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# The carbon budget of a large catchment in the Argentine Pampa plain through hydrochemical modeling

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## HIGHLIGHTS

- Hydrochemical modeling is a simple tool to estimate C budgets in water systems.
- C flux estimations are equal to 100% (I) = 11.9% (G) + 6.7% (S) + 81.4% (E).
- The main output of C is towards the Mar Chiquita lagoon and/or to the ocean.
- C fluxes to the atmosphere are very low in extremely flat environments.
- Calcite precipitation is the main C sink in the system.

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## ABSTRACT

Mar Chiquita is a coastal lagoon located in the Argentine Buenos Aires province in South America. The aim of this study is to estimate the annual contribution of inland waters to the carbon cycle in this lagoon's catchment by estimating the corresponding local carbon budget. Fifteen pairs of water samples were chosen to carry out hydrogeochemical modeling using PHREEQC software. Groundwater samples were considered as recharge water (initial solutions), while streamwater samples were taken as groundwater discharge (final solutions for inverse modeling/reference solutions for direct modeling). Fifteen direct models were performed, where each groundwater sample was constrained to calcite equilibrium under two different carbon dioxide partial pressure ($P_{CO2}$) conditions: atmospheric conditions (log $P_{CO2}$ (atm) = −3.5) and a $P_{CO2}$ value of log $P_{CO2}$ (atm) = −3. Groundwater samples are close to calcite equilibrium conditions. The calcite precipitation process is kinetically slower than gas diffusion, causing oversaturation of this reactant phase in streamwater samples. This was accompanied by a pH increase of approximately two units due to a $P_{CO2}$ decrease. From the fifteen inverse models it was estimated that, of the total carbon that enters per year in the hydrological cycle of the study area, about 11.9% is delivered to the atmosphere as $CO_2$ and around 6.7% is buried in sediments. This would indicate that 81.4% of the remaining carbon is retained in equilibrium within the system or discharged into the Mar Chiquita lagoon and/or directly to the ocean through regional flows.



## 1. Introduction

The carbon (C) cycle is the biogeochemical cycle by which carbon is exchanged among the biosphere, hydrosphere, atmosphere, lithosphere and anthroposphere of the Earth. As a result, carbon is distributed in several components of these terrestrial systems that are called “sinks”. A carbon sink is a natural or artificial reservoir that accumulates and stores some carbon-containing chemical compound for an indefinite period. Carbonate sedimentary rocks are the most important carbon sink (Bolin, 1981; IPCC, 2001; Siegenthaler and Sarmiento, 1993).

This boundless carbon cycle consists of two loops (Regnier et al., 2013): 1) the organic carbon loop, which starts with the lateral leakage of some of the organic carbon that is fixed into the terrestrial biosphere by photosynthesis. This carbon is then horizontally transferred through aquatic channels down to the coastal and open ocean, where is returned to the atmosphere as carbon dioxide ($CO_2$); and 2) the inorganic loop, which is driven by the land-based weathering of silicate and carbonate rocks that consumes atmospheric $CO_2$. Subsequently, weathering products of cations, anions and dissolved inorganic carbon are transported to the ocean, where part of the $CO_2$ is returned to the atmosphere through

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ocean carbonate sediment formation (a process that increases the $CO_2$ partial pressure, $P_{CO2}$, in seawater). The other part is returned by volcanism.

Although only about 1% of the Earth's surface is assumed to be covered by inland waters, their collective contribution to global carbon fluxes is substantial compared to terrestrial and marine ecosystems (Tranvik et al., 2009). "Inland waters" are aquatic environments located within land boundaries. These include lakes, rivers, ponds, streams, groundwater, springs, cave waters, floodplains, as well as bogs, marshes and swamps, which are traditionally grouped as inland wetlands. Streams and rivers do tend to be supersaturated with carbon dioxide when compared to the atmosphere and are a source of atmospheric $CO_2$ (Cole et al., 2007).

On a global scale, a general estimation of the inland water contribution to the carbon cycle was performed by Cole et al. (2007). They formulated a simplified mass balance to track the fate of carbon (organic plus inorganic) in an integrated freshwater and terrestrial carbon budget as (Fig. 1a):

$$I = G + S + E \tag{1}$$

where the carbon imported to aquatic systems (I) can be estimated as the net carbon gas balance of the aquatic system with the atmosphere (G), plus storage (S) and export in drainage waters (E): surface water (mostly riverine flux) and groundwater.

To the extent that I may exceed E in Eq. (1), Cole et al. (2007) proposed that freshwaters, from a mass balance point of view, would not function as neutral passive "pipes" but are a place of active transformation ("active pipes"). Following this proposal, they estimated that inland waters annually receive, from a combination of background and anthropogenically altered sources, on the order of 1.9 petagrams of carbon per year (Pg C/yr; Pg: $10^{15}$ g) from the terrestrial landscape (I). From this amount, at least 0.75 Pg C/yr (39.5%) (possibly much more) are returned to the atmosphere as gas exchange (G), 0.23 Pg C/yr (12.1%) are buried in aquatic sediments (S), while the remaining 0.9 Pg C/yr (48.4%) are delivered to the ocean (E) almost equally as inorganic and organic carbon. Recent global estimations of present-day (2000–2010) carbon fluxes were provided by Regnier et al. (2013). For these authors, the Eq. (1) of Cole et al. (2007) is equal to: 2.9 Pg C/yr = 1.35 Pg C/yr (45.8%) + 0.6 Pg C/yr (20.3%) + 1.0 Pg C/yr (33.9%) (see "Supplementary note" for further details) (Fig. 1b).

Regional studies on different environments can be useful to improve global carbon flux estimations. The understanding of local processes involving $CO_2$ outgassing and carbonate precipitation can be extrapolated at global scale in order to estimate the effects of changes in freshwater chemistry. The Pampa plain in Argentina is a large (1,500,000 $km^2$) temperate humid to sub-humid prairie. In its most southern sector, there is an extremely flat area, occupying about 90,000 $km^2$, which is known as Depressed Pampa (Tricart, 1973). This is characterized by extremely very low topographic gradients (around 0.001%), a precipitation average of 1000 mm/yr and it is crossed by small streams. Groundwater and streamwater in this environment are alkaline and bicarbonate type, the entire system being open to the atmosphere (Glok Galli et al., in press).

The aim of this study is to estimate the annual contribution of inland waters to the carbon cycle in a catchment in the Pampa's plain environment, the Mar Chiquita lagoon's catchment, by performing hydrogeochemical balances and modeling. Therefore, the derivative objective is to develop an easy method to estimate existing carbon fluxes between

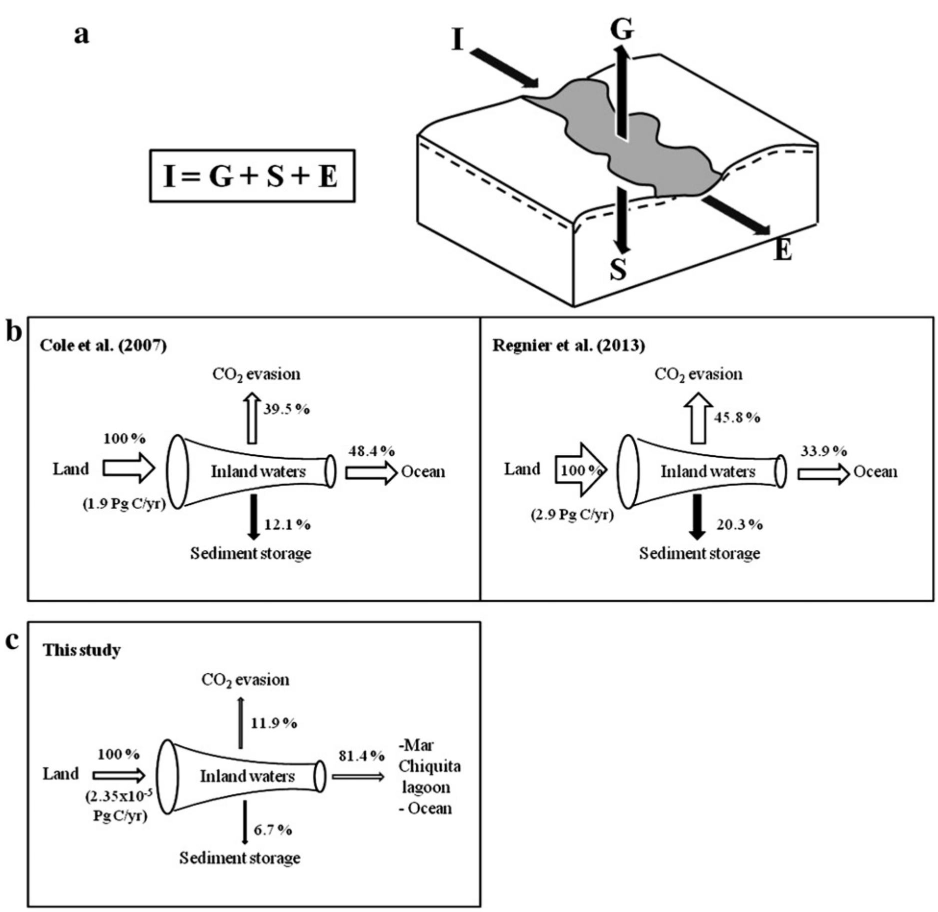


**Fig. 1.** (a) Graphical scheme illustrating the simplified mass balance (Eq. (1)) formulated by Cole et al. (2007), (b) representation of global carbon budgets estimated by Cole et al. (2007) and Regnier et al. (2013), and (c) representation of the carbon budget estimated in this study—(b) and (c) the "active pipe" concept presented by Cole et al. (2007) was applied (values represented as % C/yr).