

## Effect of seasonal biogenic silica variations on dissolved silicon fluxes and isotopic signatures in the Congo River

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### Abstract

We report 2 yr of monthly data from the Congo River (the second largest river in the world) on dissolved silicon concentrations, biogenic silica particle concentrations, isotopic signatures of dissolved silicon, and biogenic siliceous particle counts. Diatoms predominated in the biogenic silica fraction, especially during low flow; phytoliths and sponge spicules were more abundant than diatoms only during the rainy season, when biogenic silica fluxes are low. Biological processes dominated the seasonal variations of the dissolved  $\delta^{30}\text{Si}$  ratio that are superimposed on a constant abiotic  $\delta^{30}\text{Si}$  value of  $+0.70\text{‰} \pm 0.05\text{‰}$  throughout the year. The measured biogenic silica concentration is less than the amount required to explain the monthly variations of dissolved  $\delta^{30}\text{Si}$  signatures. We use these signatures and a Rayleigh isotopic fractionation model to calculate that  $82\% \pm 7\%$  of the diatoms produced each month would be exported out of the water column, probably through settling in the Malebo Pool or further upstream. The uptake of dissolved silicon by diatoms during low water flow periods could explain the absence of the dilution effect observed for the other major elements. Annual Si export to the estuary is  $1.17 \times 10^{10} \text{ mol yr}^{-1}$  in the form of biogenic silica and  $2.23 \times 10^{11} \text{ mol yr}^{-1}$  in dissolved Si form, with a mean dissolved  $\delta^{30}\text{Si}$  of  $+0.96\text{‰} \pm 0.27\text{‰}$ . Phytoliths make only a minor contribution to the annual biogenic silica flux, and dissolved Si fluxes predominate over biogenic Si fluxes.

Despite being one of the most important dissolved elements in tropical rivers, silicon (Si) is often a poor indicator of rock weathering because of its ubiquitous character and the lack of Si-specific tracers. For timescales of years to decades, it is assumed to be a stable constituent in stream water (Davis 1964; Edwards and Liss 1973; Grady et al. 2007). However, biological uptake of dissolved silicon (DSi) by organisms (e.g., diatoms, sponges, higher plants, chrysophytes) and its concomitant transformation into biogenic amorphous silica (BSi) can yield significant variations of DSi concentration. Previous studies in rivers have already emphasized the importance of the biological cycle of silicon when considering weathering (Conley 2002) but have also shown that biological uptake is an irregular process that can fluctuate in time (Grady et al. 2007), sometimes leading to DSi consumption  $> 90\%$  during diatom growth (Edwards 1974). Recent studies have highlighted that BSi concentrations in rivers can be of the same order of magnitude as DSi (Conley 1997; Humborg et al. 2006; Triplett et al. 2008). However, the scarcity of data, especially on large tropical rivers, prevents reaching a correct estimate of continental Si runoff to the ocean. Such

uncertainty has important implications on the global biogeochemical Si cycle, including for weathering calculations (Négrel and Lachassagne 2000) and for the marine Si cycle. Another unsolved question is the form of BSi. Conley (2002) and Cary et al. (2005) suggest that phytoliths might represent the main contribution of river BSi, diatoms being minor. The aim of the present contribution on the Congo River is to constrain better both DSi and BSi runoff and the major contributor to BSi through a monitoring of BSi, DSi, and Si isotopes over a 2-yr period.

Si isotopes could offer a proxy to monitor the controlling factor of the DSi concentration in the river. However, except Cardinal et al. (2010), no comprehensive studies have been published yet on silicon isotopes in tropical rivers, and only few and isolated data have been reported (De La Rocha et al. 2000; Alleman et al. 2005; Georg et al. 2009). Moreover, the only two studies of  $\delta^{30}\text{Si}$  ratio variations in rivers were both located in Europe and did not provide complete annual cycles (Georg et al. 2006; Engström et al. 2010). The exact functioning of  $\delta^{30}\text{Si}$  ratios in continental environments is complex because of the number of overlapping processes at stake (*see* Cardinal et al. 2010 for an overview). It has been shown that DSi in rivers is nearly always enriched in heavy isotopes relative to the mean values of the continental crust ( $\delta^{30}\text{Si}_{\text{continental crust}} = -0.07\text{‰} \pm 0.05\text{‰}$ ; *see* André et al. 2006 for a synthesis). This responds to different fractionation processes discriminating against heavy isotopes, including (1) secondary clay

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formation (Ziegler et al. 2005a,b; Méheut et al. 2007), (2) adsorption onto iron oxides (Delstanche et al. 2009; Opfergelt et al. 2009), and (3) BSi production, which includes uptake by diatoms (De La Rocha et al. 1997) and by higher plants (Opfergelt et al. 2006; Hodson et al. 2008). Little is known so far about the relative influence of these different processes on the silicon isotopes and on the silicon cycle in rivers, but BSi production seems the most likely to change on a short timescale (e.g., at a daily scale in the case of a diatom bloom) compared with the other processes that are supposed to act on longer time scales (seasonal to geological). Therefore, this contribution also aims to determine which among the above-mentioned fractionation processes controls the river isotopic composition at the scale of a large river basin.

To improve the quantification of BSi export and investigate the influence of biology on silicon isotopes in rivers, a 2-yr-long series of monthly samples from the Congo River was studied. The Congo River is the second largest river in the world in terms of water discharge and dissolved silicon input to the ocean (Gaillardet et al. 1999). Its drainage area covers  $3.75 \times 10^6$  km<sup>2</sup> and extends from the great lakes of the East African Rift, including Lake Tanganyika and its drainage basin, to the Atlantic Ocean. Cardinal et al. (2010) have shown that the spatial variations of Si isotopic compositions of the mainstream and tributaries of the Congo River result from different weathering characteristics and intensity at the subbasin scale. Here, we will focus more specifically on the relation between the isotopic composition of the Congo River and the biogenic silica production on a seasonal scale at a single sampling location likely to be representative of the output to the ocean. We will use Si isotopic data to understand processes controlling the Si biogeochemical cycle and, more specifically, to estimate BSi production within the river.

## Methods

*General study area settings*—The annual and interannual discharge fluctuations in the Congo River are low, and the ratio between the mean discharge at low- and high-water periods is around 1 : 2 (Olivry et al. 1995). This is explained by the central position of the watershed on the Equator and the distribution of the rainfall in both hemispheres, avoiding any real low water period at the basin-wide scale. One can however distinguish two peaks of high discharge, one in November and December and one smaller in April and May, and two periods of lower discharge, one in February and March and one, more marked, in July and August (Olivry et al. 1995). The Congo shield is essentially composed of Precambrian crystalline magmatic and metamorphic rocks with scarce carbonate and evaporite rocks (Négrelet et al. 1993; Giresse 2005), whereas the central low-lying relief area is constituted of quaternary alluvial deposits and clastic sedimentary rocks (Dürr et al. 2005). The Congo drainage area is dominated by a wet tropical climate with precipitation  $> 1500$  mm yr<sup>-1</sup> and a high mean annual temperature. The center of the basin is mainly covered by tropical rain forest and wooded savannahs (Runge 2007). The Congo basin is characterized by the

predominance of chemical weathering over physical weathering but also simultaneously by a low chemical weathering rate (Gaillardet et al. 1995) resulting from vegetation, topography, and climate. This corresponds to an erosive dynamic in its terminal phase, wherein mechanical erosion has slowed down and biogeochemical erosion acts on an already strongly leached soil (Sondag et al. 1995).

*Sampling*—The sampling took place within the framework of the Observatoire de Recherche sur l'Environnement-Hydrologie du Bassin Amazonien (ORE-HYBAM) project led by the Institut de Recherche pour le Développement (IRD) and the Centre National de la Recherche Scientifique (CNRS), whose purpose is to provide monthly data to study seasonal variations of particles and geochemical fluxes and of the flow rate at a large number of stations spread over the Amazon and the Orinoco and the Congo basins. The samples studied here were taken monthly from September 2006 to August 2008 for the water samples and from April 2006 to August 2008 for the particle samples. The sample of May 2006 is missing. The sampling was done at the subsurface in the middle of the stream at the exit of the Malebo Pool, a large widening of the Congo River, just upstream from the Kinshasa-Brazzaville urban zone (08.1536°N, 063.5361°W; Fig. 1). This place can be considered as fairly representative of the export of the river to the estuary because no major tributary enters the river downstream. Furthermore, the Congo River becomes much narrower downstream from Kinshasa-Brazzaville, with a succession of gigantic rapids unfavorable for the growth of diatoms before reaching the estuary 350 km further downstream.

Samples were stored in the dark and filtered on preweighted 0.22- $\mu$ m cellulose nitrate filters immediately on arrival at the laboratory in Brazzaville. Filters were kept for BSi analyses. Two acid-washed high-density polyethylene (HDPE) bottles were each filled with 100 mL of the filtrates, one being acidified with 200  $\mu$ L of Suprapur 14 mol L<sup>-1</sup> HNO<sub>3</sub> for the analysis of the trace elements and the other kept for the analysis of the major elements. Isotopic analyses of dissolved silicon (DSi) were performed on aliquots from the acidified or from the unacidified filtered water samples, depending on the available volume. Cardinal et al. (2010) have reported that acidification makes no difference for Si isotope analyses.

*Hydrochemical parameters*—The ORE-HYBAM project provides a database (<http://www.ore-hybam.org/>) for hydrological and geochemical data, including water discharge, suspended sediments, and concentrations of dissolved major and trace elements. Si and other major cation concentrations were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) at the Laboratoire des Mécanismes et Transferts en Géologie (LMTG) in Toulouse (France). Error on dissolved Si concentration is  $\pm 5\%$ .

*Biogenic silica*—The concentration of amorphous silica was estimated by applying a wet alkaline digestion method on the filters. Aluminum released during the digestion was

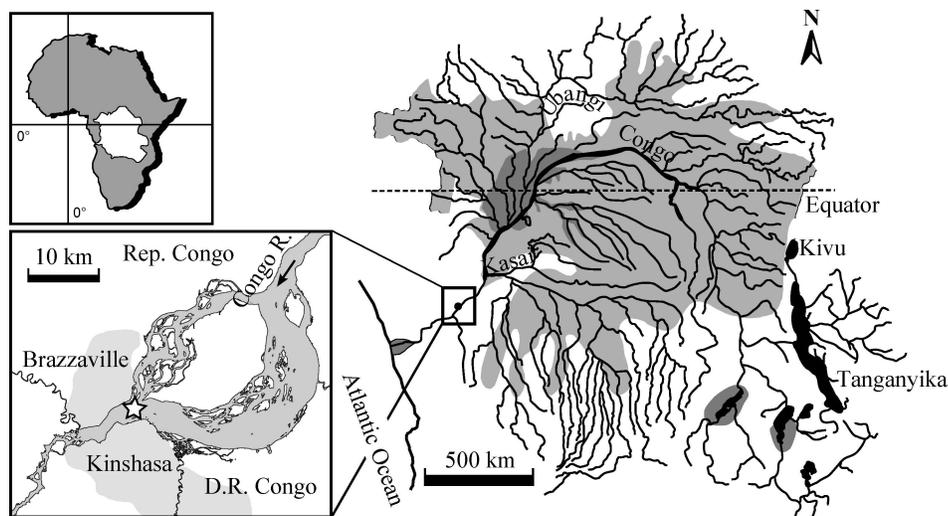


Fig. 1. Congo watershed, sampling location, and simplified vegetation map. Frame: sampling site at the exit of the Malebo pool, a large widening of the Congo River just upstream from the Kinshasa–Brazzaville urban zone (light grey). The star identifies the sampling location. Congo vegetation map: dark grey, swamps; medium grey, rain forests; light grey, wooded grassland and savannah. Vegetation map adapted from Nkounkou and Probst (1987).

used to correct for concomitant dissolution of lithogenic particles following the method of Ragueneau et al. (2005). A known fraction of the filter was submitted to a first digestion in  $0.2 \text{ mol L}^{-1}$  NaOH at  $100^\circ\text{C}$  for 40 min. At the end of this first leach, all the BSi and some lithogenic Si were supposed to be dissolved. Si and Al concentrations ( $[\text{Si}]_1$  and  $[\text{Al}]_1$ ) in the supernatant were then analyzed by high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS). After rinsing and drying, the filter was submitted to a second digestion step, identical to the first, allowing us to determine a  $(\text{Si}:\text{Al})_2$  ratio characteristic of the lithogenic particles present on the filter. This ratio is then used to correct the concentration of Si in biogenic silica form as follows:  $[\text{BSi}] = [\text{Si}]_1 - [\text{Al}]_1 \times (\text{Si}:\text{Al})_2$ . A third digestion step was added to the original method to verify that no BSi was left after the first leach.  $(\text{Si}:\text{Al})$  ratios should therefore be similar in the supernatants after the second and the third leaches. In a few cases in which all the BSi was not dissolved on the first attempt, the procedure was started over with a smaller filter fraction. Uncertainty on BSi measurements with the method from Ragueneau et al. (2005) is ca. 10% but depends on the importance of the correction. Note that the presence of Al within opal is not taken into account and could lead to a slight underestimation of [BSi]. In the Congo River, Giresse et al. (1990) measured an Al:Si ratio of 0.027 in *Aulacoseira* sp. (syn. *Melosira* sp.), which is the dominant diatom species (Gasse et al. 1989). If such an Al:Si ratio is representative of the BSi studied here, it would induce an underestimation of only ca. 4% of the measured BSi.

Among the 28 particle samples studied, 15 were chosen for microscope observation, biogenic siliceous particles counts, and biovolume calculation. A known fraction of the filter was oxidized (boiling during 2 h in  $\text{H}_2\text{O}_2$ ), rinsed with demineralized water, and reduced to a known volume (1 mL). Permanent quantitative microscope slides contain-

ing a drop of  $200 \mu\text{L}$  of the cleaned sample were made through embedding in Naphrax<sup>®</sup>. A statistically representative part of the slides was investigated, and the numbers of diatoms, phytoliths, small siliceous sponge spicules (microscleres), and cysts of Chrysophyta were counted. Approximate biovolumes of the observed items were calculated using the measured dimensions, assuming the same density (Hillebrand et al. 1999). Once the count was completed, the entire microscope slide was screened for “large” items, such as large siliceous sponge spicules (megascleres), phytoliths, and diatoms. Biovolume calculations were then used to assess the relative distribution of BSi between diatoms and other biogenic siliceous particle types within the BSi measured by the leaching method.

*Isotopic analyses*—Dissolved Si was purified by triethylamine molybdate (TEA-moly) coprecipitation and combustion in covered Pt crucibles at  $1000^\circ\text{C}$  (De La Rocha et al. 1996) then dissolved in a dilute Suprapur HF-HCl mixture (Cardinal et al. 2003). Si isotopes were measured with a Nu Plasma Multi-Collector-ICP-MS (Nu Instruments) at the Université Libre de Bruxelles, operating in dry plasma mode with a Cetac Aridus II desolvating nebulization system. Mass bias was corrected through external Mg doping (Cardinal et al. 2003), and the long-term instrumental drift was corrected by the sample-standard bracketing technique relative to the NBS28 silica sand standard (National Institute of Standard and Technology, reference 8546). This analytical method was supported by an interlaboratory comparison and proved accurate on secondary reference materials (Reynolds et al. 2007). The isobaric interference of  $^{14}\text{N}^{16}\text{O}$  on  $^{30}\text{Si}$  was solved with the use of pseudo-high resolution, which consists in analyzing the interference-free left side of the  $^{30}\text{Si}$  peak (adapted from Abraham et al. 2008). Measurements were done in different sessions distributed over

Table 1. Results of monitoring. Water flow rate and DSi values come from the ORE-HYBAM database. The water flow rate is the value observed for the day of sampling, Measured BSi is the Si in biogenic silica form measured on filters. Diatoms, phytoliths, sponge spicules, and cysts of *Chrysophyta* are given as percentages of the BSi on the basis of biovolumes calculated from counts. Standard error on  $\delta^{30}\text{Si}$  is given as the standard deviation on the replicates; where only one analysis could be done (italic values) the average analytical standard error is given.

Sampling date	Water flow rate ( $\text{m}^3 \text{ s}^{-1}$ )	DSi ( $\mu\text{mol L}^{-1}$ )	Monthly DSi flux ( $10^{10}$ mol)	Measured BSi ( $\mu\text{mol L}^{-1}$ )	% diatoms	% phytoliths	% sponge spicules	% cysts of <i>Chrysophyta</i>	$\delta^{30}\text{Si}$ (‰)	Standard error
Apr 06	35,500	240	2.20	10.5	78.4	5.1	13.9	2.5		
May 06	36,760	184	1.82							
Jun 06	34,950	208	1.89	7.7	34.8	16.0	49.1	0.0		
Jul 06	28,700	173	1.33	23.6	70.0	16.3	13.7	0.0		
Aug 06	28,940	162	1.26	37.9	88.4	9.4	2.2	0.0		
Sep 06	33,120	175	1.50	12.2	38.6	27.4	34.0	0.0	1.00	0.15
Oct 06	38,470	170	1.76	9.2	4.9	46.7	48.4	0.0	1.02	0.07
Nov 06	47,070	165	2.01	3.8	80.5	10.6	6.5	2.4	0.87	0.05
Dec 06	61,330	171	2.81	0.9	11.8	67.5	20.6	0.0	0.78	0.22
Jan 07	57,040	173	2.64	1.7	67.9	12.3	19.8	0.0	0.73	0.07
Feb 07	42,240	190	1.94	8.2	4.2	58.5	37.3	0.0	0.88	0.07
Mar 07	37,160	189	1.88	24.1	99.9	0.0	0.0	0.1	0.94	0.12
Apr 07	34,930	194	1.76	5.9					0.87	0.01
May 07	36,560	192	1.88	5.9					0.75	0.02
Jun 07	35,300	177	1.62	3.3					0.69	0.04
Jul 07	33,720	179	1.62	4.9					0.93	0.09
Aug 07	32,100	111	0.95	40.8	99.9	0.0	0.0	0.0	1.89	0.12
Sep 07	37,580	159	1.55	6.1					0.93	0.07
Oct 07	44,920	162	1.95	3.2					0.82	0.04
Nov 07	53,950	171	2.39	1.4					0.73	0.12
Dec 07	60,700	156	2.54	1.6	22.9	69.8	7.3	0.0	0.72	0.04
Jan 08	55,750	184	2.75	2.7					0.76	0.11
Feb 08	44,230	154	1.65	4.9					0.85	0.00
Mar 08	36,930	158	1.56	9.6					0.99	0.04
Apr 08	38,840	138	1.39	21.0	99.5	0.3	0.1	0.0	1.46	0.04
May 08	40,100	139	1.49	19.1					1.21	0.03
Jun 08	35,220	158	1.44	13.2	99.8	0.0	0.2	0.0	1.10	0.05
Jul 08	32,800	166	1.46	18.2					0.78	0.02
Aug 08	32,000	148	1.27	11.2	60.0	22.7	16.9	0.3	1.26	0.05
average	40,238	171	1.80	11.2	60	23	17	0.3	0.96	0.07
SD	9244	24	0.47	10.4	36	24	17	0.8	0.27	0.05
Mean annual fluxes	1307 km <sup>3</sup>	2.23×10 <sup>11</sup> mol		1.17×10 <sup>10</sup> mol					0.91‰	±0.09

several months. The accuracy of the Si isotope ratio measurements during runs was checked on a daily basis with the use of a well-constrained secondary reference material (diatomite). In this study, all results were measured and are expressed as  $\delta^{30}\text{Si}$  (‰) relative to NBS28, with an average precision and accuracy of  $\pm 0.07\text{‰}$  ( $\pm 1 \sigma_{\text{SD}}$ ) following:

$$\delta^{30}\text{Si} = \left[ \frac{\left( \frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_{\text{sample}}}{\left( \frac{^{30}\text{Si}}{^{28}\text{Si}} \right)_{\text{NBS28}}} - 1 \right] \times 1000 \quad (1)$$

Among the 24 samples analyzed for  $\delta^{30}\text{Si}$ , 20 have been replicated. Note that because of the high lithogenic Si contribution during the first NaOH leaching ( $56\% \pm 24\%$  of the total Si released during the first leaching) and because of the low amount of BSi present in comparison, we were not able to analyze the  $\delta^{30}\text{Si}$  of the BSi.

## Results

**Dissolved silicon**—For the period studied, the dissolved silicon (DSi) concentration is rather stable and ranges from 111 to 240  $\mu\text{mol L}^{-1}$ , with a mean value of  $171 \pm 24 \mu\text{mol L}^{-1}$  (Table 1; Fig. 2a). These results are similar to the mean value of  $156 \pm 14 \mu\text{mol L}^{-1}$  found by Sondag et al. (1995) just upstream from the Malebo pool during a 5-yr-long monthly sampling series from 1988 to 1992. From April 2006 to August 2008, a significant decrease was observed from 196  $\mu\text{mol L}^{-1}$  to 146  $\mu\text{mol L}^{-1}$  ( $R^2 = 0.34$ ,  $p < 0.001$ ), and a minimum at 111  $\mu\text{mol L}^{-1}$  was registered in August 2007, which coincides with a minimum in water discharge. However, no clear global relationship between dissolved silicon concentration and flow rate can be deduced (Fig. 3a).

**Biogenic silica**—Twenty-eight samples of suspended matter representing  $> 2$  yr of monthly records were analyzed for BSi concentration. Results range from

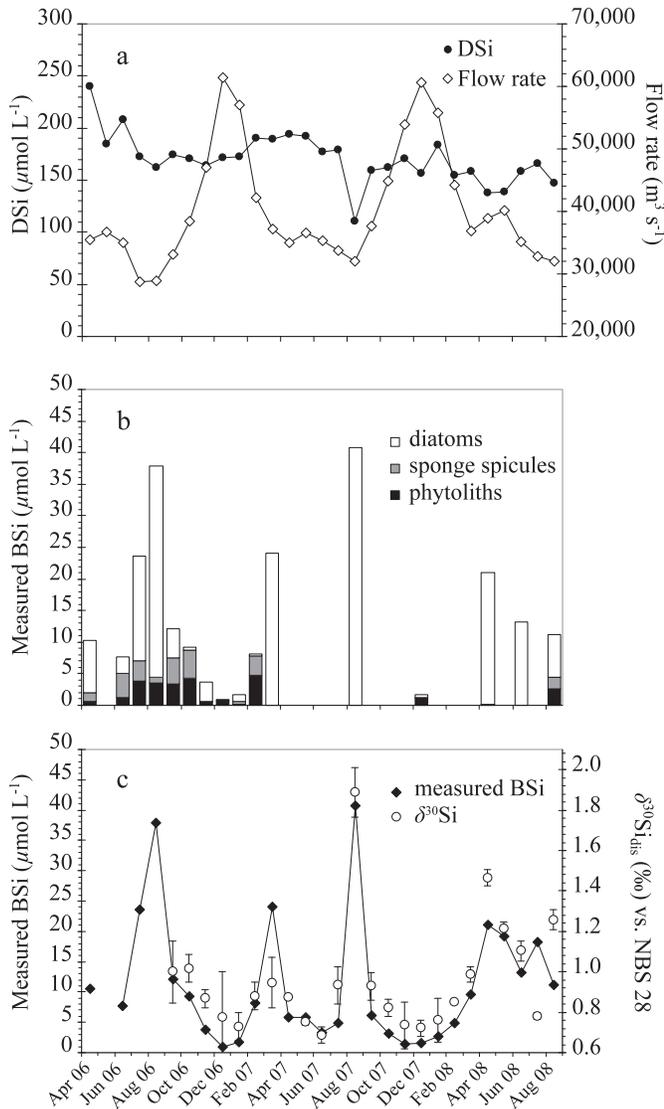


Fig. 2. Temporal evolution of (a) DSi concentration. (b) Proportions of diatoms (white), sponge spicules (grey), and phytoliths (black) estimated by biogenic siliceous particle counts reported to the total measured BSi concentration. (c)  $\delta^{30}\text{Si}$  measured in dissolved silicon and measured BSi concentration.

$0.9 \mu\text{mol L}^{-1}$  BSi up to  $40.8 \mu\text{mol L}^{-1}$  with a mean value of  $9.7 \pm 9.4 \mu\text{mol L}^{-1}$ . This is three to four times less than the average BSi concentration measured just upstream from the Malebo pool by Giresse et al. (1990). As shown hereinafter, settling within the pool could partly explain the lower concentration of BSi observed in our samples. Despite the relative stability of the river flow, a strong negative power relationship is observed between the BSi concentration we measured and the seasonal discharge variations of the Congo River ( $R^2 = 0.68$ ,  $n = 28$ ,  $p < 0.001$ ; Fig. 3b).

An overview of the relative BSi distribution estimated by microscopic counts is given in Table 1 and Fig. 2b. Among the samples counted, most of the BSi belongs to diatoms ( $57\% \pm 37\%$ ;  $\pm 1 \sigma_{\text{SD}}$ ). This is especially true for high BSi

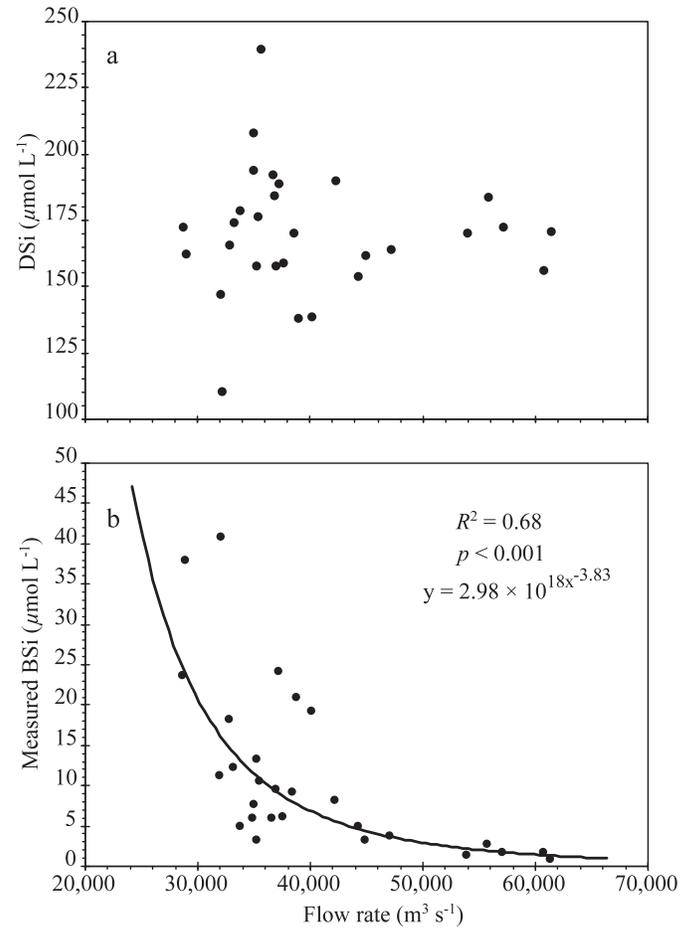


Fig. 3. (a) The absence of relation between the flow rate and the concentration of dissolved Si. (b) The relation between the flow rate and the measured BSi concentration. A strong negative power relationship is observed between our measured BSi concentration and the seasonal variations of the flow rate of the Congo River. The range  $40,000\text{--}45,000 \text{ m}^3 \text{ s}^{-1}$  constitutes a sort of limit above which no important BSi concentration is observed.

concentrations ( $> 15 \mu\text{mol L}^{-1}$ ), in which diatoms represent 70%–100% of the total BSi biovolume. Phytoliths and sponges spicules are of similar relative importance, with a mean concentration equivalent to 26% and 16%, respectively. In opposition to diatoms, the relative abundance of phytoliths is the highest at low BSi concentrations (reaching twice  $\sim 70\%$  when BSi is  $< 2 \mu\text{mol L}^{-1}$ ). Cysts of Chrysophytes never reached a significant proportion of the BSi (maximum of 2.5% in April 2006).

Diatoms from the genus *Aulacoseira* (belonging to the genus *Melosira sensu lato*) are the most common (mostly *Aulacoseira granulata* (Ehrenb.) Simonsen). *Aulacoseira* is a major component of the diatom flora in large African rivers, and their dominance in the Congo River has already been reported (Gasse et al. 1989; Giresse et al. 1990; Uliana et al. 2001). An epiphytic species (*Gomphonema zairensis* Compère) dominated only in March 2007 (93.2% of all diatom valves). Preservation of the diatoms in the studied samples was very good; between 76% and 99.9% of the observed valves were intact (in November 2006 and March

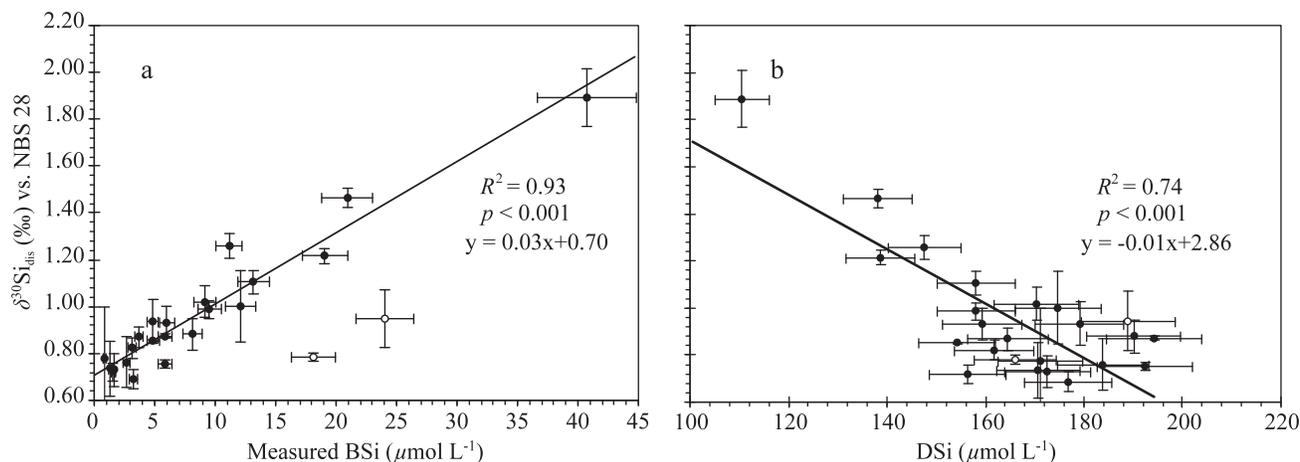


Fig. 4. Relationship between (a) the  $\delta^{30}\text{Si}$  measured in dissolved silicon and the measured BSi concentration, (b) the  $\delta^{30}\text{Si}$  measured in dissolved silicon and the DSi (the two outliers are in white and are excluded from the linear regressions).

2007, respectively). Most observed broken valves belong to species of the dominant genus *Aulacoseira*.

**Isotopic composition**— $\delta^{30}\text{Si}$  signatures of the dissolved phase vary  $> 1.1\text{‰}$ , ranging from  $+0.69\text{‰}$  up to  $+1.89\text{‰}$ , with a mean value of  $+0.96\text{‰} \pm 0.27\text{‰}$  ( $\pm 1\sigma_{\text{SD}}$ ,  $n = 24$ ; Table 1). These new results show a clear seasonal pattern that is expressed by the large standard deviation and strong correlations between  $\delta^{30}\text{Si}$  and BSi (Fig. 2c), except for two outliers in March 2007 and July 2008 (linear model,  $R^2 = 0.93$ ,  $n = 22$  without the two outliers; Fig. 4a). In contrast, no clear correlation is observed between  $\delta^{30}\text{Si}$  and DSi concentration until the latter decreases below ca.  $150 \mu\text{mol L}^{-1}$  (Fig. 4b)—most probably as a consequence of biological uptake.

## Discussion

**Seasonal and annual DSi and BSi fluxes**—The mean annual DSi flux to the estuary measured for the period 2006–2008 is  $2.23 \times 10^{11} \text{ mol yr}^{-1}$ , close to the  $2.3 \times 10^{11} \text{ mol yr}^{-1}$  reported by van Bennekom and Berger (1984) and within the range of  $1.9\text{--}2.3 \times 10^{11} \text{ mol yr}^{-1}$  estimated by Probst et al. (1992). DSi concentrations measured in our study are also similar to those reported in previous studies (van Bennekom and Berger 1984; Sondag et al. 1995). Therefore, it is unlikely that the slight time-related decrease observed in DSi concentration during monitoring (Fig. 2a) corresponds to a long-term trend.

The mean annual BSi flux to the estuary during the studied period is  $1.17 \times 10^4 \text{ mol}$ , about 5.1% of the annual (DSi + BSi) flux. On a monthly scale, BSi represents 0.5%–26.9% of the total (DSi + BSi) flux. An increase of BSi during low flow periods in the Congo River has been reported by Giresse et al. (1990), and a very similar negative power relationship between chlorophyll content and estimates of discharge in the Danube has also been found by Schmidt (1994). Considering the correlation we observe between the measured BSi and the flow rate, past periods of higher or lower discharge of the Congo River described by Laraque et al. (2001)—1960–1970 and 1982–

1993, respectively—might have had a significant influence on the BSi concentration and, to a lesser extent, on DSi concentration. These results could explain the slightly lower (ca. 10%) average DSi concentration found by Sondag et al. (1995), in that the average flow rate during that study was about 10% lower ( $\sim 37,500 \text{ m}^3 \text{ s}^{-1}$  compared with  $\sim 41,800 \text{ m}^3 \text{ s}^{-1}$  during our study). This could also partially explain the difference between BSi concentrations we measured and those measured by Giresse et al. (1990):  $11.2 \pm 10.4 \mu\text{mol L}^{-1}$  vs.  $37.3 \pm 21.2 \mu\text{mol L}^{-1}$ , respectively. Several other factors can explain this difference. First, the XRD method used by Giresse et al. (1990) has been shown to overestimate slightly the BSi concentration (Conley 1998). Furthermore, the samples from Giresse et al. (1990) were taken upstream of the Malebo Pool, where settling can happen and thereby explain the lower concentration of BSi observed in our samples.

The counts of biogenic siliceous particles have shown that even if diatoms are not always dominant in the samples, they represent by far the main BSi reservoir when the BSi concentration rises to  $> 13 \mu\text{mol L}^{-1}$  (Fig. 2b). The other groups show rather stable concentrations throughout the year in comparison. Respective contributions of these groups to the annual BSi flux (i.e., monthly concentrations weighted for discharge) can be estimated for April 2006 to March 2007, for which only the particle count of May 2006 is missing. For this period, diatoms, phytoliths, and sponge spicules represent 65%, 17%, and 17% of the annual BSi flux, respectively. The relative contribution from May 2006 is assumed to be the average of April and June 2006. A previous study by Cary et al. (2005) in Cameroonian rivers stated a predominance of phytoliths over diatoms (about 90% of the BSi load) and an extremely low BSi concentration ( $1.07\text{--}2.85 \mu\text{mol L}^{-1}$ ). We ascribe this feature to the fact that samples from Cary et al. (2005) were collected during the rainy season, which constitutes unfavorable conditions for the growth of diatoms but probably favorable conditions for the export of phytoliths through runoff. This explanation reconciles both the results from Cameroon and Congo, in that low BSi concentration and high phytolith content in Cameroonian rivers (Cary et

al. 2005; Opfergelt et al. 2009) are consistent with the values found in our Congolese samples collected during high discharge periods. In the Congo River, the proportion of BSi in the mean annual (DSi + BSi) flux (5.1%) is also rather low compared with the world mean of 16% estimated by Conley (1997). Although implementation of BSi monitoring on other large rivers is necessary to quantify BSi fluxes properly at the global scale, our study suggests that BSi export by rivers to estuaries is minor compared with DSi, although not negligible.

*$\delta^{30}\text{Si}$  signatures and the role of BSi*—The mean annual dissolved  $\delta^{30}\text{Si}$  signature exported by the Congo River, calculated from monthly values weighted for the DSi concentration and for the flow rate following Eq. 2, is  $+0.91\% \pm 0.09\%$ .

$$\sum \left[ \frac{\delta^{30}\text{Si} \times Q \times \text{DSi}}{\sum (Q \times \text{DSi})} \right] = \text{mean } \delta^{30}\text{Si} \text{ export} \quad (2)$$

These results are in good agreement with a previous study of the Congo–Oubangui main stem on the basis of samples from November 1989 ( $+1.01\% \pm 0.12\%$ ,  $n = 13$ ; Cardinal et al. 2010). They are within the range of most of the rivers already studied around the world, although the only other large tropical river studied so far, the Ganges–Brahmaputra system, shows heavier  $\delta^{30}\text{Si}$  ( $1.51 \pm 0.19$ ,  $n = 6$ ) which probably reflects the differences in overall weathering intensity (Georg et al. 2009).

BSi formation removes silicon from solution while the remaining DSi is enriched in heavy isotopes. The strong correlation ( $R^2 = 0.93$ ,  $p < 0.001$ ,  $n = 22$ , two outliers excluded) in the Congo River between BSi and  $\delta^{30}\text{Si}$  (Fig. 4a) points to a likely control of biological activity on the seasonal variation of the dissolved Si isotopic composition. For the two outliers, the microscopic count available for March 2007 shows that it is the only sample in which *Aulacoseira* was not the dominant diatom genus. The dominant diatom species in this sample was *Gomphonema zairensis*, an epiphytic diatom, which contrasts with the planktonic *Aulacoseira* species found in the other samples. Because *Aulacoseira granulata* is a heavily silicified diatom, it is then possible that the silicification or the ecology of the diatom frustules between these two genera differs. Because of their specificity, the two outliers identified in Fig. 4a will not be taken into account for the discussion on isotopes.

By applying a linear regression on the trend from Fig. 4a, we can extrapolate a  $\delta^{30}\text{Si}$  of  $+0.70\% \pm 0.05\%$  ( $\pm 2 \sigma_{\text{SD}}$ ) for the intercept at BSi = 0. Considering the good  $\delta^{30}\text{Si}$ –BSi correlation, this lower limit could be interpreted as the constant abiotic Si isotopic value that is yearly maintained in the Congo River and on which the effects of biologic activity are added. This is an approximation because the small contribution of phytoliths—which are not supposed to influence the  $\delta^{30}\text{Si}$  within the river—to BSi is included in the regression calculation. However, because of the predominance of diatoms over phytoliths and spicules in the biogenic component, this value can be roughly regarded as the diatom-free initial isotopic composition of the Congo River. The possibility of a

constant abiotic  $\delta^{30}\text{Si}$  background on an annual timescale seems coherent in regard to the overall constancy of chemical denudation in the Congo Basin found by Gaillardet et al. (1995).

The rather constant flow rate of the Congo River also prevents the relative contribution from rivers with extreme  $\delta^{30}\text{Si}$  values, like the black rivers (close to 0‰; Cardinal et al. 2010), to vary considerably. The dissolution of BSi is likely to influence the initial  $\delta^{30}\text{Si}$  background value but must have a negligible effect on the seasonal variation in  $\delta^{30}\text{Si}$  because it is a slow process that acts on a longer timescale than BSi formation. This assertion is supported by the very good preservation state of freshwater diatoms in the surface sediments of the Congo deep-sea fan (Gasse et al. 1989; Uliana et al. 2001) and those in suspension in the river itself (our own observations). Potential human influences such as deforestation are limited in this pristine watershed (Meybeck 2003), especially because they are buffered by the high flow rate. Therefore, BSi formation is likely the major controlling factor of the seasonal  $\delta^{30}\text{Si}$  variations in the Congo. The  $\delta^{30}\text{Si}$  ratio in the river would then result from the activity of diatoms that is to be added on top of a constant mineral-derived basin-average initial value of  $+0.70\%$ . Compared with the mean annual  $\delta^{30}\text{Si}$  export ( $+0.91\%$ ), this would mean, on a yearly basis, the biological activity induces an increase of at least  $0.21\%$   $\delta^{30}\text{Si}$  on the total DSi exported by the Congo River.

*Estimating the total BSi production using  $\delta^{30}\text{Si}$* —Regarding the good correlation between the  $\delta^{30}\text{Si}$  value and the measured BSi concentrations, it is appealing to use  $\delta^{30}\text{Si}$  as a proxy to quantify BSi production. Two models are generally used to describe the Si isotope fractionation: the Rayleigh model for closed systems, wherein the product (BSi) does not exchange any more with the reservoir (DSi), and the steady-state model for open systems at an isotopic equilibrium between DSi and BSi,

$$\text{Rayleigh : } \delta^{30}\text{Si} = \delta^{30}\text{Si}_0 + \varepsilon(\ln f_{\text{Si}}) \quad (3)$$

$$\text{Steady state : } \delta^{30}\text{Si} = \delta^{30}\text{Si}_0 - \varepsilon(1 - f_{\text{Si}}) \quad (4)$$

where  $\delta^{30}\text{Si}$  is the isotopic composition of the dissolved silicon,  $\delta^{30}\text{Si}_0$  is the isotopic composition of the dissolved silicon source before any biological uptake,  $f_{\text{Si}}$  is the fraction of the dissolved silicon remaining in the dissolved phase after removal by biologic activity, and  $\varepsilon$  is the fractionation factor in per-mil units. If we consider the production of BSi as the only output of DSi for a given water parcel, then  $f_{\text{Si}} = \text{DSi}/(\text{DSi} + \text{BSi})$ , and one can then rewrite the equations as:

$$\text{Rayleigh : } \text{BSi} = \text{DSi} \times \left[ \exp\left(\frac{\delta^{30}\text{Si}_0 - \delta^{30}\text{Si}}{\varepsilon}\right) - 1 \right] \quad (5)$$

$$\text{Steady state : } \text{BSi} = \text{DSi} \times \left( \frac{\varepsilon}{\delta^{30}\text{Si} - \delta^{30}\text{Si}_0 + \varepsilon} - 1 \right) \quad (6)$$

$\delta^{30}\text{Si}_0$  is set at  $+0.70\%$  using the value extrapolated for BSi = 0 (Fig. 4a). The fractionation factor ( $\varepsilon$ ) has not been

Table 2. Amount of BSi in total Si. Measured BSi is the Si in biogenic silica form measured on filters. The calculated BSi concentration is calculated from Eq. 5 with  $\epsilon = -1.1\%$ . Total Si is the sum of the calculated BSi concentration and the measured dissolved silicon DSi concentration. The percentage of total Si as BSi is the part of BSi in total Si.

Sampling date	Measured BSi ( $\mu\text{mol L}^{-1}$ )	Calculated BSi Rayleigh model ( $\mu\text{mol L}^{-1}$ )	Total Si ( $\mu\text{mol L}^{-1}$ )	% of total Si as BSi
Sep 06	12.2	54.8	224.3	22
Oct 06	9.2	57.0	221.9	23
Nov 06	3.8	27.0	189.1	13
Dec 06	0.9	12.1	182.2	6
Jan 07	1.7	4.4	176.6	2
Feb 07	8.2	33.5	220.7	14
Mar 07	24.1	47.1	231.7	18
Apr 07	5.9	31.6	223.1	13
May 07	5.9	9.5	201.1	4
Jun 07	3.3	-2.2	174.8	0
Jul 07	4.9	42.2	217.4	18
Aug 07	40.8	215.1	297.7	63
Sep 07	6.1	37.0	193.0	17
Oct 07	3.2	18.8	179.0	10
Nov 07	1.4	5.4	175.7	3
Dec 07	1.6	2.9	159.1	2
Jan 08	2.7	10.2	193.2	5
Feb 08	4.9	22.7	174.9	12
Mar 08	9.6	46.8	200.5	21
Apr 08	21.0	138.5	261.0	47
May 08	19.1	82.7	212.9	35
Jun 08	13.2	70.0	221.3	29
Jul 08	18.2	12.8	177.7	7
Aug 08	11.2	97.5	234.9	37

determined directly here, but studies on marine diatoms have shown  $\epsilon$  ranging from  $-0.7\%$  to  $-2.0\%$ , with a mean value of  $-1.2\% \pm 0.5\%$  for in situ measurements (see synthesis in Fripiat et al. 2011). A similar  $\epsilon$  value ( $-1.1\% \pm 0.4\%$ ) has also been found by Alleman et al. (2005) in Lake Tanganyika (recalculated as  $\delta^{30}\text{Si} = \delta^{29}\text{Si} \times 1.93$ ; Georg et al. 2006). We will use this latter value of  $\epsilon$  because we expect it to be more representative of the diatoms of the Congo River while being not significantly different from the whole average.

The steady-state model appears to be incompatible with the observed isotopic ratios. Some  $\delta^{30}\text{Si}$  being impossible with an  $\epsilon$  of  $-1.1$ , and even when using an extreme value for  $\epsilon$  of  $-1.5\%$  (Alleman et al. [2005] value  $-1 \sigma_{\text{SD}}$ ) it would imply a consumption of the DSi up to 80%, which is unrealistic given the limited DSi decrease observed in our samples ( $171 \pm 24 \mu\text{mol L}^{-1}$ ). When applying the Rayleigh-type fractionation model (Table 2; Fig. 5), a linear correlation is observed between calculated and measured BSi concentration, with more realistic DSi uptakes for the highest  $\delta^{30}\text{Si}$  measured (maximum  $215 \mu\text{mol L}^{-1}$  of DSi consumed in August 2007 for  $\epsilon = -1.1\%$ , equivalent to 66% consumption). This suggests that the system is closed at the timescale considered for biological activity; that is, diatoms in the water column remain surrounded by the water parcels in which they consumed Si. Assuming that the DSi is homogeneous in the water column (Négre 1992), so that measured  $\delta^{30}\text{Si}$  are representative of the whole water column and that

biological activity is the only parameter driving seasonal  $\delta^{30}\text{Si}$  variations, we can then use isotopic signatures to estimate the total production of BSi. The comparison of the measured BSi concentrations with the results of Eq. 5 shows that measured and calculated values diverge by a factor of  $5.5 \pm 2.1$  for  $\epsilon = -1.1\% \pm 0.4\%$ . This indicates that despite the rather good correlation observed between the measured BSi concentrations and the  $\delta^{30}\text{Si}$ , the measured BSi concentrations are insufficient to explain

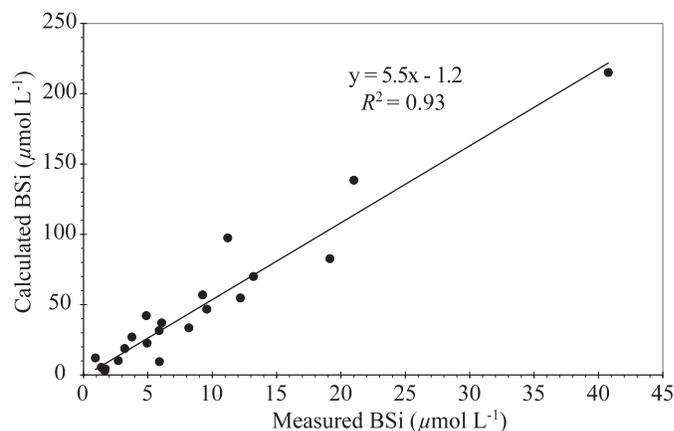


Fig. 5. Relation between the measured and calculated BSi concentration using the Rayleigh model for a fractionation factor of  $-1.1\%$ . The steady state clearly presents unlikely high BSi production for the larger  $\delta^{30}\text{Si}$  values.

the variations of the isotopic ratio in the Congo River according to known fractionation factors. Even when considering an extreme  $\varepsilon = -1.7\text{‰}$  (mean  $-1 \sigma_{SD}$ ), the difference remains within a factor of 2.9. This difference between measured BSi concentration and calculated BSi production suggests a massive sedimentation of the BSi: The measured BSi concentration is lowered by this export while the isotopes in the dissolved phase keep the imprint of the total BSi produced. This settling would correspond to a loss of  $82\% \pm 7\%$  of the BSi particles, which could happen when crossing the Malebo Pool, but also upstream in the central zone of the Congo Basin where the river is wide and shallow. If our estimates of this settlement are confirmed by further studies, then this process probably plays an important role in the riverine Si cycle of the Congo Basin. At this stage, more detailed studies of sedimentation and dissolution processes of BSi in the Congo River are clearly needed. Moreover, this result is based on the mean in situ  $\varepsilon$  value of the literature, but it is obvious that a more accurate measurement of  $\varepsilon$  is needed to estimate the real BSi lost by settling. Using the BSi values calculated with the Rayleigh model for  $\varepsilon = -1.1\text{‰} \pm 0.4\text{‰}$ , however, we can try to estimate the ratio between DSi and BSi. On a monthly basis, produced BSi would represent on average  $17.5\% \pm 15.6\%$  of the initial Si reservoir ( $DSi_0$ ) and could have reached 63% in August 2007. This confirms the minor but nonnegligible role of BSi in the Si budget of the Congo River.

Although more intensive studies under different weathering conditions are clearly needed for a better understanding of the factors controlling the silicon cycle and to better constrain the fractionation factor of freshwater diatoms, this monitoring gives new insights on the Si fluxes in large tropical rivers and on the functioning of the silicon isotopes in such environments.

*The buffering role of BSi on seasonal variations of DSi*—Different factors generally affect the concentration of dissolved silicon in rivers, including geochemical, hydrological, and biological processes (Grady et al. 2007). Edwards and Liss (1973) noted that the DSi concentration in rivers is remarkably constant from one river to another on a worldwide scale and is often insensitive to change in discharge compared with other major dissolved constituents. This phenomenon was already well observed in the Congo River by Probst et al. (1992) and by Sondag et al. (1995). Our monitoring also shows that the relationship between DSi and water discharge seems barely nonexistent (Fig. 3a), whereas it is clearly observed for other major elements. One could have expected DSi to be lower during high discharge events because of the dilution effect. This relative insensitivity of DSi to changes in river discharge has been observed in various contexts (Lesack et al. 1984; Jennerjahn et al. 2006), but the causes of this phenomenon remain poorly studied. In some cases, it has been partly attributed to the uptake of DSi by diatoms during the season of low discharge (Saunders and Lewis 1989; Grady et al. 2007; Carbone et al. 2009) and by marsh recycling (Struyf et al. 2005). Edwards and Liss (1973), however, also suggested an abiotic buffering mechanism based on

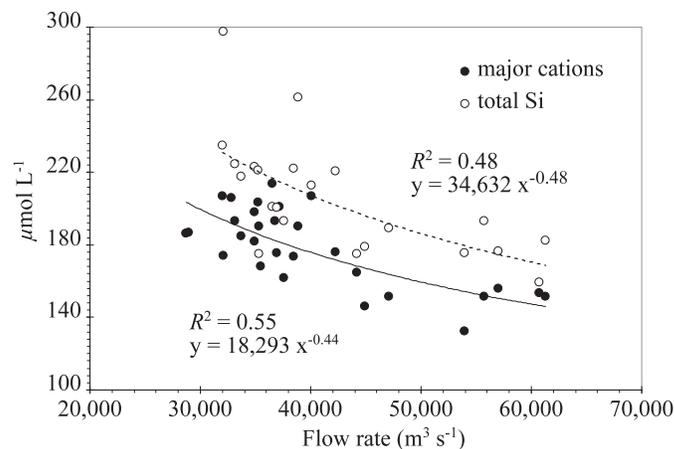


Fig. 6. The dilution effect on a higher flow rate. Once corrected for the calculated BSi uptake, the concentration of Si (white circles) correlates with the flow rate following a similar negative power relationship, as observed for major dissolved cations (Na, Ca, Mg, K; black circles).

adsorption and desorption from soil particles. In the Congo River, the large swampy area in the central part of the basin could act as a regulator for DSi flux; wetlands have indeed been shown to act as a BSi recycler, resupplying DSi to the river (Struyf et al. 2005).

Using our estimations of the real BSi production, we can test to see whether it explains the absence of a relation between the DSi and flow rate. The total Si (sum of DSi and calculated BSi) exhibits a range of seasonal variations of  $\pm 70 \mu\text{mol L}^{-1}$  (Table 2), which is slightly higher than those for total dissolved cations ( $\pm 40 \mu\text{mol L}^{-1}$ ). Total Si is correlated with the flow rate following a similar negative power relationship, as observed for major dissolved cations ( $R^2 = 0.48$ ;  $n = 22$ ; Fig. 6). This suggests that dissolved Si concentrations in the Congo River are also subject to a dilution effect but that this effect is hidden by the activity of diatoms, which preferentially takes place during low flow rate (i.e., at a time when DSi concentrations should be high). Then, the transfer of silicon from the DSi pool to the BSi pool dampens the seasonal variation of the DSi compared with the other cations (less affected by aquatic biology), yielding to a relative stability of the DSi concentrations in the Congo River throughout the year. Whether this feature can be extrapolated to other rivers is unsure. Indeed the seasonality of diatom production in the Congo River is rather limited. Therefore, it is possible that in high-latitude rivers, diatoms have a stronger seasonal effect on DSi and  $\delta^{30}\text{Si}$ . It is necessary to acquire seasonal data on BSi, DSi, and diatom production from other rivers to confirm such a hypothesis.

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