Inorganic carbon speciation and fluxes in the Congo River

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Received 20 November 2012; revised 9 January 2013; accepted 11 January 2013; published 14 February 2013.

[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 CO3**, the sum of dissolved CO2 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 CO3** and bicarbonate fluxes accounted for ~57% and 43% of the DIC flux, respectively. Congo River surface water released CO2 at a rate of ~109 mol m−2 yr−1. The basin-wide DIC yield was ~8.84 × 104 mol km−2 yr−1. The discharge normalized DIC flux to the ocean amounted to 3.11 × 1011 mol yr−1. The DIC 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 (~8.3 × 1017 mol yr−1 or 1.0 × 1015 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 (HCO3) is the dominant species in TA such that DIC ≈ TA ≈ HCO3. 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]:

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

\[
\text{TA} = [\text{HCO}_3^-] + 2 \times [\text{CO}_2^+] + \text{[OrgAlk]} + \text{[other Alk]} + [\text{OH}^-] - [\text{H}^+] \quad (2)
\]

where CO3** is the sum of dissolved CO2 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, CO3** contributes a large proportion to the DIC pool, driving DIC values away from TA and making DIC estimates from TA inaccurate.

[3] Water pH regulates the DIC speciation, thus controlling the partial pressure of CO2 (pCO2) and the CO2 flux across the air-water interface. Global rivers and streams release an estimated 1.7–5.0 × 1013 mol C yr−1 (2.0–6.0 × 1014 g C yr−1) to the atmosphere as a result of air-water CO2 exchange [Austen, 2011; Cole et al., 2007]. Many of the available pCO2 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 pCO2 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 (~45,000 m3 s−1) and drainage basin area (3.7 × 106 km2), the Congo River exports ~1.2 × 1012 mol C yr−1 (1.4 × 1013 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 HCO3 flux has been previously estimated as ~2.7 × 1011 mol C yr−1 (3.2 × 1012 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...
affecting pH and DIC speciation, and (3) estimate the CO₂ outgassing rate and inorganic carbon fluxes to the ocean.

2. Methods

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 µm cartridge filters into 250 mL borosilicate glass bottles using a peristaltic pump. Each sample was poisoned with 60 µL of saturated mercuric chloride and sealed with a greased, ground-glass stopper [Dickson et al., 2007]. DOC samples were filtered into pre-combusted (550°C for 8 h) glass vials, acidified (pH ~ 2), and refrigerated (4°C) in the dark [Mann et al., 2012].

Discrete DIC samples were measured on a DIC autoanalyzer (AS-C3, Apollo SciTech) via sample acidification followed by non-dispersive infrared CO₂ 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 ± 0.1°C. The Gran titration determines total titration alkalinity that includes contributions from all weak acid anions, such as CO₃²⁻, HCO₃⁻, and deprotonated organic acid anions (equation (2)) [Morel and Hering, 1993]. DIC and TA values were reported in µmol kg⁻¹ after being corrected for water density and mercuric chloride addition. Both DIC and TA measurements had a precision and accuracy of ±2.0 µmol kg⁻¹.

Sample pH was measured using a ROSS combination electrode (Thermo Scientific) at 22.0 ± 0.1°C. The electrode was calibrated using three National Bureau of Standards (NBS) solutions (pH = 4.01, 7.00, and 10.01). The pH precision and accuracy was ±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].

Other inorganic carbon parameters, HCO₃⁻, CO₂*, and pCO₂, were calculated using measured pH and DIC data via the CO₂ program by Pierrot et al. [2006] using the freshwater option. Non-carbonate alkalinity (nCAlk) 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 CO₂ system calculations instead of the pH-TA pair to avoid large calculation errors introduced by undefined nCAlk in TA as illustrated by a large discrepancy in pCO₂ 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 µmol kg⁻¹) in all samples (data not shown).

Riverine DIC, TA, HCO₃⁻, and CO₂* 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].
The CO₂ fluxes were calculated based on the one-dimensional flux model: $\text{CO}_2 \text{ Flux} = k \times K_0 \times (p\text{CO}_2 - p\text{CO}_2\text{air})$, where $k$ (m d⁻¹) is the gas transfer velocity, $K_0$ (mol m⁻³ atm⁻¹) is the solubility of CO₂ [Weiss, 1974], and $p\text{CO}_2$ and $p\text{CO}_2\text{air}$ represent $\text{CO}_2$ 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 m d⁻¹ with a range 2.23–2.47 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 CO₂ outgassing at the surface (see details in section 3.3). The global atmospheric mean $p\text{CO}_2$ (390 µatm in 2010) was used as $p\text{CO}_2\text{air}$.

3. Results and Discussion

3.1. Hydrology and Inorganic Carbon System

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±29 (1σ) µmol 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 (85–235 µmol 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±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 CO₂ parameters (Figure 1c) had a slight clockwise hysteresis with higher values during the rising stage of $Q$. This pattern was more evident when $Q > 33,000$ m³ s⁻¹.

Low pH values in the Congo River resulted in elevated values of $\text{CO}_2^*$ (70–237 µmol kg⁻¹; Figure 1d) and negligible carbonic ion concentrations ([CO₂⁻] < 0.1 µmol 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 HCO₃⁻ and became the major species in DIC when $Q > 33,000$ m³ s⁻¹ (pH < 6.4; Figures 1c and 1d). The $p\text{CO}_2$ (2018–6853 µatm) 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 [Aafdenkampe et al., 2011; Richey et al., 2002]. HCO₃⁻ was negatively correlated with $Q$ and accounted for 17–72% of DIC, but 46–92% of TA. Using TA values to estimate HCO₃⁻ and DIC in the Congo River is thus problematic and may cause large inaccuracies.

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

As the dominant form (>80%) of organic carbon [Coyne et al., 2005], Congo River DOC has a mean concentration of ~880 µmol kg⁻¹ (10.6 mg L⁻¹), more than three times greater than the mean DIC concentration (258 µmol 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].

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 (pH = 7.34 and TA = 294 µmol kg⁻¹) when DOC = 0. At this condition, the calculated DIC would be 323 µmol kg⁻¹. The DIC maximum (301 µmol kg⁻¹) measured at low flow, low DOC condition (Figure 1c) is close to this hypothetical value.

Riverine discharge has a strong, positive control over Congo River DOC [Coyne et al., 2005; Spencer et al., 2012a]. Consistently, when DOC (and organic acids) reached its annual maximum, the pH, TA, and HCO₃⁻ values were near their annual minima, while $\text{CO}_2^*$ and $p\text{CO}_2$ were at their
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 (HA) concentration with TA and pH. Following the empirical organic acid model [Morel and Hering, 1993], HA concentration can be estimated as 

\[ [HA] = 883 \times [DOC] \]  

where 883 is the average number of ionizable acid groups per unit mole of DOC. Congo River HA concentration (51–135 μmol kg\(^{-1}\)) was linearly correlated with the percentage of non-carbonate alkalinity in TA (nCalk%) (R\(^2\)=0.77; Figure 2b), suggesting that organic acids affected the relative importance of nCalk and contributed proportionally to total alkalinity. A stronger, but negative linear relationship was found between water pH and [HA] (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 [HA] 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 25–56 μmol kg\(^{-1}\) organic alkalinity, which represents 11–61% (mean 33 ± 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 nCalk, using DIC in CO\(_2\) calculations is more accurate than using TA to evaluate CO\(_2\) and other carbonate species fluxes. Daily DIC and CO\(_2^{*}\) fluxes, both positively correlated with discharge, varying by a factor of approximately 3 (4.7–14.3 × 10\(^{-3}\) mol d\(^{-1}\)) and 10 (1.4–13.3 × 10\(^{-3}\) mol d\(^{-1}\)), respectively (Figure 3). In contrast, daily HCO\(_3\) fluxes were negatively correlated with Q and had a lower range (2.4–4.2 × 10\(^{-3}\) mol d\(^{-1}\)). During the period of highest Q (October–February), daily CO\(_2^{*}\) fluxes accounted for >50% of daily DIC fluxes, while daily 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].

[22] Closely following daily CO\(_2^{*}\) fluxes, daily surface CO\(_2\) fluxes at Brazzaville-Kinshasa varied between 133 and 506 mmol m\(^{-2}\) d\(^{-1}\), with a mean of 298 ± 135 mmol m\(^{-2}\) d\(^{-1}\). These values are comparable with the Amazon main stem (259–691 mmol m\(^{-2}\) d\(^{-1}\)) [Richey et al., 2002], but were much higher than the Oubangui River at Bangui (23–46 mmol m\(^{-2}\) d\(^{-1}\)), where higher pH (6.6–8.2) and TA (220–600 μmol kg\(^{-1}\)) and lower pCO\(_2\) 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 × 10\(^{11}\) mol C (Table 1), in which the HCO\(_3\) flux (1.19 × 10\(^{11}\) mol C yr\(^{-1}\)) accounted for 43%, while the CO\(_2^{*}\) flux made up the rest. The CO\(_2^{*}\) flux was negligible (<1%). Although 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 km\(^3\) yr\(^{-1}\)), annual fluxes of DIC species (except the CO\(_2\) flux) increased by 14% (Table 1), as our sampling period had relatively low discharge (Q = 1108 km\(^3\) yr\(^{-1}\)). These results represent, to our knowledge, the first comprehensive estimate of all DIC species and 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 × 10\(^4\) mol km\(^{-2}\) 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

<table>
<thead>
<tr>
<th></th>
<th>DIC</th>
<th>HCO(_3)</th>
<th>CO(_2^{*})</th>
<th>TA</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010–2011 flux (×10(^{11}) mol yr(^{-1}))</td>
<td>2.88</td>
<td>1.19</td>
<td>1.67</td>
<td>1.64</td>
</tr>
<tr>
<td>Discharge normalized flux* (×10(^{11}) mol yr(^{-1}))</td>
<td>3.28</td>
<td>1.36</td>
<td>1.90</td>
<td>1.87</td>
</tr>
<tr>
<td>2010–2011 yield (×10(^{3}) mol km(^{-2}) yr(^{-1}))</td>
<td>7.77</td>
<td>3.22</td>
<td>4.51</td>
<td>4.42</td>
</tr>
<tr>
<td>Discharge normalized yield* (×10(^{3}) mol km(^{-2}) yr(^{-1}))</td>
<td>8.84</td>
<td>3.66</td>
<td>5.13</td>
<td>5.03</td>
</tr>
<tr>
<td>Surface CO(_2) flux to the atmosphere (mol m(^{-2}) yr(^{-1}))</td>
<td>109</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2010–2011 DIC flux to the ocean* (×10(^{3}) mol yr(^{-1}))</td>
<td>2.73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Discharge normalized DIC flux to the ocean (×10(^{3}) mol yr(^{-1}))</td>
<td>3.11</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

*Discharge normalized values were calculated by dividing the 2010–2011 values with the annual discharge and multiplying the 1990–2011 mean discharge.

*Yield was calculated by dividing the annual fluxes by the Congo River drainage area.

*The DIC flux to the ocean was calculated by correcting DIC loss due to CO\(_2\) outgassing downstream Brazzaville-Kinshasa (see text).
To more accurately estimate actual DIC flux into the ocean, DIC loss via CO₂ 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⁻¹ 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 CO₂ outgassing: enhancing CO₂ outgassing by increasing turbulence, but reducing total flux by shortening transit time. Small DIC differences (<5 μmol kg⁻¹) 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 CO₂ 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 CO₂ outgassing would range 6–24 μmol kg⁻¹, 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 × 10¹¹ mol yr⁻¹ (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 CO₂ outgassing.

4. Implication

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 CO₂ 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 (pCO₂, pH, DIC, and TA) are required to characterize the CO₂ 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 pCO₂-DIC pairs would be better to characterize the CO₂ 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 CO₂ system.

References


