

## Inorganic carbon speciation and fluxes in the Congo River

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[1] Seasonal variations in inorganic carbon chemistry and associated fluxes from the Congo River were investigated at Brazzaville-Kinshasa. Small seasonal variation in dissolved inorganic carbon (DIC) was found in contrast with discharge-correlated changes in pH, total alkalinity (TA), carbonate species, and dissolved organic carbon (DOC). DIC was almost always greater than TA due to the importance of  $\text{CO}_2^*$ , the sum of dissolved  $\text{CO}_2$  and carbonic acid, as a result of low pH. Organic acids in DOC contributed 11–61% of TA and had a strong titration effect on water pH and carbonate speciation. The  $\text{CO}_2^*$  and bicarbonate fluxes accounted for ~57% and 43% of the DIC flux, respectively. Congo River surface water released  $\text{CO}_2$  at a rate of  $\sim 109 \text{ mol m}^{-2} \text{ yr}^{-1}$ . The basin-wide DIC yield was  $\sim 8.84 \times 10^4 \text{ mol km}^{-2} \text{ yr}^{-1}$ . The discharge normalized DIC flux to the ocean amounted to  $3.11 \times 10^{11} \text{ mol yr}^{-1}$ . The DOC titration effect on the inorganic carbon system may also be important on a global scale for regulating carbon fluxes in rivers. **Citation:** Wang, Z. A., D. J. Bienvenu, P. J. Mann, K. A. Hoering, J. R. Poulsen, R. G. M. Spencer, and R. M. Holmes (2013), Inorganic carbon speciation and fluxes in the Congo River, *Geophys. Res. Lett.*, *40*, 511–516, doi:10.1002/grl.50160.

### 1. Introduction

[2] Total dissolved inorganic carbon (DIC) contributes ~38% of the global riverine carbon flux to the ocean ( $\sim 8.3 \times 10^{13} \text{ mol yr}^{-1}$  or  $1.0 \times 10^{15} \text{ g yr}^{-1}$ ) [Cai, 2011; Meybeck, 1993]. DIC fluxes have historically been assessed primarily based on total alkalinity (TA) measurements. In many rivers, such as the Mississippi and Changjiang [Cai *et al.*, 2008], this assessment is robust as the bicarbonate ion ( $\text{HCO}_3^-$ ) is the dominant species in TA such that  $\text{DIC} \approx \text{TA} \approx \text{HCO}_3^-$ . In other systems, a large difference between DIC and TA values may exist. This stems from their definitions and basic aquatic chemistry [Morel and Hering, 1993]:

$$\text{DIC} = [\text{CO}_2^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (1)$$

$$\text{TA} = [\text{HCO}_3^-] + 2 \times [\text{CO}_3^{2-}] + [\text{OrgAlk}] + [\text{other Alk}] + [\text{OH}^-] - [\text{H}^+] \quad (2)$$

[3] where  $\text{CO}_2^*$  is the sum of dissolved  $\text{CO}_2$  and carbonic acid; the sum of the first two terms in equation (2) is called carbonate alkalinity (CAlk), and OrgAlk represents organic alkalinity. Similar to CAlk, OrgAlk results from the contribution of deprotonated organic acid anions in natural waters. In low pH water,  $\text{CO}_2^*$  contributes a large proportion to the DIC pool, driving DIC values away from TA and making DIC estimates from TA inaccurate.

[4] Water pH regulates the DIC speciation, thus controlling the partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) and the  $\text{CO}_2$  flux across the air-water interface. Global rivers and streams release an estimated  $1.7\text{--}5.0 \times 10^{13} \text{ mol C yr}^{-1}$  ( $2.0\text{--}6.0 \times 10^{14} \text{ g C yr}^{-1}$ ) to the atmosphere as a result of air-water  $\text{CO}_2$  exchange [Aufdenkampe *et al.*, 2011; Cole *et al.*, 2007]. Many of the available  $p\text{CO}_2$  data sets use estimates calculated from measured pH and TA data, based on the traditional inorganic carbon system model. However, when large amounts of undefined acid-base species such as OrgAlk exist, the calculated  $p\text{CO}_2$  values may bear large uncertainties [Butman and Raymond, 2011; Hunt *et al.*, 2011], which are difficult to assess without comprehensive measurements of the DIC pool alongside other related species (e.g., dissolved organic carbon, DOC).

[5] As the world's second largest river by discharge ( $\sim 45,000 \text{ m}^3 \text{ s}^{-1}$ ) and drainage basin area ( $3.7 \times 10^6 \text{ km}^2$ ), the Congo River exports  $\sim 1.2 \times 10^{12} \text{ mol C yr}^{-1}$  ( $1.4 \times 10^{13} \text{ g C yr}^{-1}$ ) of organic carbon to the Atlantic Ocean [Coynel *et al.*, 2005]. Typically, over 80% of this flux is in the form of DOC due to low suspended sediment concentrations [Spencer *et al.*, 2012a]. Based on TA measurements, the Congo River  $\text{HCO}_3^-$  flux has been previously estimated as  $\sim 2.7 \times 10^{11} \text{ mol C yr}^{-1}$  ( $3.2 \times 10^{12} \text{ g C yr}^{-1}$ ) [Probst *et al.*, 1992], less than 25% of the DOC flux. In comparison to other major global rivers, such as the Amazon and Arctic Rivers, the Congo has received limited study with respect to its biogeochemistry [Spencer *et al.*, 2010]. Recent studies, however, have addressed the organic carbon fluxes and biogeochemistry for the Congo main stem and tributaries [Spencer *et al.*, 2010; Spencer *et al.*, 2012a] as well as the inorganic carbon system on one of the major tributaries, the Oubangui River [Bouillon *et al.*, 2012].

[6] We herein describe a comprehensive set of inorganic carbon parameters (DIC, TA, and pH) measured from monthly samples collected near Brazzaville-Kinshasa in the Congo River. The study aimed to (1) examine temporal variations in the inorganic carbon chemistry of Congo main stem waters near its mouth, (2) evaluate the role of DOC in

All supporting information may be found in the online version of this article.

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affecting pH and DIC speciation, and (3) estimate the  $\text{CO}_2$  outgassing rate and inorganic carbon fluxes to the ocean.

## 2. Methods

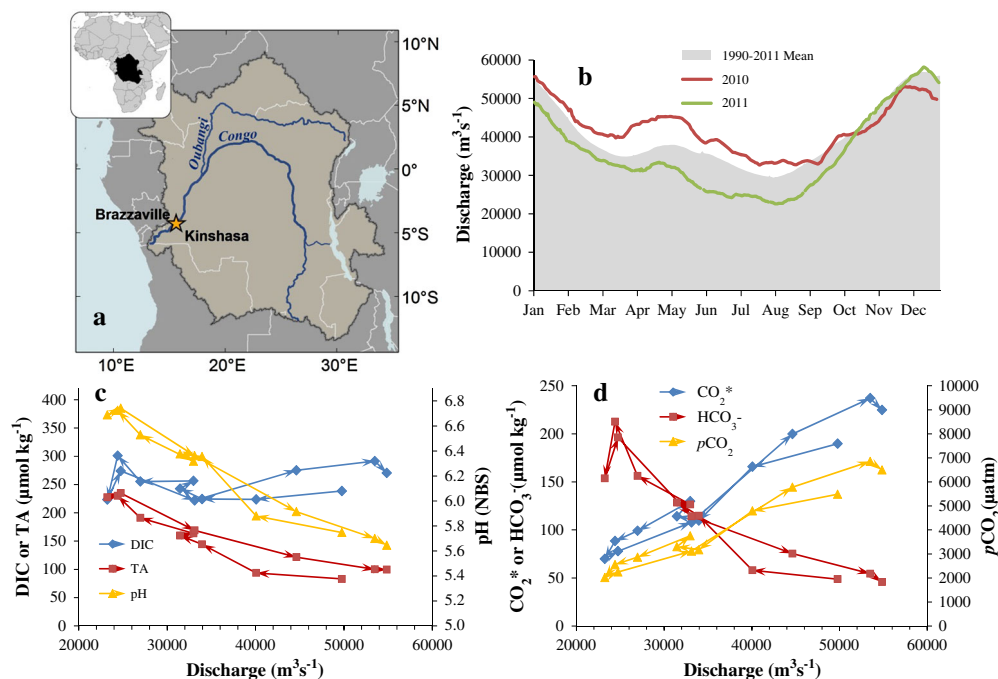
[7] Monthly sampling was conducted between December 2010 and December 2011 at Brazzaville-Kinshasa, approximately 350 km above the head of the Congo River estuary (Figure 1a). Subsurface samples for DIC, TA, and pH were pumped through  $0.45 \mu\text{m}$  cartridge filters into 250 mL borosilicate glass bottles using a peristaltic pump. Each sample was poisoned with  $60 \mu\text{L}$  of saturated mercuric chloride and sealed with a greased, ground-glass stopper [Dickson *et al.*, 2007]. DOC samples were filtered into pre-combusted ( $550^\circ\text{C}$  for 8 h) glass vials, acidified ( $\text{pH} \sim 2$ ), and refrigerated ( $4^\circ\text{C}$ ) in the dark [Mann *et al.*, 2012].

[8] Discrete DIC samples were measured on a DIC auto-analyzer (AS-C3, Apollo SciTech) via sample acidification followed by non-dispersive infrared  $\text{CO}_2$  detection (LiCOR 7000). The instrument was calibrated with certified reference material (CRM) from Dr. A.G. Dickson at the Scripps Institution of Oceanography. A modified Gran titration procedure [Wang and Cai, 2004] was used to determine TA with an automated titrator (AS-ALK2, Apollo SciTech) and CRM-calibrated HCl at  $22.0 \pm 0.1^\circ\text{C}$ . The Gran titration determines total titration alkalinity that includes contributions from all weak acid anions, such as  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , and deprotonated organic acid anions (equation (2)) [Morel and Hering, 1993]. DIC and TA values were reported in  $\mu\text{mol kg}^{-1}$  after being corrected for water density and mercuric chloride addition. Both DIC and TA measurements had a precision and accuracy of  $\pm 2.0 \mu\text{mol kg}^{-1}$ .

[9] Sample pH was measured using a ROSS combination electrode (Thermo Scientific) at  $22.0 \pm 0.1^\circ\text{C}$ . The electrode was calibrated using three National Bureau of Standards (NBS) solutions ( $\text{pH} = 4.01, 7.00, \text{and } 10.01$ ). The pH precision and accuracy was  $\pm 0.01$ , and the data were corrected to in situ temperature for reporting. DOC was determined via high-temperature combustion using a Shimadzu TOC-V organic carbon analyzer. The overall precision of independent replicates was  $< 2\%$  [Mann *et al.*, 2012].

[10] Other inorganic carbon parameters,  $\text{HCO}_3^-$ ,  $\text{CO}_2^*$ , and  $p\text{CO}_2$ , were calculated using measured pH and DIC data via the  $\text{CO}_2$  program by Pierrot *et al.* [2006] using the freshwater option. Non-carbonate alkalinity (nAlk) was calculated from the difference between measured TA and pH-DIC calculated TA [Cai *et al.*, 1998; Hunt *et al.*, 2011]. The pH and DIC data were used for  $\text{CO}_2$  system calculations instead of the pH-TA pair to avoid large calculation errors introduced by undefined nAlk in TA as illustrated by a large discrepancy in  $p\text{CO}_2$  between pH-DIC based and TA-DIC based calculations for the Congo River (Figure S1 in the Supporting Information). The contribution from phosphate and silicate to TA was negligible ( $< 1 \mu\text{mol kg}^{-1}$ ) in all samples (data not shown).

[11] Riverine DIC, TA,  $\text{HCO}_3^-$ , and  $\text{CO}_2^*$  fluxes were estimated using the United States Geological Survey (USGS) LOADEST program (<http://water.usgs.gov/software/loadest>; Table S1 in the Supporting Information). The discharge data were obtained from the Groupe de Recherche en Sciences Exactes et Naturelles in the Republic of Congo. Daily discharge was calculated using flow-stage rating curves based on water stage and automated flow meter measurements. The method was developed by the Institute of Research for Development in France [ORSTOM, 1979].



**Figure 1.** (a) The Congo River basin and time series sampling site at Brazzaville-Kinshasa (yellow star); (b) annual discharge; (c) variations of DIC, TA, and pH (NBS) with discharge; (d) variations of  $\text{HCO}_3^-$ ,  $\text{CO}_2^*$ , and  $p\text{CO}_2$  (calculated from pH and DIC data) with discharge. Arrows in Figures 1c and 1d indicate sampling sequence from December 2010 to December 2011.

[12] The  $\text{CO}_2$  fluxes were calculated based on the one-dimension flux model:  $\text{CO}_2 \text{ Flux} = k \times K_0 \times (p\text{CO}_{2w} - p\text{CO}_{2\text{air}})$ , where  $k$  ( $\text{m d}^{-1}$ ) is the gas transfer velocity,  $K_0$  ( $\text{mol m}^{-3} \text{atm}^{-1}$ ) is the solubility of  $\text{CO}_2$  [Weiss, 1974], and  $p\text{CO}_{2w}$  and  $p\text{CO}_{2\text{air}}$  represent  $p\text{CO}_2$  in surface water and overlying air, respectively. No measured  $k$  values have been reported for the Congo River, although a wide range of  $k$  values and parameterization of calculating  $k$  for estuaries and rivers elsewhere have been reported [Alin et al., 2011; Zappa et al., 2007]. We chose to use the upper mean value of the in situ  $k$  constant ( $2.47 \text{ m d}^{-1}$  with a range  $2.23\text{--}2.47 \text{ m d}^{-1}$ ) measured in the main stem of the Amazon River [Alin et al., 2011] due to the similarity in physical forcing (i.e., meteorology and hydrology) between the two rivers. The upper mean  $k$  value was used to gauge the upper boundary for DIC loss through  $\text{CO}_2$  outgassing at the surface (see details in section 3.3). The global atmospheric mean  $p\text{CO}_2$  ( $390 \mu\text{atm}$  in 2010) was used as  $p\text{CO}_{2\text{air}}$ .

### 3. Results and Discussion

#### 3.1. Hydrology and Inorganic Carbon System

[13] The Congo River at Brazzaville-Kinshasa has a bimodal hydrological cycle with maximum discharge ( $Q$ ) in December and May and minimum  $Q$  in August and March (Figure 1b). Riverine DIC concentrations varied slightly over the annual cycle  $258 \pm 29$  ( $1\sigma$ )  $\mu\text{mol kg}^{-1}$  and did not show a clear relationship with  $Q$  (Figure 1c). Both TA and pH showed a strong negative correlation with  $Q$ . TA values ( $85\text{--}235 \mu\text{mol kg}^{-1}$ ) were among the lowest for large rivers globally [Cai et al., 2008], and the  $Q$ -normalized values are 20–30% lower than those measured previously by Probst et al. [1992]. Bouillon et al. [2012] also found ~30% lower TA values compared to historical data in the Oubangui River [Probst et al., 1992], a major tributary of the Congo. River water pH values were relatively low with a mean  $6.20 \pm 0.40$  pH units, as compared to those previously reported [Dupre et al., 1996]. Annual DIC variation was decoupled from that of TA and pH, except when  $Q$  reached its lowest level. The differences between DIC and TA generally increased with increased discharge. All three measured  $\text{CO}_2$  parameters (Figure 1c) had a slight clockwise hysteresis with higher values during the rising stage of  $Q$ . This pattern was more evident when  $Q > 33,000 \text{ m}^3 \text{ s}^{-1}$ .

[14] Low pH values in the Congo River resulted in elevated levels of  $\text{CO}_2^*$  ( $70\text{--}237 \mu\text{mol kg}^{-1}$ ; Figure 1d) and negligible carbonate ion concentrations ( $[\text{CO}_3^{2-}] < 0.1 \mu\text{mol kg}^{-1}$ ). This caused higher DIC concentrations than TA values during most of the year (Figure 1c), because  $\text{CO}_2^*$

contributes only to DIC, not TA (equations (1) and (2)).  $\text{CO}_2^*$  was positively correlated with  $Q$ , and accounted for 28–83% of the DIC pool.  $\text{CO}_2^*$  surpassed  $\text{HCO}_3^-$  and became the major species in DIC when  $Q > 33,000 \text{ m}^3 \text{ s}^{-1}$  ( $\text{pH} < 6.4$ ; Figures 1c and 1d). The  $p\text{CO}_2$  ( $2018\text{--}6853 \mu\text{atm}$ ) mimicked the  $\text{CO}_2^*$  variation and was supersaturated with respect to the atmosphere. These  $p\text{CO}_2$  values are comparable to the main stems of the Amazon River and other tropical rivers [Aufdenkampe et al., 2011; Richey et al., 2002].  $\text{HCO}_3^-$  was negatively correlated with  $Q$  and accounted for 17–72% of DIC, but 46–92% of TA. Using TA values to estimate  $\text{HCO}_3^-$  and DIC in the Congo River is thus problematic and may cause large inaccuracies.

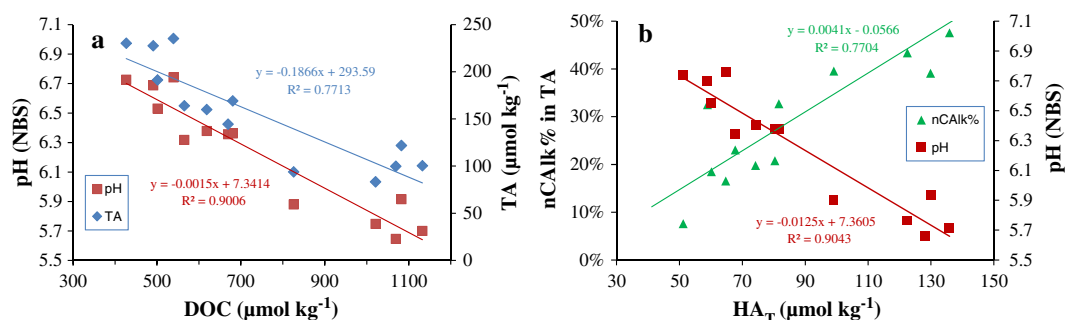
[15] Seasonal variations in the inorganic carbon parameters in the Congo River (Figures 1c and 1d) suggest that river discharge may strongly affect inorganic carbon speciation likely by influencing water pH, but exert limited control on DIC concentrations.

#### 3.2. Inorganic Carbon Speciation and DOC

[16] As the dominant form (>80%) of organic carbon [Coynel et al., 2005], Congo River DOC has a mean concentration of  $\sim 880 \mu\text{mol kg}^{-1}$  ( $10.6 \text{ mg L}^{-1}$ ), more than three times greater than the mean DIC concentration ( $258 \mu\text{mol kg}^{-1}$ ). As such, organic acids in DOC may exert a significant control upon water pH and alkalinity in the Congo River. Low pH and a large amount of unaccounted negative charges for Congo River water have been attributed to the dissociation of organic acids, where organic anions were not included in the charge balance [Dupre et al., 1996].

[17] The effect of DOC on the inorganic carbon system in the Congo River is supported by strong negative linear relationships between DOC and pH and between DOC and TA (Figure 2a). The implication is that (1) the DOC pool has a titration effect on the river water TA and pH; and (2) TA, pH, and other inorganic carbon species would have shown limited seasonal variation if DOC concentrations were low in the river water. The two intercepts of the lines in Figure 2a represent the background pH and TA values ( $\text{pH} = 7.34$  and  $\text{TA} = 294 \mu\text{mol kg}^{-1}$ ) when  $\text{DOC} = 0$ . At this condition, the calculated DIC would be  $323 \mu\text{mol kg}^{-1}$ . The DIC maximum ( $301 \mu\text{mol kg}^{-1}$ ) measured at low flow, low DOC condition (Figure 1c) is close to this hypothetical value.

[18] Riverine discharge has a strong, positive control over Congo River DOC [Coynel et al., 2005; Spencer et al., 2012a]. Consistently, when DOC (and organic acids) reached its annual maximum, the pH, TA, and  $\text{HCO}_3^-$  values were near their annual minima, while  $\text{CO}_2^*$  and  $p\text{CO}_2$  were at their



**Figure 2.** The (a) pH (NBS)-DOC and TA-DOC relationships, and (b) nAlk% (nAlk as a percentage in TA)-HA<sub>T</sub> and pH (NBS)-HA<sub>T</sub> relationships. Straight lines are best fitted lines.

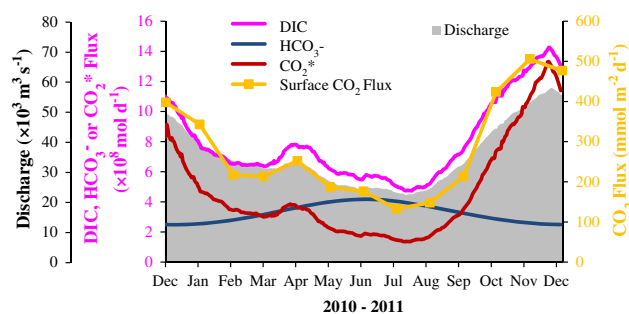
annual maxima (Figures 1 and 2). The hydrological control on riverine DOC in the Congo River may thus have an indirect but significant titration effect on the DIC pool.

[19] The Congo River exhibits relatively high chromophoric dissolved organic matter absorbance normalized to DOC concentration in relation to a range of other rivers, and this attribute has been linked to elevated organic acid concentrations [Spencer *et al.*, 2009, 2012b]. The titration effect can be further demonstrated by comparing total organic acid ( $\text{HA}_T$ ) concentration with TA and pH. Following the empirical organic acid model [Morel and Hering, 1993],  $\text{HA}_T$  concentration can be estimated as  $[\text{HA}_T] (\mu\text{mol kg}^{-1}) \approx 833 \times [\text{DOC}] (\mu\text{mol kg}^{-1})$ , where 833 is the average number of ionizable acid groups per unit mole of DOC. Congo River  $\text{HA}_T$  concentration ( $51\text{--}135 \mu\text{mol kg}^{-1}$ ) was linearly correlated with the percentage of non-carbonate alkalinity in TA (nCAIk%) ( $R^2=0.77$ ; Figure 2b), suggesting that organic acids affected the relative importance of nCAIk and contributed proportionally to total alkalinity. A stronger, but negative linear relationship was found between water pH and  $[\text{HA}_T]$  ( $R^2=0.90$ ; Figure 2b), indicating that the amount of organic acids in the water is a major driver of water pH. Furthermore, this affects speciation of the inorganic carbon system. Note that  $[\text{HA}_T]$  in the Congo River is similar to TA values due to relatively high DOC contents (Figure 2), thus resulting in a visible titration effect.

[20] The above Morel and Hering's model further predicts 40–50% of total organic acid in the Congo River water, depending on water pH, would contribute  $25\text{--}56 \mu\text{mol kg}^{-1}$  organic alkalinity, which represents 11–61% (mean  $33 \pm 18\%$ ) of measured TA values. A large proportion of TA in the Congo River water was thus attributed to organic alkalinity.

### 3.3. Inorganic Carbon Fluxes

[21] Due to the large contribution of nCAIk, using DIC in  $\text{CO}_2$  calculations is more accurate than using TA to evaluate  $\text{CO}_2$  and other carbonate species fluxes. Daily DIC and  $\text{CO}_2^*$  fluxes, both positively correlated with discharge, varying by a factor of approximately 3 ( $4.7\text{--}14.3 \times 10^8 \text{ mol d}^{-1}$ ) and 10 ( $1.4\text{--}13.3 \times 10^8 \text{ mol d}^{-1}$ ), respectively (Figure 3). In contrast, daily  $\text{HCO}_3^-$  fluxes were negatively correlated with  $Q$  and had a lower range ( $2.4\text{--}4.2 \times 10^8 \text{ mol d}^{-1}$ ). During the period of highest  $Q$  (October–February), daily  $\text{CO}_2^*$  fluxes accounted for >50% of daily DIC fluxes, while daily  $\text{HCO}_3^-$  fluxes dominated during the lower  $Q$  months (March–September). Given the DOC titration effect, these findings are consistent with the positive correlation between the DOC flux and discharge observed from this and past studies [Coyne *et al.*, 2005].



**Figure 3.** The 2010–2011 temporal variations of DIC,  $\text{HCO}_3^-$ ,  $\text{CO}_2^*$ , surface  $\text{CO}_2$  outgassing fluxes, and river discharge at Brazzaville, Congo River.

[22] Closely following daily  $\text{CO}_2^*$  fluxes, daily surface  $\text{CO}_2$  fluxes at Brazzaville–Kinshasa varied between 133 and  $506 \text{ mmol m}^{-2} \text{ d}^{-1}$ , with a mean of  $298 \pm 135 \text{ mmol m}^{-2} \text{ d}^{-1}$ . These values are comparable with the Amazon main stem ( $259\text{--}691 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) [Richey *et al.*, 2002], but were much higher than the Oubangui River at Bangui ( $23\text{--}46 \text{ mmol m}^{-2} \text{ d}^{-1}$ ), where higher pH (6.6–8.2) and TA ( $220\text{--}600 \mu\text{mol kg}^{-1}$ ), and lower  $p\text{CO}_2$  were observed [Bouillon *et al.*, 2012].

[23] The annual DIC flux of the Congo River at Brazzaville–Kinshasa between December 2010 and December 2011 was estimated at  $2.88 \times 10^{11} \text{ mol C}$  (Table 1), in which the  $\text{HCO}_3^-$  flux ( $1.19 \times 10^{11} \text{ mol C yr}^{-1}$ ) accounted for 43%, while the  $\text{CO}_2^*$  flux made up the rest. The  $\text{CO}_3^{2-}$  flux was negligible (<1%). Although  $\text{HCO}_3^-$  constituted >50% of DIC during half of the year (Figure 2), it corresponded to the low flow period and resulted in <50% of the DIC flux. Normalized to the 1990–2011 mean discharge ( $Q=1261 \text{ km}^3 \text{ yr}^{-1}$ ), annual fluxes of DIC species (except the  $\text{CO}_2$  flux) increased by 14% (Table 1), as our sampling period had relatively low discharge ( $Q=1108 \text{ km}^3 \text{ yr}^{-1}$ ). These results represent, to our knowledge, the first comprehensive estimate of all DIC species and  $\text{CO}_2$  fluxes from the Congo River. The discharge normalized annual TA flux is 34% lower than that reported previously [Probst *et al.*, 1992], due to lower TA measured during this study. The discharge normalized DIC yield at Brazzaville–Kinshasa was  $8.84 \times 10^4 \text{ mol km}^{-2} \text{ yr}^{-1}$ ; it ranks only 23rd out of the 25 largest rivers in the world [Cai *et al.*, 2008]. In terms of total DIC flux, the Congo River ranks 18th among the world's rivers. Compared to the other two large tropical rivers, the Amazon and Orinoco, the Congo annual DIC flux is about 1/7 and 2/3 of their respective estimates [Cai *et al.*, 2008; Meybeck, 1993].

**Table 1.** Congo River Inorganic Carbon Fluxes Near Brazzaville–Kinshasa, Congo

	DIC	$\text{HCO}_3^-$	$\text{CO}_2^*$	TA
2010–2011 flux ( $\times 10^{11} \text{ mol yr}^{-1}$ )	2.88	1.19	1.67	1.64
Discharge normalized flux <sup>a</sup> ( $\times 10^{11} \text{ mol yr}^{-1}$ )	3.28	1.36	1.90	1.87
2010–2011 yield ( $\times 10^4 \text{ mol km}^{-2} \text{ yr}^{-1}$ )	7.77	3.22	4.51	4.42
Discharge normalized yield <sup>b</sup> ( $\times 10^4 \text{ mol km}^{-2} \text{ yr}^{-1}$ )	8.84	3.66	5.13	5.03
Surface $\text{CO}_2$ flux to the atmosphere ( $\text{mol m}^{-2} \text{ yr}^{-1}$ )	109			
2010–2011 DIC flux to the ocean <sup>c</sup> ( $\times 10^{11} \text{ mol yr}^{-1}$ )	2.73			
Discharge normalized DIC flux to the ocean ( $\times 10^{11} \text{ mol yr}^{-1}$ )	3.11			

<sup>a</sup>Discharge normalized values were calculated by dividing the 2010–2011 values with the annual discharge and multiplying the 1990–2011 mean discharge.

<sup>b</sup>Yield was calculated by dividing the annual fluxes by the Congo River drainage area.

<sup>c</sup>The DIC flux to the ocean was calculated by correcting DIC loss due to  $\text{CO}_2$  outgassing downstream Brazzaville–Kinshasa (see text).

[24] To more accurately estimate actual DIC flux into the ocean, DIC loss via CO<sub>2</sub> outgassing downstream of Brazzaville-Kinshasa (~350 km) needs to be assessed. The mean transit time from Brazzaville-Kinshasa to the ocean is on the order of 1–3 days, using mean flow velocities of 1.4–3.6 m s<sup>-1</sup> in the lower Congo River [Oberg et al., 2009]. The presence of a large number of rapids in the lower Congo River may have opposing effects on CO<sub>2</sub> outgassing: enhancing CO<sub>2</sub> outgassing by increasing turbulence, but reducing total flux by shortening transit time. Small DIC differences (<5 μmol kg<sup>-1</sup>) were observed before and after a large stretch of rapids near Brazzaville-Kinshasa in November 2010, suggesting rapids may have a limited net effect on DIC. Assuming similar CO<sub>2</sub> flux rates (Figure 3) and using a mean water depth of ~64 m [Oberg et al., 2009] and 3 days as the upper bound in transit in the lower Congo, the DIC loss via CO<sub>2</sub> outgassing would range 6–24 μmol kg<sup>-1</sup>, only accounting for 3–8% of measured concentrations. Although this first-order estimate needs to be further studied, limited in-water processing of carbon in the lower Congo is supported by little modification of organic carbon signatures between Brazzaville-Kinshasa and the head of the estuary [Spencer et al., 2012a]. Taking this DIC loss into account, the discharge-normalized Congo River DIC flux to the ocean would be 3.11 × 10<sup>11</sup> mol yr<sup>-1</sup> (Table 1), only 5% less than the flux from Brazzaville-Kinshasa. These findings imply that most of the DIC flux passing Brazzaville-Kinshasa is exported to the ocean even with a high rate of CO<sub>2</sub> outgassing.

#### 4. Implication

[25] Impacts of DOC on the DIC pool are found in other DOC-rich rivers [Cai et al., 1998; Hunt et al., 2011]. The DOC pools of the other two major tropical rivers, the Amazon and Orinoco, also potentially influence their inorganic carbon systems [Mayorga et al., 2005; Paolini et al., 1987; Richey et al., 1990]. The DOC titration effect may be important in organic-rich blackwater rivers as well. To what extent this phenomenon affects the inorganic carbon fluxes, including CO<sub>2</sub> fluxes, globally remains an important question. Concurrent measurements of multiple inorganic parameters and DOC in river water are rare, which makes assessment of such impacts difficult. Two of the four primary inorganic carbon parameters (pCO<sub>2</sub>, pH, DIC, and TA) are required to characterize the CO<sub>2</sub> system in aquatic systems. Since the traditional view that TA primarily consists of carbonate alkalinity can be challenged by significant contribution from undefined acid-base species (e.g., organic acids), such as in the Congo River case, pH-DIC or pCO<sub>2</sub>-DIC pairs would be better to characterize the CO<sub>2</sub> system (see the Supporting Information). In addition, TA should be measured concurrently to provide key information to assess the effects of non-carbonate acid-base species on the CO<sub>2</sub> system.

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