Terrestrial and fluvial carbon fluxes in a tropical watershed: Nyong basin, Cameroon

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ABSTRACT

The Nyong watershed, with an area of 27 800 km^2 and a mean annual discharge of 390 m^3 s^{-1}, is the second largest river in Cameroon. The Nyong watershed serves as an outstanding study area for the examination of carbon fluxes in humid tropical environments because of its limited anthropogenic impact and homogeneous silicate bedrock. Between April 2005 and April 2007, we sampled water at seven stations, from the small watershed of the Mengong (0.6 km^2) to the Nyong at Edea (24 500 km^2), and monitored temperature, pH, dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) contents, as well as the isotopic composition of DIC ($\delta^{13}C_{DIC}$) and DOC ($\delta^{13}C_{DOC}$). We estimated terrestrial net ecosystem productivity in the Nyong River watershed and measured fluvial fluxes of carbon to the ocean and the atmosphere. The Nyong River basin sequesters significant amounts of carbon on an annual basis: ~7 920 000 t C year^{-1} (300 g C m^{-2} year^{-1}). The combined dissolved organic, dissolved inorganic and atmospheric fluxes of carbon from the Nyong River only export 3% of this flux from the basin on an annual basis. This includes a minimum CO_2 outgassing of 1487 g C m^{-2} year^{-1}, comparable to 115% of the annual flux of DOC and four times greater than the flux of DIC.

1. Introduction

The exchange of carbon between the terrestrial biosphere and the atmosphere is an important yet poorly constrained portion of the global carbon cycle (Houghton et al., 2001), particularly in tropical environments. Though terrestrial carbon cycling has a strong influence on atmospheric pCO_2, quantitative estimates of production and respiration at the watershed scale are rare. Rivers play an important role in the global carbon cycle by linking terrestrial systems and oceans, transporting on average 1 ± 0.2 Gt of carbon per year in particulate and dissolved forms (Amiotte-Suchet et al., 2003). Rivers also actively degas carbon to the atmosphere as CO_2 (Devol et al., 1987).

While tropical rivers contribute nearly 60% of the global water discharge and the bulk of the carbon flux to the world's oceans and tropical river watersheds cover a significant portion of the Earth's surface, there have been few studies which quantify both terrestrial and fluvial fluxes of carbon in tropical rivers. Increased concern over carbon emissions necessitates an improved understanding of carbon cycling both on a global and a watershed scale. Furthermore, an understanding of carbon cycling in unmodified tropical watersheds will prove important in assessing the impacts of their deforestation.

Dissolved inorganic carbon (DIC), estimated to account for 40% of the total fluvial carbon inputs to the ocean (Ludwig et al., 1996), originates mainly from three sources: (1) atmospheric CO_2, (2) biogenic CO_2 produced by root respiration and organic matter decay, and (3) dissolution of carbonate rocks. Stable isotopes of carbon have proven to be useful tracers to distinguish DIC originating from atmospheric CO_2, soil organic matter, and the dissolution of carbonates, and for understanding the modifications that biogeochemical processes in the river itself impart on DIC.

In this study we use the distribution of the stable isotopes in rainfall and river water to constrain the annual water and carbon fluxes in the Nyong River basin. We quantify the flux of organic and inorganic carbon from the river to the ocean and atmosphere by tracing the carbon isotopic evolution from the small watershed of the Mengong (less than 1 km^2) to the whole drainage basin of the Nyong (Fig. 1). The lack of carbonates in the Nyong basin restricts the source
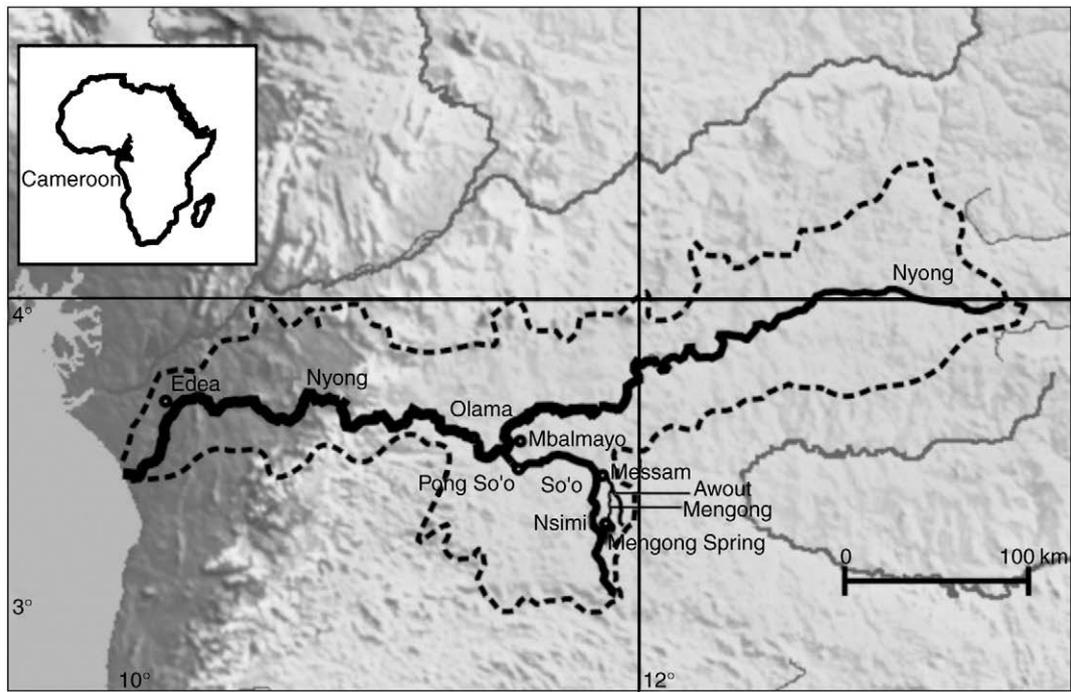
Fig. 1. The Nyong basin, sampling sites (shown in bold), and rivers sampled.

of DIC to either biogenic or atmospheric CO_2 and enables us to elucidate the fluvial transport of carbon, the role of swampy zones, and the exchange with atmospheric CO_2.

2. Methods

2.1. Study area

The Nyong River is the second largest river in Cameroon, with a drainage basin of 27 800 km². The entire basin is within tropical latitudes, between 2°48′N to 4°32′N and 9°54′E to 13°30′E. In this study, six sub-basins were sampled every two weeks from April 28, 2005 to April 16, 2007: the small watershed of the Mengong at Nsimi, the Awout watershed (tributary of the So'o) at Messam, the So'o watershed (tributary of the Nyong) at Pont So'o, the Nyong at Mbalmayo, Olama (after the confluence with the So'o), and downstream at Edea (Fig. 1). Samples were also collected at the source of the Mengong from a spring, which provides approximately 20% of this tributary's water supply (Ndam Ngoupayou, 1997). The geographic and hydrologic characteristics of these six sub-basins are summarized in Table 1.

The vegetation cover in the entire watershed is dominated by semi-deciduous forests on hill slopes and by raffia in the low-lying swampy zones (Boeglin et al., 2003). In the eastern-most portion of

the basin, the Nyong River flows through permanent swamp forests and permanently and seasonally inundated grass swamps 2–3 km in width. Downstream the basin is dominated by rounded hills covered in semi-deciduous forest (60%) and cropland (40%), predominantly tubers, manioc, palms and plantain (Letouzey, 1985).

In the south of the basin, the bedrock consists of granitoids of the 2900 Ma Liberian orogeny. In the northern part of the basin, the bedrock is primarily gneiss and migmatites of the Yaoundé series, metasomatised and metamorphosed during the 600 Ma Panafrican orogeny (Vicat, 1988). The morphology of the upper watershed, the southern Cameroon plateau, and the So'o sub-basin (including Awout and Mengong), is typified by eroded hills with an elevation of 650 to 850 m and by large swampy zones in the riverbeds. The Nyong River itself flows westward with a very low slope (0.15‰) until its confluence with the So'o. Downstream, the riverbed steepens to a mean slope of 6.7‰ and a series of falls (Olivry, 1986).

The climate of the region is of a Guinean type with four seasons: two rainy seasons, March to May and September to November, separated by short (June to August) and long (December to February) dry seasons. Boeglin (2002) reports average 1998–2002 annual values for precipitation and runoff at Olama as 1631 mm and 343 mm, respectively (Table 1). During our sampling period, the mean annual discharge at Olama was 269 mm, significantly lower than the long-term average discharge.

Table 1
Geographic and hydrologic characterization of the six sub-basins.

| River	Station	Drainage area (km²)	Mean annual precipitation (mm year^{-1})	Mean annual discharge (m³ s^{-1})	Runoff (mm year^{-1})		
					1998–2002[a]	2005	2006
Mengong	Nsimi	0.6	1779 ± 254	7.6 ± 2.6[b]	397 ± 133	190	–
Awout	Messam	206	1779 ± 254	3.6 ± 1.48	551 ± 226	231	257
So'o	Pont So'o	3070	1749 ± 225	43.9 ± 15.7	451 ± 161	285	304
Nyong	Mbalmayo	13 555	1759 ± 159	133.8 ± 31.5	311 ± 73	259	242
Nyong	Olama	18 510	1631 ± 181	201.3 ± 47	343 ± 80	268	270
Nyong	Edea	24 450	–	–	–	–	–

[a] Boeglin, (2002).
[b] Discharge in L s^{-1}.
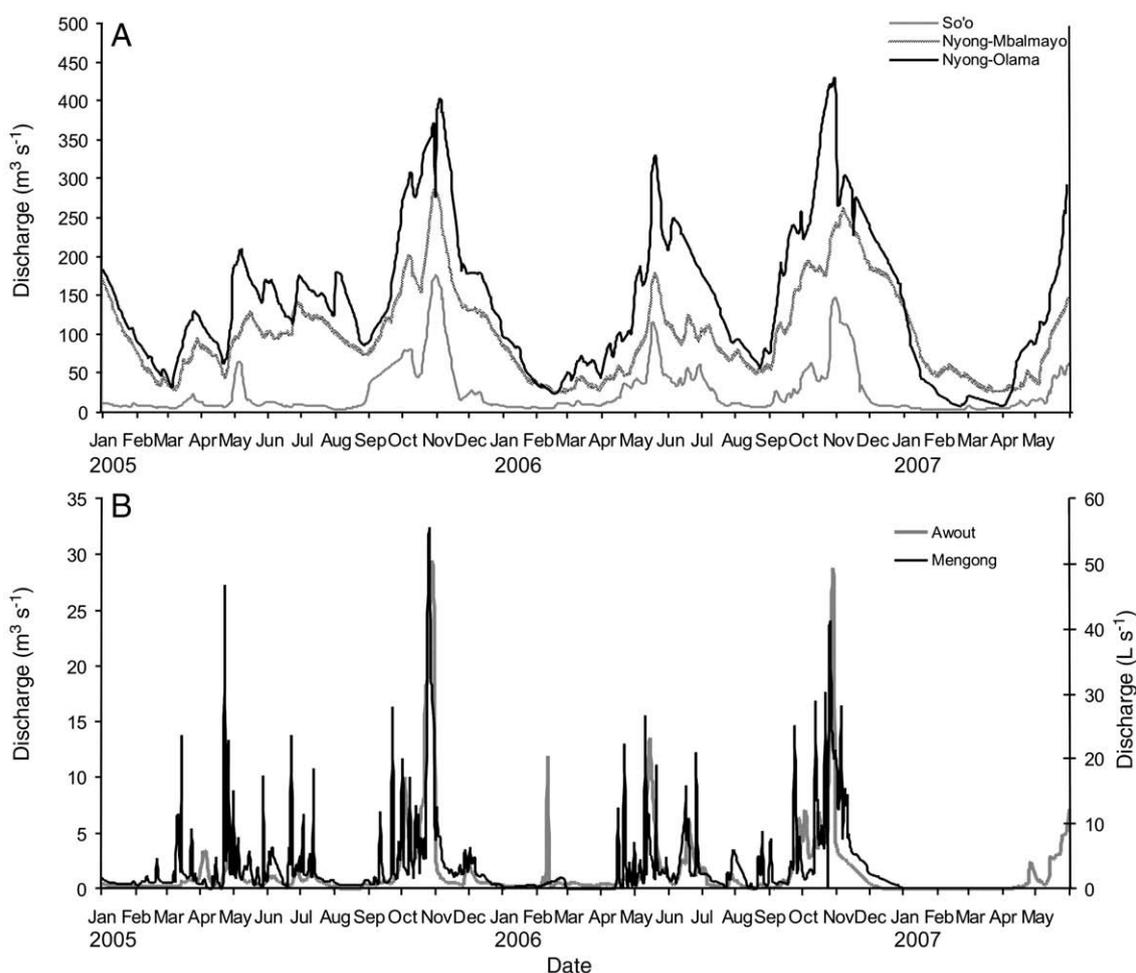
Fig. 2. Daily discharge of the Nyong River (A) and its tributaries (A and B), in $m^3 s^{-1}$, except for the Mengong where the discharge is in $L s^{-1}$.

Daily discharges of the Nyong and its tributaries during our sampling period are shown in Fig. 2. For the Mengong and Awout, the seasons are well marked, with rapid variations in flow, mainly in response to precipitation events. During the long dry season (December to March) several days with no flow were observed. The 2006 and 2007 dry seasons were more pronounced and longer than that of 2005. For the So'o and the Nyong, the maximum wet season discharge was observed in October 2005 and seasonal wet/dry patterns are clearly recognizable.

2.2. Sampling and laboratory procedures

Water samples were collected from bridges in the middle of the river. pH (pH 330i/SET probe, manufactured by WTW), temperature and conductivity (LF 325-B/SET probe, manufactured by WTW) were measured in the field. Water samples were filtered in the field through a 0.45 μm glass fibre filter, the filtrate treated with $HgCl_2$ to prevent microbiological activity, and stored in 40 mL TraceClean EPA Vials (pre-cleaned amber borosilicate) taking care that no trapped air remained in contact with the sample. For each sample, 3 vials were collected. A second septum (Flexseal disc, Teflon/Rubber 22 m, Chromatographic Specialties Inc cat#C8850522C) was added to each vial to avoid exchange with the atmosphere. Due to logistic problems, the second septa were not available for 3 months, from November 30, 2005 to February 28, 2006. Subsequently, we continued sampling with two septa, but also collected an additional sample with a single septum to test for possible distortion of results during the 3-month

interval. The comparison of the DIC concentrations and their isotopic compositions showed significant deterioration of the DIC pool in the vials without the second septum. Samples from this period were therefore deleted from the present report.

Samples for DIC, DOC, $\delta^{13}C_{DIC}$ and $\delta^{13}C_{DOC}$ were analyzed at the G. G. Hatch Isotope Laboratory on an OI Analytical "TIC–TOC" Analyser and a Finnigan Mat DeltaPlus isotope ratio mass spectrometer, following the procedure outlined by St-Jean (2003). Samples were analyzed with bracketing standards within a sequence and standard deviation of isotopic samples was ± 0.2‰. All carbon isotope values are reported against Vienna PeeDee Belemnite, as ‰ VPDB.

The partial pressure of CO_2 in the river was calculated using the DIC concentration, pH and temperature (Stumm and Morgan, 1996; Szaran, 1998). Excess of pCO_2 ($epCO_2$) is defined as the ratio of the pCO_2 in the river to the atmospheric pCO_2 value (Neal, 1988). The atmospheric value used in this study is 378 ppmV. For example, for $epCO_2$ of 10 the pCO_2 is 10 times higher than the atmosphere pressure of CO_2.

2.3. Interpretation of stable isotopes of carbon in river water

The isotopic composition of dissolved inorganic carbon in a river, $\delta^{13}C_{DIC}$, reflects the sources of inorganic carbon (Fig. 3). Atmospheric CO_2 has a $\delta^{13}C$ value of about -8‰ VPDB. Dissolution and gas transfer into water are both isotopically fractionating processes, yielding $\delta^{13}C$ values near -1‰ for dissolved inorganic carbon originating from atmospheric CO_2 (Zhang et al., 1995). Soil organic matter has an
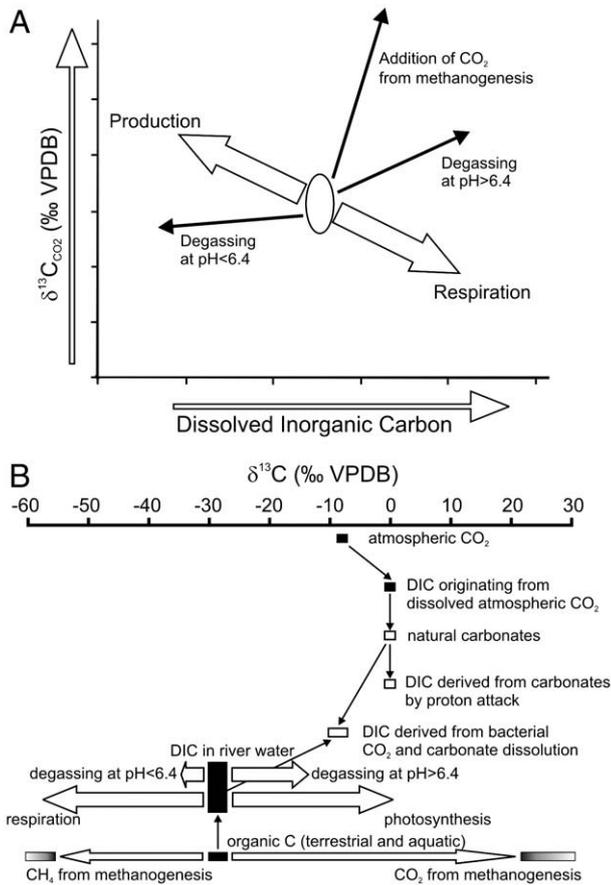
Fig. 3. (A) General effects of production (photosynthesis), respiration, methanogenesis and degassing on the isotopic composition and concentration of dissolved inorganic carbon in an aquatic system. (B) Carbon isotopic signature of various components of the carbon cycle in rivers. The effects of biogeochemical processes on $\delta^{13}C$ are shown with arrows.

isotopic composition between -24 and $-34‰$ (O'Leary, 1988). The isotopic signature of soil CO_2 that originates from the decomposition of terrestrial organic matter dominated by C3 plants averages about $-27‰$ (Vogel, 1993). Mineralization of this organic carbon imparts little isotopic fractionation, but the steep CO_2 concentration gradient between soil and air can cause kinetic fractionation of about 4‰ (Cerling et al., 1991). Furthermore, dissolution of CO_2 into water is also a fractionating process (Zhang et al., 1995) so that the final $\delta^{13}C$ of CO_2 in soil water is about $-24‰$. DIC from carbonate dissolution has an average $\delta^{13}C_{DIC}$ of about 0‰ (Salomons and Mook, 1986), though there are no carbonates in the Nyong watershed.

Within the river, biogeochemical processes will affect the isotopic composition of carbon. Aquatic photosynthesis preferentially consumes ^{12}C, leaving the residual inorganic carbon pool enriched in ^{13}C (Baird et al., 2001), with the magnitude of the enrichment depending on the amount of CO_2 available to photosynthesizing organisms. As a result, the organic matter produced by aquatic photosynthesis is isotopically depleted. Reported fractionation factors for photosynthesis vary widely and range from 0 to 20‰ lighter than the isotopic composition of the dissolved CO_2 (Leggett et al., 1999; Bade et al., 2006; Cole et al., 2002). The competing process, in situ respiration, consumes this depleted organic matter and produces CO_2 with a similarly depleted isotopic composition (Keough et al., 1998). When an aquatic system is oversaturated in CO_2, degassing under non-equilibrium conditions can lead to isotope enrichment of the remaining CO_2 pool (Marlier and O'Leary, 1984). The methane and carbon dioxide produced during methanogenesis are depleted and

enriched, respectively, with ^{13}C by up to 58‰ in freshwater environments (Whiticar, 1999).

2.4. Carbon fluxes

2.4.1. Terrestrial carbon fluxes

Ferguson and Veizer (2007) used stable isotopes of oxygen and hydrogen in river water and precipitation to examine the water balance of a series of rivers distributed globally, including the Nyong River, and that publication contains a detailed description of their methodology. Briefly, the annual water input into the basin from precipitation is balanced by the annual outflow from the river plus evapotranspiration, ET. Using an approach that relies on measurements of the isotopic composition of $\delta^{18}O$ and δ^2H in precipitation and the isotopic enrichment that occurs during evaporation, Ferguson and Veizer (2007) partitioned ET into evaporation and transpiration (T) fluxes in the Nyong basin.

The above transpiration flux can be used to approximate net primary productivity (NPP) in the watershed (Telmer and Veizer, 2000; Lee and Veizer, 2003). During transpiration, CO_2 diffuses inwards while O_2 and H_2O diffuse outward via leaf stomata. The number of moles of water that diffuses outward for each mole of carbon that diffuses inward is termed the water use efficiency (WUE). Large differences in WUE occur between different plant species and are mainly related to the photosynthetic pathway used. Average long term WUE for C_3 plants is 1 mol CO_2 to 925 ± 506 mol H_2O (Jones, 1992) and for C_4 plants 1 mol CO_2 per 425 ± 96 mol H_2O (Molles, 2002). The proportion of C3 to C4 plants in the Nyong watershed is determined from the land cover data in Mayaux et al. (2004) and Still et al. (2003). Knowing the proportion of C_3 to C_4 plants and the annual transpiration flux, NPP for the watershed can be estimated:

$$NPP(\text{molCa}^{-1}) = T(\text{moles H}_2\text{Oa}^{-1}) / WUE(\text{moles H}_2\text{O} / \text{molCO}_2). \quad (1)$$

While NPP is an important component of the terrestrial carbon cycle, sequestering large amounts of CO_2 from the atmosphere annually, soil respiration returns a significant portion of this sequestered CO_2 to the atmosphere. The net accumulation of carbon in the Nyong watershed, net ecosystem exchange (NEE), can be estimated from NPP and heterotrophic soil respiration (R_h):

$$NEE = NPP - R_h \quad (2)$$

Positive NEE indicates that a watershed is a net sink and negative a net source of CO_2 to the atmosphere. Total soil respiration is derived from the global soil efflux database described in Raich and Potter (1995) which consists of a grid of mean annual C emissions from terrestrial soils on a 0.5° longitude/latitude scale. Total soil respiration was then divided into its components of autotrophic soil respiration (R_a, root respiration) and heterotrophic soil respiration (bacterial activity). According to Hanson et al. (2000), the percentages of R_a to R_h in forested and non-forested areas are ~60 and ~46%, respectively.

2.4.2. DIC and DOC fluxes

Average annual fluxes of dissolved organic and inorganic carbon (F) in the Nyong and its sub-basins were calculated from mean annual discharge (Q_{ma}), instantaneous DIC and DOC concentrations (C_i), and instantaneous discharge rates (Q_i):

$$F = 365 Q_{ma} \left[\frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \right] \quad (3)$$

following Helie et al.(2002). During the sampling periods, discharge data were not available for the station at Edea, but Olivry (1986)

observed a close relationship between discharge at Olama and discharge at Edea, where Q at Edea = (1.84 ± 0.14) and Q at Olama + (11.13 ± 37.7) ($r^2 = 0.97$, $p < 0.001$). We used this relationship to estimate discharge at Edea from measured discharge at the upstream station at Olama.

2.4.3. Atmospheric CO_2 fluxes

We estimated evasion of CO_2 to the atmosphere from the flux equation:

$$F = \frac{D}{z}(C_{eq} - C) \qquad (4)$$

where F is the diffusive flux of CO_2 to the atmosphere, D is the CO_2 diffusion coefficient in water, z is the empirical thickness of the boundary layer and C_{eq} and C are concentrations of dissolved CO_2 in equilibrium with the atmosphere and measured CO_2, respectively. Richey et al. (1990) found the average measured D/z in the Amazon to be 15 cm h^{-1}, a value representative of moderately stirred water (Mook, 1970). The latter author also found that stagnant waters had a D/z value of 8 cm h^{-1}. In turbulent waters D/z is much higher, 115 cm h^{-1} (Mook, 1970). Atmospheric CO_2 fluxes in the Nyong and the tributaries were calculated with a D/z value of 8 cm h^{-1} to estimate minimum fluxes from the river to the atmosphere. Average widths of each segment of river were used to calculate the total flux of CO_2 from the Nyong to the atmosphere.

2.5. Statistical analysis

All statistical tests and confidence intervals are reported at the $\alpha = 0.05$ critical level. The precision of chemical and isotopic measurements are reported as confidence intervals (± one standard error (SE) of the mean of n determinations multiplied by the student t distribution (t) for $n - 1$ degrees of freedom, where SE = SD / $(n)^{1/2}$ and SD is the standard deviation). Variables used in linear regressions were tested against the standard normal distribution with a Chi-squared goodness of fit test. Non-normal variables were log-transformed and used as such in multiple regressions. For linear regressions, all regression parameters were bootstrapped 1000 times and standard errors are reported.

3. Results

An earlier study (Ndam Ngoupayou, 1997) showed that the spring water accounted for only a subordinated portion of the water budget in the Mengong River, a proposition entirely compatible with the dissimilar isotopic and chemical signals of the Mengong Spring and waters of the rivers in the Nyong watershed (Table 2). We therefore discuss the two ecosystems as separate entities.

3.1. Mengong Spring

In the Mengong Spring, DIC concentrations are on average significantly higher (16.4 ± 0.9 mg L^{-1}, Table 2), and DOC concentrations (1.3 ± 0.1 mg L^{-1}, see also Viers et al., 1997) are notably lower than in
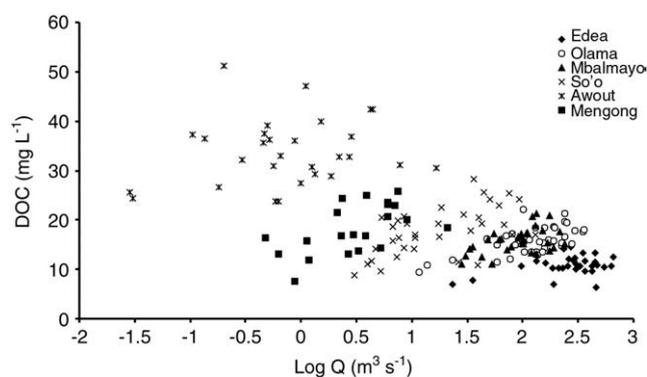

Fig. 4. DOC concentration versus log of discharge (log Q, m^3 s^{-1}, $r = -0.62$, $n = 187$,) at the various sampling stations. When the stations are considered individually, there is a positive correlation between DOC concentration and log Q at all stations except Awout (Edea, $r = 0.40$, $p = 0.03$; Olama, $r = 0.63$, $p < 0.001$; Mbalmayo, $r = 0.45$, $p = 0.01$; So'o, $r = 0.57$, $p < 0.001$; Awout, $r = 0.17$, $p = 0.18$; Mengong, $r = 0.56$, $p = 0.001$).

the rivers. epCO$_2$ was elevated, on average 99.2 ± 6.2, and dropped four fold between the Mengong Spring and the Mengong sampling station 850 m downstream. $\delta^{13}C_{DIC}$ was significantly more depleted in ^{13}C in the Mengong Spring than at the river stations (-21.8 ± 0.5‰), while $\delta^{13}C_{DOC}$ was slightly enriched (-27.3 ± 0.2‰).

3.2. Nyong and tributaries

3.2.1. DOC, DIC and epCO$_2$

In the Nyong and the tributaries DOC concentrations ranged from 6.4 to 51 mg L^{-1} and averaged 16 ± 1.3 mg L^{-1} (Appendix A). Concentrations in the tributaries were significantly higher than in the main channel (Fig. 4) and, overall, they further declined downstream (Table 2). Concentrations of DOC increased rapidly with the start of the rainy seasons (September and April, Appendix A) and all stations except for Awout when considered individually exhibit therefore significant positive correlations with discharge (Fig. 4).

DIC concentrations in the entire Nyong basin were relatively low (Appendix A), reflective of the lack of carbonates in the watershed, and declined downstream (Table 2). Overall, the DIC content was not significantly correlated with either discharge or DOC content. When the two sampling years were considered separately, DIC content correlated negatively with pH in 2005 ($r = -0.52$, $p < 0.001$, $n = 75$), but there was no significant correlation in 2006–07.

In the Nyong and its tributaries, all samples were oversaturated in CO_2, with epCO$_2$ ranging from 3 to 86 and averaging 19 ± 1 ($n = 187$, Fig. 5). epCO$_2$ decreased downstream along the entire length of the Nyong and it was consistently lowest at the furthest downstream station of Edea, where it averaged 12 ± 2.3 (Table 2).

3.2.2. $\delta^{13}C_{DOC}$ and $\delta^{13}C_{DIC}$

Within the Nyong and its tributaries there was little variation in $\delta^{13}C_{DOC}$, which ranged from -28.3‰ to -29.6‰ and averaged $-29.0 \pm$

Table 2

Average biogeochemical and isotopic measurements at each sampling site between May 2005 and 2007: temperature (T, °C), pH, dissolved organic carbon (DOC mg L^{-1}), isotopic composition of DOC ($\delta^{13}C_{DOC}$, ‰VPDB), dissolved inorganic carbon (DIC, mg L^{-1}), log partial pressure of carbon dioxide (log pCO$_2$, µatm), excess pCO$_2$ (epCO$_2$), isotopic composition of DIC ($\delta^{13}C_{DIC}$, ‰VPDB).

Station	T	pH	DOC	$\delta^{13}C_{DOC}$	DIC	log pCO$_2$	epCO$_2$	$\delta^{13}C_{DIC}$
Mengong Spring	23.5 ± 0.5	4.7 ± 0.1	1.3 ± 0.1	−27.3 ± 0.2	16.4 ± 0.9	−1.4 ± 0.0	99.2 ± 6.2	−21.8 ± 0.5
Mengong at Nsimi	24.1 ± 0.5	5.3 ± 0.1	18.4 ± 1.7	−29.4 ± 0.1	4.2 ± 0.5	−2.1 ± 0.1	23.7 ± 3.1	−15.8 ± 1.0
Awout at Messam	24.8 ± 0.6	4.9 ± 0.1	33.5 ± 2.4	−29.2 ± 0.1	3.8 ± 0.4	−2.1 ± 0.1	23.3 ± 3.1	−16.4 ± 1.3
So'o at Pont So'o	24.2 ± 0.5	5.5 ± 0.1	17.8 ± 1.6	−29.1 ± 0.1	3.3 ± 0.3	−2.2 ± 0.0	17.3 ± 2.0	−14.6 ± 1.0
Nyong at Mbalmayo	25.7 ± 0.3	5.7 ± 0.1	15.8 ± 0.9	−28.7 ± 0.1	4.0 ± 0.4	−2.1 ± 0.0	20.2 ± 2.4	−13.1 ± 0.9
Nyong at Olama	25.7 ± 0.4	5.7 ± 0.1	15.7 ± 0.8	−28.8 ± 0.1	3.6 ± 0.3	−2.2 ± 0.1	17.7 ± 2.3	−13.2 ± 1.2
Nyong at Edea	26.1 ± 0.6	6.2 ± 0.1	10.8 ± 0.7	−28.9 ± 0.1	3.1 ± 0.3	−2.4 ± 0.1	12.0 ± 2.3	−11.3 ± 1.3

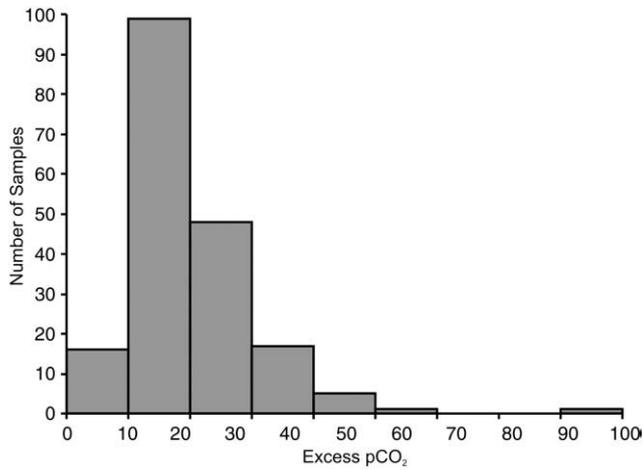Confidence intervals are at the $\alpha = 0.05$ critical level.

Fig. 5. epCO$_2$ (ratio of river pCO$_2$ to atmospheric pCO$_2$) in the Nyong River and its tributaries between April 2005 and 2007 ($n = 187$).

0.04‰ (Appendix A). These values are broadly consistent with the predominance of C3 vegetation in the watershed, which likely sourced the DOC (Fig. 3).

The isotopic composition of DIC varied significantly between sampling stations. In the tributaries (Mengong, Awout, and So'o) $\delta^{13}C_{DIC}$ averaged -15.7 ± 0.7‰ and in the Nyong -12.6 ± 0.7‰, with progressive enrichment in ^{13}C downstream, from an average of -13.1 ± 1.0‰ at Mbalmayo to -11.3 ± 1.3‰ at Edea (Table 2). $\delta^{13}C_{DIC}$ was positively correlated with discharge (Fig. 6) but only when considered for data from all stations together. No correlations were observed at individual stations.

When the two sampling years were considered separately, $\delta^{13}C_{DIC}$ was significantly negatively correlated with pCO$_2$ (Fig. 7A) and DOC content (Fig. 7B) and positively correlated with pH (Fig. 8).

3.3. Carbon fluxes

3.3.1. Riverine carbon fluxes

Fluxes of DOC and DIC at each sampling station are listed in Table 3. At all of the Nyong sampling site, the flux of organic carbon was between three and ten times larger than that of inorganic carbon. (Fig. 9). At Edea, the furthest downstream station, annual fluxes of DOC and DIC averaged 94 000 and 26 000 t C year^{-1} respectively.

Average annual atmospheric CO$_2$ fluxes for each river segment are shown in Table 4. Atmospheric carbon fluxes per unit area were highest in the headwaters and decreased downstream. Note that the unit area
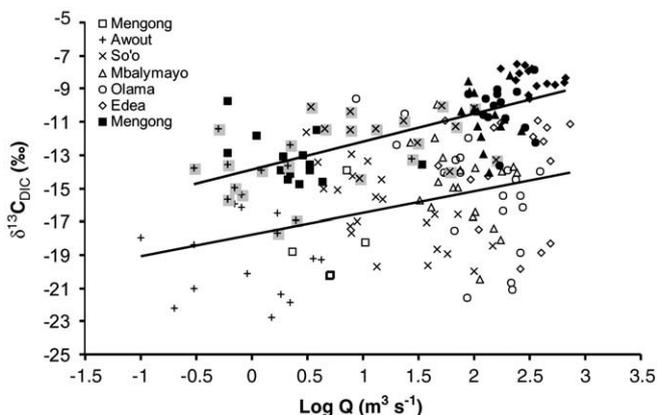

Fig. 7. $\delta^{13}C_{DIC}$ (‰) versus (A) log pCO$_2$ (µatm) and (B) DOC concentration (mg L^{-1}) in the Nyong and the tributaries. Samples collected in 2005 are shown with solid symbols and samples collected in 2006–07 with open symbols. In A, $\delta^{13}C_{DIC}$ was negatively correlated with log pCO$_2$ when the sampling years were considered separately (2005: $r^2 = 0.47$, $p < 0.001$, $n = 85$; 2006–07: $r^2 = 0.21$, $p < 0.001$, $n = 133$). In B, $\delta^{13}C_{DIC}$ was negatively correlated with DOC (2005: $r^2 = 0.36$, $p < 0.001$, $n = 83$; 2006–07: $r^2 = 0.37$, $p < 0.001$, $n = 125$).

flux was particularly high in the Mengong Spring, at 38 g C m^{-2} day^{-1}. Over the entire course of the river, the minimum average annual flux of CO$_2$ to the atmosphere was 108 000 t C year^{-1}, almost as great as the total amount of carbon transported to the Gulf of Guinea as DIC and DOC.

Fig. 6. $\delta^{13}C_{DIC}$ concentration versus log of discharge (log Q). Samples collected in 2005 are shown with solid symbols and samples collected in 2006–07 with open symbols.
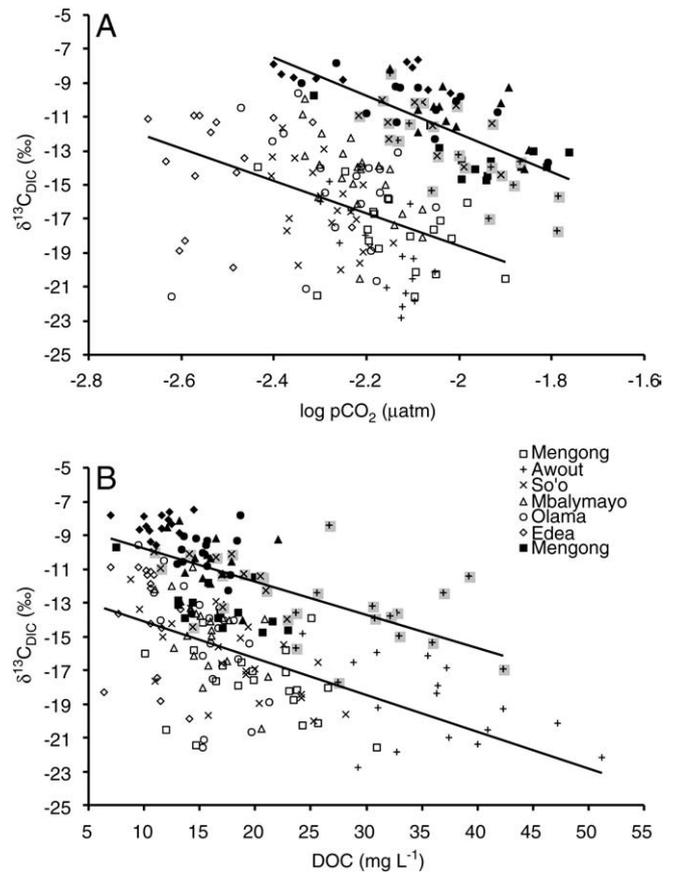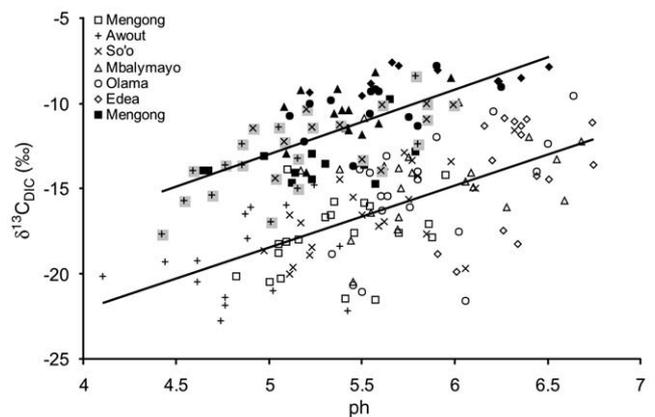

Fig. 8. $\delta^{13}C_{DIC}$ (‰) versus pH in the Nyong and the tributaries. Samples collected in 2005 are shown with solid symbols ($r^2 = 0.57$, $n = 88$) and samples collected in 2006–07 with open symbols ($r^2 = 0.57$, $n = 137$).

Table 3
Average discharge, dissolved inorganic and organic carbon contents (DOC, DIC, g m^{-3}), and fluxes of dissolved inorganic and organic carbon from the Nyong and its tributaries between April 2005 and 2007.

Station	Average discharge (m³ s⁻¹)			DOC (g m⁻³)			DIC (g m⁻³)			DOC flux (10³ t C year⁻¹)			DIC Flux (10³ t C year⁻¹)		
	2005–06	2006–07	2005–07	2005–06	2006–07	2005–07	2005–06	2006–07	2005–07	2005–06	2006–07	2005–07	2005–06	2006–07	2005–07
Mengong	3.1×10^{-3}			16.8 ± 2.1	20.7 ± 2.4	18.8 ± 1.7	5.0 ± 0.7	3.5 ± 0.5	4.2 ± 05	2.1×10^{-3}			4.5×10^{-4}		
Awout	1.5	1.5	1.5	33.0 ± 3.1	35.5 ± 3.9	34.1 ± 2.4	4.4 ± 0.6	3.0 ± 0.3	3.8 ± 0.4	1.7	1.6	1.8	0.19	0.21	0.16
Pont So'o	27	28	27	18.2 ± 2.0	17.4 ± 2.5	17.8 ± 1.6	3.8 ± 0.5	2.8 ± 0.2	3.3 ± 0.3	17	15	19	2.9	3.2	2.5
Mbalmayo	101	106	104	15.7 ± 1.1	15.8 ± 1.4	15.8 ± 0.9	4.4 ± 0.4	3.6 ± 0.6	4.0 ± 0.4	52	49	55	12	14	11
Olama	146	150	148	15.7 ± 0.8	15.7 ± 1.5	15.7 ± 0.8	3.9 ± 0.5	3.3 ± 0.4	3.6 ± 0.6	78	76	80	16	17	14
Edea	279	286	283	11.2 ± 0.8	10.3 ± 1.1	10.8 ± 0.7	3.5 ± 0.3	2.6 ± 0.4	3.1 ± 0.3	94	101	88	26	30	22

3.3.2. Terrestrial carbon fluxes

Utilizing an approach based on $\delta^{18}O_{H_2O}$ and $\delta^2 D$ measurements of precipitation and river water, Ferguson and Veizer (2007) estimated the transpiration flux in the Nyong River basin to be $1130 \pm 183 \times 10^3$ g H$_2$O m^{-2} year^{-1}. The vegetation in the Nyong River basin was completely dominated by C3 plants (Still et al., 2003) and we therefore utilize the water use efficiency of 925 ± 506 mol H$_2$O mol C^{-1} in Eq. (1). This yields net primary productivity for the entire Nyong River basin of 21 489 600 t C or 814 ± 462 g C m^{-2} year^{-1}.

The global soil efflux database (Raich and Potter, 1995) shows that total soil respiration in the Nyong River basin is approximately 1200 g C m^{-2} year^{-1}. From land cover data (Mayaux et al., 2004) we estimate that eighty percent of the Nyong River basin is forested while the remaining 20% is used as cropland. Taking the percentages of autotrophic to heterotrophic soil respiration for forested and non-forested land as given in Hanson et al. (2000), we estimate heterotrophic soil respiration, R_h, to be about 513 g C m^{-2} year^{-1}. A *first order* estimate of NEE calculated from Eq. (2) is therefore 300 g C m^{-2} year^{-1}. The Nyong River watershed covers 2.64×10^{10} m^2 (Ferguson and Veizer, 2007) and the total annual NEE for the basin therefore amounts to about 7 920 000 t C.

4. Discussion

4.1. Mengong Spring

Both concentrations and isotopes of DOC and DIC in the Mengong Spring are significantly different from the river water samples (Table 2). The low concentrations of DOC and high concentrations of DIC typify water that has been extensively influenced by interaction with the bedrock, although the highly negative $\delta^{13}C_{DIC}$ signal argues for DIC derivation from oxidation of organic matter.

Between the Mengong Spring and the Mengong sampling station, only 850 m downstream, DIC concentrations decrease four-fold while DOC concentrations increase fourteen times and $\delta^{13}C_{DIC}$ increases by 6‰ (Table 2). Over this distance, the Mengong descends 10 m and flows through a wide swampy area. The notable difference between spring water and river water suggests that the majority of the river water is supplied not by the spring water, but by the wetlands. Indeed, an earlier study by Ndam Ngoupayou (1997) concluded that only about 20% of the flow of the Mengong between 1995 and 1996 was spring fed.

4.2. Nyong and tributaries

4.2.1. epCO₂, DIC and DOC

For the entire Nyong basin pCO$_2$ averaged 7240 ± 428 µatm, within the higher range of values reported in literature. For comparison, pCO$_2$ in the Ottawa River averaged 1200 µatm (Telmer and Veizer, 1999), in the Changjiang River estuary it ranged from 650 to 1440 µatm, in the Huangpujiang River 1000–4600 µatm (Zhai et al., 2007) and in the Xinjiang River, a subtropical monsoon river in China, from 600 to 7200 µatm in the mainstream and from 700 to 11 000 in the tributaries (Yao et al., 2007). In the Amazon, pCO$_2$ varied from 2950 µatm in the mainstream to over 44 000 µatm on the floodplain (Richey et al., 2002).

This consistent oversaturation of CO$_2$ in rivers in general and in the Nyong in particular indicates that the DIC does not originate from invasion of atmospheric CO$_2$. Because there are no carbonates in the Nyong basin, an observation consistent with the low pH of its rivers
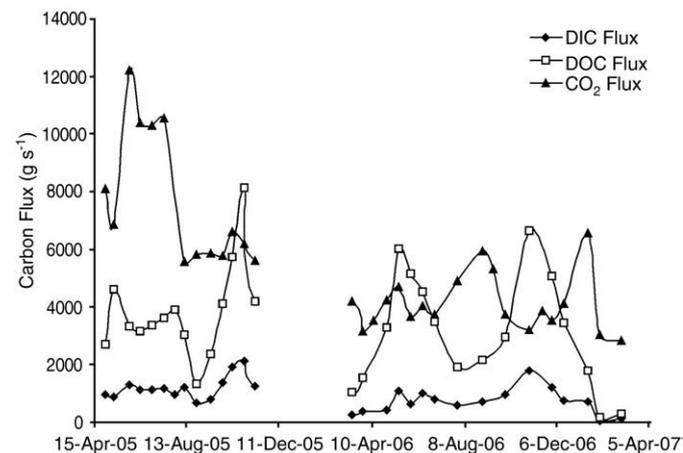

Fig. 9. Fluvial carbon fluxes over the sampling period. DOC and DIC flux estimates are shown for the furthest downstream station, Edea, while the calculated minimum flux of CO$_2$ to the atmosphere is shown for the entire Nyong and its tributaries.

Table 4
Atmospheric fluxes of CO$_2$ from the Nyong and its tributaries between April 2005 and 2007.

Segment	Length (km)	Width (m)	Average flux (g C m⁻² day⁻¹)			Total flux (10³ t C year⁻¹)		
			2005–06	2006–07	2005–07	2005–06	2006–07	2005–07
Mengong Spring–Nsimi	0.85	1	38	38	39	0.01	0.01	0.01
Nsimi–Messam	30	10	10	7	9	1.1	0.8	1.0
Messan–Pont So'o	107	28	9	5	7	10	5.4	8.0
Pont So'o–Confluence with Nyong	5	38	7	5	6	0.5	0.4	0.4
Headwaters of Nyong–Mbalmayo	360	38	8	6	7	41	30	36
Mbalmayo–Olama	56	100	7	5	6	14	11	13
Olama–Edea	135	129	3	3	3	18	16	18
Edea–Gulf of Guinea	99	330	3	3	3	34	31	33
Total						119	94	108

(Table 2), their riverine DIC must originate from the oxidation of organic carbon.

Concentrations of DOC were consistently higher in the tributaries and increased rapidly with the start of the rainy seasons (September and April), caused by flushing of organic matter from swampy zones. The observed positive correlations of DOC and discharge (Fig. 4) at specific stations are a reflection of this seasonal flushing process. The decline in DOC in the Nyong, compared to the tributaries (Table 2), is therefore an outcome of oxidation of DOC within the main channel coupled with dilution of swampy waters from the uplands by less DOC-rich waters from the downstream portion of the watershed.

The average DOC concentration in the Nyong, 18.6 ± 1.3 mg L^{-1}, is within the upper range of values reported for other tropical rivers, such as the Godavari River in India, with an average concentration of 1.24 mg L^{-1} (Balakrishna et al., 2006), the Indus River with 14.4 mg L^{-1} (Ludwig et al., 1996), and three tributaries of the Amazon, the Madeira, Solimoes, and Negro with 6.1 mg L^{-1}, 5.83 mg L^{-1} and 12.7 mg L^{-1}, respectively (Moreira-Turcq et al., 2003). Discharge weighted average DOC concentration in the Amazon is 5.1 mg L^{-1} (Moreira-Turcq et al., 2003). Considered in qualitative terms, the high DOC concentrations in the swampy headwaters and the subsequent decline downstream are therefore consistent with a scenario that involved advancing oxidation of DOC, generation of DIC and CO$_2$ outgassing as controlling processes of down-river carbon cycle dynamics. Do isotope data support this proposition?

4.3. $\delta^{13}C_{DOC}$ and $\delta^{13}C_{DIC}$ in the Nyong

The isotopic composition of organic carbon in the soil depends on the type of vegetation cover in the watershed. Bird et al. (1993, 1998) documented that the seasonal organic carbon fluxes for two areas in the Sanaga basin, Cameroon, one covered by forest (C3 plants) and another by savannah (C4 plants), have $\delta^{13}C$ of -28‰ and -12‰, respectively. In the Nyong watershed, the vegetation is mainly deciduous forest on the hills and raffia in the low-lying zones, both C3 plants. The measured $\delta^{13}C_{DOC}$ in the Nyong River and its tributaries of -29.0 ± 0.04‰ ($n = 199$), is therefore in agreement with the C3 nature of the vegetation and is comparable to the average value of -28.7‰ in the tropical Amazon (Quay et al., 1992).

As there are no carbonates in the Nyong River watershed and pCO$_2$ is constantly oversaturated in the river and its tributaries (Fig. 4), DIC in the river can only originate from the oxidation of organic matter. $\delta^{13}C_{DIC}$ in the water of the Nyong and its tributaries ranged from -22.8‰ to -7.5‰ (Appendix A), reflecting variable contributions from different carbon sources or differing impacts of processes that fractionate isotopes of carbon, such as respiration, production and evasion. Considering that variations in $\delta^{13}C_{DOC}$ are only 1.3‰, variable sources of carbon cannot be held responsible for the observed range in $\delta^{13}C_{DIC}$. In contrast, because $\delta^{13}C_{DIC}$ correlates positively with pH (Fig. 8) and negatively with pCO$_2$ and DOC (Fig. 7), aquatic respiration and photosynthesis are the most likely controlling processes of the and DIC signals within the watershed. The offset in $\delta^{13}C_{DIC}$ between the sampling years (Figs. 6 and 7) likely relates to differences in hydrologic regimes, since the annual discharge in 2005 was higher than in 2006–07. This could lead to additional flooding of low-lying land and thus amplification of changes in $\delta^{13}C_{DIC}$ and DOC and DIC contents.

The above trends from tributaries to the Nyong River continued, albeit at a lesser gradient, downstream (Table 2). We therefore interpret all these overall decreases in pCO$_2$ and increases in $\delta^{13}C_{DIC}$ to be the results of a combination of CO$_2$ degassing and aquatic biological productivity.

As shown in Section 3.3.1, the carbon dioxide flux from the Nyong to the atmosphere is significant and the isotopic effect of degassing is pH dependent. Under open system conditions, favorable for rapid exchange of CO$_2$, kinetic isotope fractionation can result in greater

isotope enrichment than is expected for equilibrium conditions. In an experimental setting, Marlier and O'Leary (1984) measured kinetic isotope fractionation as large as 14.7‰. In a natural setting, in the first 500 m of the Sleepers River the pCO$_2$ decline coincided with an increase in $\delta^{13}C_{DIC}$ of 3‰ to 5‰ (Doctor et al., 2007). Note, however, that these experimental and observational kinetic fractionations occurred at pH values between 6.5 and 8, where DIC is predominantly HCO$_3^-$ (Marlier and O'Leary, 1984; Doctor et al., 2007), while in our case pH averaged 5.6 ± 0.08 and DIC was thus predominantly H$_2$CO$_3$. Yet, the kinetic isotope fractionation factor between H$_2$CO$_3$ and CO$_{2(g)}$ is -0.81 ± 0.16‰ at 21 °C (Zhang et al., 1995) and -1.03 ± 0.02‰ at 25 °C (Szaran, 1998). Thus, while outgassing is primarily responsible for the large losses of CO$_2$ from the river, it is unlikely that it can account for the progressive downstream increase in $\delta^{13}C_{DIC}$, unless it is accompanied by rapid pH increases towards the crossover point at pH = 6.4, where DIC is predominantly HCO$_3^-$ (Stumm and Morgan, 1996) and significant isotopic enrichment can occur.

It is therefore more realistic to propose that at least some of the progressive downstream increase in $\delta^{13}C_{DIC}$ results from photosynthesis that preferentially consumes ^{12}C (Fig. 3). Still, $\delta^{13}C_{DIC}$ averaged from -16.4‰ at Awout to -11.3‰ at the furthest downstream station, while the $\delta^{13}C_{DOC}$, the apparent the original source of the DIC, was everywhere close to -29‰. Nevertheless, while the combination of the above processes may account for the downstream isotopic trends, it is difficult to conceive how they could explain the large DIC–DOC isotopic shift evident already in the headwaters. We therefore postulate that this initial isotopic shift is inherited already from the swamp waters that source the rivers. These swamps are likely characterized by intense methanogenesis that produces isotopically enriched CO$_2$ (and DIC, Fig. 3), with isotopic fractionations of up to 58‰ (Whiticar, 1999).

4.4. Carbon fluxes

4.4.1. Atmospheric CO$_2$ fluxes

The estimates and the importance of CO$_2$ flux via atmospheric evasion from terrestrial water bodies, relative to the total carbon export vary significantly. Richey et al. (2002) argued that outgassing of CO$_2$ to the atmosphere was an important pathway for carbon loss in the Amazon basin, amounting to 120 ± 30 g C m^{-2} year^{-1}. In the Xinjiang River atmospheric CO$_2$ fluxes ranged from 830 to 1560 g C m^{-2} year^{-1} (Yao et al., 2007), but in the Changjiang River they were much lower at 186–411 g C m^{-2} year^{-1}, representing only 2–5% of the DIC export into the East China Sea (Zhai et al., 2007). For the Ottawa River, Telmer and Veizer (1999) estimated the flux of CO$_2$ to the atmosphere to be 170 g C m^{-2} year^{-1}, or 30% of the river's annual flux of DIC.

In the Nyong, the elevated pCO$_2$ levels result in an unusually high efflux of CO$_2$ to the atmosphere from 1000 g C m^{-2} year^{-1} in the downstream reaches to 2600 g C m^{-2} year^{-1} in the headwaters of the tributaries. Near the Mengong spring, atmospheric carbon flux was nearly 15 000 g C m^{-2} year^{-1}. Our estimate for an average annual outgassing in the Nyong is 1487 g C m^{-2} year^{-1}, or 108 000 t C year^{-1}. This atmospheric carbon loss was four times the river's annual flux of DIC to the Gulf of Guinea and 115% of the river's annual DOC flux.

It should be noted that, while our estimates of CO$_2$ flux to the atmosphere are high, they represent minimum estimates as the D/z value used in Eq. (3) applies to still waters (Mook, 1970). Increasing the D/z from 8 cm h^{-1} to 15 cm h^{-1}, a value representative of moderately mixed waters (Mook, 1970; Richey et al., 1990; Yang et al., 1996) would raise estimates of CO$_2$ flux to the atmosphere by 53%. Applying a value of 115 cm h^{-1} to the stretches of water with turbulent flow (Mook, 1970), would increase it still further.

4.4.2. Terrestrial carbon fluxes

Our estimate of NPP in the Nyong River basin, 814 ± 462 g C m^{-2} year^{-1}, is high relative to other riverine systems that have been

studied by the same method. The NPP in the Volta River watershed of West Africa was calculated to be 428 g C m^{-2} year^{-1} (Freitag et al., 2008), in the Great Lakes basin 346 g C m^{-2} year^{-1} (Karim et al., 2008), in the Mississippi River basin 355 g C m^{-2} year^{-1} (Lee and Veizer, 2003) and in the Great Plains Region of North America 325 g C m^{-2} year^{-1} (Ferguson et al., 2007). However, these are mostly savannah-type and temperate climate watersheds. For tropical forest ecosystems, the literature review of carbon fluxes admitted by other approaches, suggests an average NPP of 864 ± 54 g C m^{-2} year^{-1} ($n = 12$, Luyssaert et al., 2007), similar to our estimate for the Nyong watershed.

Our *first-order* estimate of NEE in the Nyong River basin indicates therefore that this terrestrial ecosystem sequesters large quantities of carbon on an annual basis. Our NEE, ~300 g C m^{-2} year^{-1} (7 920 000 t C year^{-1}), is comparable to estimates from other tropical forest ecosystems of 403 ± 96 g C m^{-2} year^{-1} ($n = 7$, Luyssaert et al., 2007). The combined dissolved organic, dissolved inorganic and atmospheric fluxes of carbon from the Nyong River only export about 3% of this flux from the basin on an annual basis. We do not have any estimate for the potential export of carbon via the postulated methanogenesis in the swamps, but consider it unlikely to be large enough for closing the carbon budget of the watershed. In summary, it appears that tropical ecosystems are net carbon sinks of considerable magnitude, in contrast to temperate ecosystems studied by us previously that appear to have import/export balances close to equilibrium.

5. Summary

The Nyong watershed serves as a suitable study area for tracing the fate of carbon in a humid tropical river ecosystem because of its limited anthropogenic impacts and homogeneous silicate bedrock. Over the entire sampling period and at all sites sampled, the consistent and strong oversaturation of CO_2 indicates that dissolved inorganic carbon in the river cannot originate from dissolution of atmospheric CO_2, but rather from the oxidation of organic matter.

In the river samples, the seasonal hydrologic cycle is super-imposed on the down-river evolution; the onset of the rainy season results in the enlargement of swampy zones, which provide organic-rich water with high DOC from biogenic sources. At each station we observed higher concentrations of DOC at times of increased discharge. However, at individual stations, changing levels of discharge were not reflected in the isotopic composition of DIC. Instead, downstream evolution of water affected both $\delta^{13}C_{DIC}$ and pCO_2. $\delta^{13}C_{DIC}$ was progressively enriched downstream while DIC content decreased, reflecting the effect of both degassing and aquatic photo-synthesis on DIC.

When examining total carbon fluxes from rivers with low pH, estimates of CO_2 flux to the atmosphere should not be excluded. In the Nyong, we found that the atmospheric evasion of CO_2 was at least 115% of the annual flux of DOC and four times greater than the flux of dissolved inorganic carbon. Nearly as much carbon evaded to the atmosphere as was transported to the Gulf of Guinea as DOC and DIC. Despite its relatively small size and low concentrations of DIC, we estimate the minimum total annual flux of carbon from the Nyong is 228 000 t C year^{-1}.

However, this fluvial flux of carbon was minor when compared with terrestrial net ecosystem exchange in the Nyong River basin. Our *first order* estimate of NEE shows that net primary productivity exceeded heterotrophic respiration by ~300 g C m^{-2} year^{-1} or 7 920 000 t C year^{-1}. The combined dissolved organic, dissolved inorganic and atmospheric fluxes of carbon from the Nyong river only export 3% of this flux from the basin on an annual basin, indicating that tropical forest watersheds that receive large amounts of precipitation can sequester considerable amounts of carbon on an annual basis.

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