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Effect of evapotranspiration on dissolved inorganic carbon and stable carbon isotopic evolution in rivers in semi-arid climates: The Okavango Delta in North West Botswana

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ABSTRACT

Study region: Okavango Delta, Middle Kalahari, NW Botswana.
Study focus: We investigated the effect of evapotranspiration on the evolution of dissolved inorganic carbon (DIC) and stable carbon isotopes of DIC ($\delta^{13}C_{DIC}$) in the Okavango River. We measured the DIC concentrations and the $\delta^{13}C_{DIC}$ for samples collected over a 400 km reach of the river in the Okavango Delta during flood conditions and non-flood conditions. In addition, we incubated river samples collected from the proximal portion (Mohembo) and the distal portion (Maun) of the Delta and subsequently evaporated the samples by ~90% under ambient conditions.
New hydrological insights: We found a 379% and 500% increase in the DIC concentrations and a $\delta^{13}C_{DIC}$ increase of 3.9‰ and 6.1‰ in the river during the flood non-flood conditions, respectively. The DIC concentrations of evaporated river samples increased by 535% for the Mohembo and by 850% for the Maun samples. The increase in the $\delta^{13}C_{DIC}$ of the evaporated river samples resulted from $CO_{2(g)}$ loss during chemical equilibrium with atmospheric $CO_{2(g)}$ followed by carbon exchange between DIC and atmospheric $CO_{2(g)}$. Although the $\delta^{13}C_{DIC}$ increased spatially for the Okavango River, it never reached the value of ~0‰ expected for equilibration of river DIC with atmospheric $CO_{2(g)}$. The results of the evaporated river samples suggest that isotopic enrichment from equilibration in Okavango River was balanced by respiration and photo-oxidation of carbon-depleted dissolved organic matter.

1. Introduction

The carbon in riverine dissolved inorganic carbon (DIC; $CO_{2(aq)} + HCO_3^- + CO_3^{2-}$) pool constantly interacts with atmospheric $CO_{2(g)}$, making rivers an important interface in the transfer of terrestrial and aquatic carbon to the atmosphere (Meybeck, 1982; Richey et al., 2002; Cole et al., 2007). In fact, it is estimated globally that 50% of riverine carbon is trans-

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ferred to the atmosphere before rivers discharge to the oceans (Cole et al., 2007). Carbon cycling investigations in rivers have focused in tropical and temperate regions and because rivers in these regions empty into the ocean; they are useful for the quantification of global carbon cycling (e.g., Hope et al., 1994; Telmer and Veizer, 1999; Raymond and Cole, 2001; Hélie et al., 2002; Richey et al., 2002; Brunet et al., 2005; Kanduč et al., 2007; Billett and Moore, 2008; Johnson et al., 2008). Studies of carbon cycling in river systems that do not discharge into the ocean are limited perhaps because they do not export carbon to the ocean and are assumed to be unimportant in the global carbon cycle. River systems that do not empty into the oceans are endorheic and largely exist in arid environments and prominent ones, such as the Amu Darya River and the Chari and Logone Rivers are characterized by the presence of former large lakes at their terminus (e.g., Seeley et al., 2002). The cycling of carbon in endorheic river systems will be different from that of tropical and temperate river systems because of fundamental differences in water cycle processes. For example, in arid environments, discharge tends to decrease down river due mostly to evaporative loses and an influent hydrologic flow regime. In tropical and temperate environments, discharge generally increases down river due to effluent hydrologic conditions. At the terminus of endorheic rivers in arid environments, water is retained temporally at the surface where it is subjected to further evaporation and/or recharges groundwater. While the cycling of carbon in an endorheic river basin occurs entirely within the terrestrial/atmospheric reservoirs, the role of these endorheic rivers systems in local, regional or global carbon cycling remains unclear.

We can predict that carbon at the terminus of an endorheic rivers is going to be stored in solid (organic and inorganic) forms, in the dissolved form in groundwater (as DIC or dissolved organic carbon) or transferred into the atmosphere. However, the balance and interplay between the physical, chemical and biological processes and the hydrologic and climatic controls on carbon cycling are not clearly understood. The link between riverine carbon and the atmospheric $CO_{2(g)}$ is via DIC and variations in the DIC concentrations in the riverine DIC pool commonly reflect input/output of carbon that is in part controlled by river-atmosphere interaction. Nevertheless, increases in the DIC concentrations in rivers in arid environments where high rates of evaporation occur may not always be due to carbon input (e.g., Akoko et al., 2013).

The stable carbon isotope ratio of DIC ($\delta^{13}C_{DIC}$) in the river water changes when carbon is (1) added (e.g., dissolution of $CO_{2(g)}$, weathering of $CaCO_3$ or from organic matter oxidation), (2) removed (e.g., photosynthesis, evasion or precipitated as carbonates), or (3) exchanged between the DIC pool and atmospheric $CO_{2(g)}$. Carbon from different sources has unique isotopic composition and the transformation of carbon by several of the processes involve in carbon cycling cause isotopic fractionation (e.g., Clark and Fritz, 1997). Thus, the $\delta^{13}C_{DIC}$ in river water represents a bulk property whose value is influenced by (1) source of carbon, (2) processes that cause ^{13}C vs. ^{12}C partitioning and (3) the extent to which the processes that cause ^{13}C vs. ^{12}C partitioning affect the DIC pool.

We can use the spatial and temporal variations in DIC concentrations and the $\delta^{13}C_{DIC}$ to evaluate the effects of hydrology, chemistry and river-atmosphere interaction in carbon cycling in an endorheic river system. We selected the Okavango Delta at the terminus of the Okavango River basin for this study. The Okavango Delta is at the terminus of an endorheic river basin and occurs in a semiarid environment (Seeley et al., 2002). The Okavango River flows for over 400 km for 4–6 months through a wetland complex. The long residence time exposes river water to evaporation and transpiration which affects solute chemistry and the dense aquatic and wetland vegetation allows for extensive river water-vegetation-atmosphere interactions which affect carbon cycling. A previous study by Akoko et al. (2013) suggested that evapotranspiration was responsible for the spatial increases observed in the DIC concentrations across the Okavango Delta. Also, despite the occurrence of extensive vegetation and organic matter in the delta, Akoko et al. (2013) suggested that equilibration of carbon in the river DIC and atmospheric $CO_{2(g)}$ dominated DIC and $\delta^{13}C_{DIC}$ evolution. To assess the role of evapotranspiration in DIC concentration changes and the role of respiration of organic matter on the $\delta^{13}C_{DIC}$, we collected, incubated and evaporated river water from the proximal end of the delta before significant evapotranspiration and from the distal end after extensive evapotranspiration. Our objective was to use the temporal DIC concentrations and the $\delta^{13}C_{DIC}$ results of the evaporated river water interacting with the atmosphere to assess the DIC and $\delta^{13}C_{DIC}$ evolutionary behavior for river water spatially across the Okavango Delta during flood and non-flooding seasons. These results provide greater insights into the DIC evolutionary behavior and into the cycling of carbon at the terminus of an endorheic river system in a semiarid environment.

2. Study site

The Okavango River (Fig. 1) is located in semiarid NW Botswana. The Okavango River at its terminus consists of a Panhandle region and a series of distributaries (The Okavango Delta) developed on an alluvial fan (>22,000 km^2) that supports Africa's largest pristine wetland complex (McCarthy et al., 1993). The vegetation type, distribution and density have been described and define different wetland ecotones (Fig. 1): permanently flooded, seasonally flooded and occasional flooded regimes (e.g., McCarthy et al., 1993).

The hydrology of the Okavango Delta is characterized by an annual flood pulse which travels down the delta in 4–6 months. High water conditions occur in the dry season (April to October) when the delta is flooded by discharge from subtropical watersheds in Angola, while low water conditions occur during the rainy season (November to March) when local rainfall estimated annually at 450 mm (e.g., McCarthy et al., 2012; Milzow et al., 2009) produces no or limited flooding across the delta. Within the Okavango Delta, groundwater in the local watershed does not recharge the river as groundwater table depths are several tens of meters below river level ((McCarthy et al., 1998). Since the hydraulic gradient is from the