relatively low (Ca+Mg):Al ratios, and low suspended matter content, and (*ii*) waters with low Al:Si ratios, high δ^{30}Si (+1.0‰), relatively higher (Ca+Mg):Al ratios, and suspended matter content.

4.2.1. Origin of the Heavy Isotopic Signatures

[9] Clay and/or phytolith formation are two possible mechanisms to explain the isotopically heavy end-member. Recent studies in Cameroon by *Opfergelt et al.* [2008, 2010] have confirmed the results of the pioneering work by *Ziegler et al.* [2005b] by showing that the δ^{30}Si value of crystalline clays fraction becomes more negative with increasing degree of soil weathering and that clay formation should produce a soil solution enriched in ^{30}Si. Although the suspended sediments transported by the Congo Rivers were not analysed here, a Si isotopic mass budget can be attempted. We use the average suspended sediment contents of the Congo River [*Dupré et al.*, 1996] and their average mineralogical composition [*Jouanneau et al.*, 1990] to yield a Si mass distribution in the Oubangui-Congo river main branch of 56% as solute and 44% as suspended particles (Text S3). We then ascribe δ^{30}Si signatures to the different Si fractions. δ^{30}Si values for the particulate matter (mostly clays) are obtained from the literature, whilst δ^{30}Si data for the dissolved phase is taken from this study. This balance leads to a river bulk (dissolved + solid) δ^{30}Si signature of the Si source of −0.08 ± 0.26‰, similar to the expected bedrock crustal signature, suggesting that all significant reservoirs were taken into account. This isotopic budget has neglected the phytolith component because most of the amorphous silica in Congo suspended particles is constituted by diatoms with rare phytoliths [*Giresse et al.*, 1990; *Hughes et al.*, 2009]. Using the soil Si budget made in a Congolese rainforest [*Alexandre et al.*, 1997], we show that a typical stable phytolith pool stored in soils representing 20–25% of the exported Si would not have impacted the output water signature (Text S3). This does not mean that plants do not impact or even control the Si cycle in the Congo Basin but rather that the isotopic fractionation they are responsible for remains restricted to the soil-plant system and does not significantly impact the δ^{30}Si value of the river. Kaolinitic clay neoformation is therefore the most likely mechanism to account for the high δ^{30}Si end-member and is in agreement with the dominance of kaolinite in clay minerals fractions representing 58% of Congo soil clays [*Alexandre et al.*, 1997] and 80% of suspended clays in the Congo River [*Jouanneau et al.*, 1990]. *Braun et al.* [2005] have moreover observed that soil solutions in equilibrium with kaolinite in a Cameroon watershed have Al:Si and (Ca+Mg):Al ratios close to 8mg/g and 40g/g respectively, in the range of those found here for the ^{30}Si-enriched end-member. This indicates a residual character of kaolinite-rich soils in which Si and Al are reprecipitated, the cations being mostly leached from soil towards the river drainage.

4.2.2. Origin of the Light Isotopic Signatures

[10] The second end-member has a much lighter isotopic composition and is found in the Al-rich Black Rivers, with the lowest suspended matter load (e.g., 6mg/l in Likouala). Such low δ^{30}Si value can not derive from clay formation but

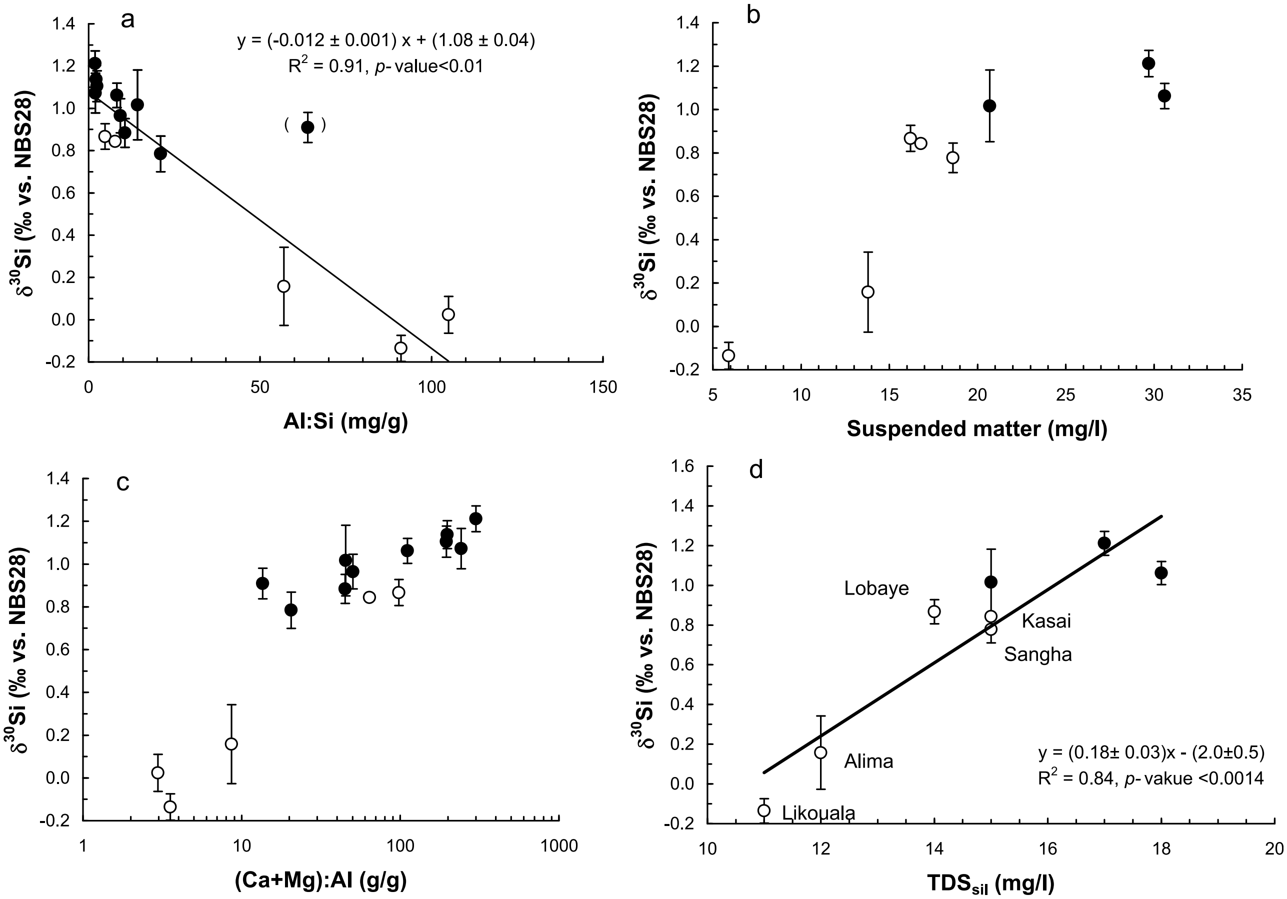

Figure 3. (a–d) Dissolved δ^{30}Si as function of major element contents. Filled circles: Oubangui-Congo main branch. Open circles: Tributaries. Error bars are $\pm 1\sigma_{SD}$ of replicates or ±1 standard error of analysis (cf. Table S1). TDS_{sil} is an estimate of the sum of concentration of dissolved Ca, Na, Mg, K, SO_4 derived from silicate weathering and SiO_2 [*Gaillardet et al.,* 1995]. In the correlation line shown on Figure 3a, one outlier has been removed from the calculation. Note the log scale in Figure 3c.

could be inherited from either clay and/or rock dissolution. Congo Black Rivers have the same range of Al:Si (50–100mg/g) as the Black Rivers studied in an experimental catchment in a rainforest and swampy area in Cameroon [*Viers et al.*, 1997; *Oliva et al.*, 1999] where it was shown that Al, in contrast to Si, is complexed with colloidal organic matter. The absence of clay minerals there clearly show that in these hydromorphic soils, organic matter enhances kaolinite dissolution in upper soil even though kaolinite is formed in the deeper horizons [*Oliva et al.*, 1999]. A typical δ^{30}Si kaolinite value of −2.2‰ [*Ziegler et al.*, 2005a; *Opfergelt et al.*, 2010] implies an Al:Si ratio of ~300mg/g and a (Ca+Mg):Al ratio lower than 2g/g (Figure 3), which are compatible with the chemistry of other African organic-rich waters [*Viers et al.*, 1997]. Since granite congruent dissolution at a large scale is unlikely, our data suggest that δ^{30}Si values in the Black Rivers are more likely to be inherited from the mixing of dissolved Si with high δ^{30}Si released at the weathering front, where isotopically light clays are precipitated and waters rich in organic acids which have dissolved clay minerals originally formed in the deeper horizons. Overall the isotopic composition of the ultimate source (bedrock) is obtained.

4.3. Implications

[11] The two types of weathering processes identified by the δ^{30}Si end-members confirm a recent work based on Ge/Si ratios in a tropical granitic weathering environment: *Lugolobi et al.* [2010] show on the one hand incongruent weathering with associated chemical fractionation and the production of a residual solid, and on the other hand dissolution of that residual solid, having the opposite fractionation effect on the leaching waters. Congo δ^{30}Si values are positively correlated ($r^2 = 0.84$, p-value <0.0014) with the concentration of solutes derived from silicate weathering, (TDS_{sil}, Total Dissolved Solids originating from weathering of silicates [*Gaillardet et al.*, 1995]) and suspended matter concentration (Figure 3), while a weak correlation, statistically not significant is observed with weathering fluxes ($r^2 = 0.64$, p-value > 0.06 (Figure S1)). This indicates that δ^{30}Si signature is more sensitive to the intensity of weathering than to fluxes. Compared to other large rivers' basins, low relative weathering rates (i.e., when reported per km^2) characterize the lowland areas of the Congo Basin in conjunction with intense chemical weathering, while the periphery of the Basin has developed lateritic soils with important clay formation [*Gaillardet et al.*, 1995, 1999].

There is also a good positive correlation of δ^{30}Si with pH (Figure S1) which holds true for Tanganyika tributaries which have higher δ^{30}Si (+1.6 ± 0.5‰) and higher pH (8–9), in an area with less vegetation cover and higher topography [*Alleman et al.*, 2005]. Hence, at geological time scales, Congo river δ^{30}Si data would be sensitive to changes of the hydrological cycle associated to climate, topography and geodynamic changes.

5. Conclusions

[12] The δ^{30}Si signatures of rivers in the Congo Basin reflect weathering processes occurring at a large scale in the drainage basin. We proposed a Si isotopic and mass budget in the Congo Basin rivers which was in equilibrium with the expected bedrock signature. This approach further highlighted the contrast between two types of weathering regimes present in the central Congo Basin: one in which formed clays remain stable, light Si isotopes being sequestered in clay minerals and one in swampy areas in which the action of organic matter dissolved the clays, resulting in the delivery of light Si isotopes to rivers. This supports a significant role of organic acids in controlling weathering processes and our data suggest that they might control riverine δ^{30}Si signatures in low relief and flooded areas. Furthermore, our data indicate that δ^{30}Si signatures in rivers are more sensitive to the intensity of silicate weathering rather than to fluxes. Changes in the weathering intensity and/or in the extent of wetlands (e.g., through topography, climate, ecosystem changes…) will therefore lead to changes in the isotopic signal of Si delivered to the ocean. The substantial contribution of Black waters to the Congo River in the central basin calls for more extended sampling and adequate representation of these waters when studying large tropical basins such as the low-lying relief areas of Central Africa and Central America.

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