



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



M. Glok Galli^{a,b,c,1}, D.E. Martínez^{a,b,c}, E.E. Kruse^{a,d}

^a Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Av. Rivadavia 1917, C1033AAJ Ciudad Autónoma de Buenos Aires, Argentina

^b Instituto de Investigaciones Marinas y Costeras (IIMyC), CONICET-Universidad Nacional de Mar del Plata (UNMDP), Funes 3350, 7600 Mar del Plata, Argentina

^c Instituto de Geología de Costas y del Cuaternario (IGCyC)-UNMDP, Casilla de correo 722, 7600 Mar del Plata, Argentina

^d Facultad de Ciencias Naturales y Museo-Universidad Nacional de La Plata (UNLP), Calle 60 y 122, 1900 La Plata, Argentina

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.

ARTICLE INFO

Article history:

Received 19 March 2014

Received in revised form 5 June 2014

Accepted 10 June 2014

Available online xxxx

Editor Eddy Y. Zeng

Keywords:

Carbon budget

Mar Chiquita lagoon's catchment

Hydrogeochemical modeling

pH

CO₂ partial pressure

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 CO₂ 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.

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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 (CO₂); and 2) the inorganic loop, which is driven by the land-based weathering of silicate and carbonate rocks that consumes atmospheric CO₂. Subsequently, weathering products of cations, anions and dissolved inorganic carbon are transported to the ocean, where part of the CO₂ is returned to the atmosphere through

E-mail address: gloggalli@mdp.edu.ar (M. Glok Galli).

¹ Tel.: +54 223 475 3150.

ocean carbonate sediment formation (a process that increases the CO_2 partial pressure, P_{CO_2} , 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):

$$I = G + S + E \quad (1)$$

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

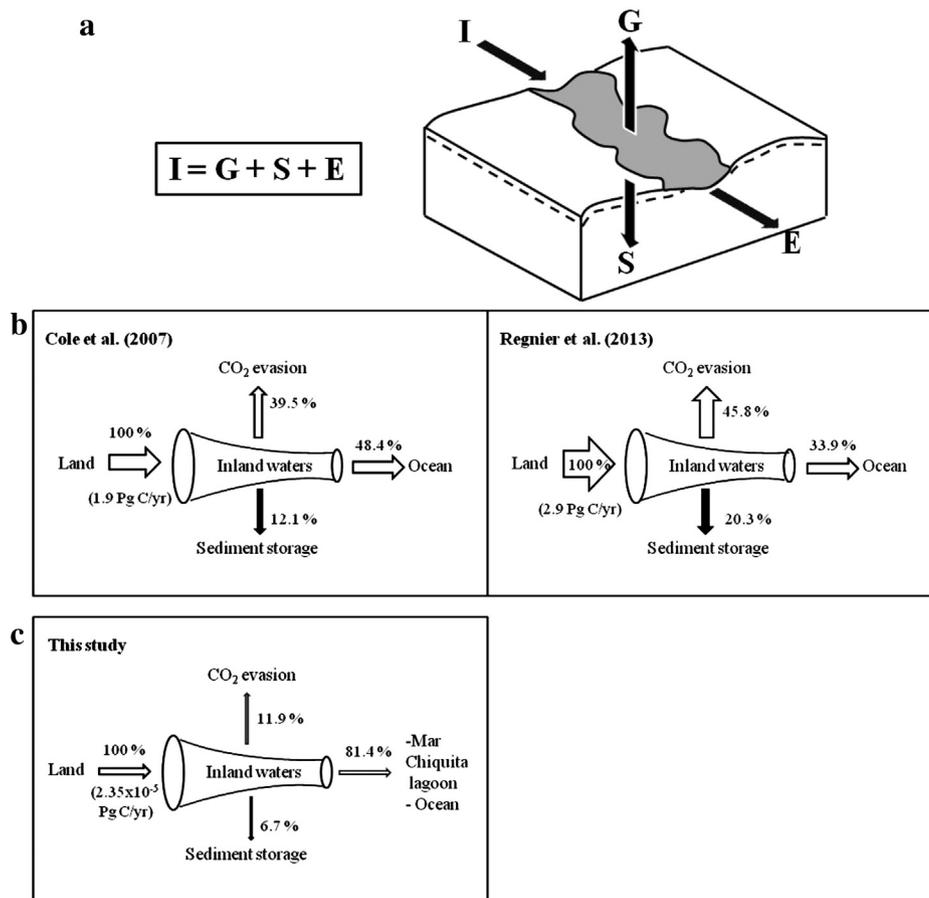


Fig. 1. (a) Graphical scheme illustrating the simplified mass balance (Eq. (1)) formulated by Cole et al. (2007), (b) representation of global carbon budgets estimated by Cole et al. (2007) and Regnier et al. (2013), and (c) representation of the carbon budget estimated in this study—(b) and (c) the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

the hydrological cycle components and the atmosphere/lithosphere (study area's sediments).

2. Hydrogeological and hydrogeochemical description

Mar Chiquita lagoon's catchment is located in the southeast of the Depressed Pampa's plain, covering an area of approximately 10,000 km² (Fasano, 1980) (Fig. 2). This lagoon receives the discharge of many streams draining the catchment and has a mouth open to the ocean having an estuarine behavior. The geomorphology of the region is characterized by the presence of the Tandilia Mountain System, located in the most western section and where the tributaries conforming the catchment have their sources. This is surrounded by a zone of hills and fluvial–aeolian plain, which ends in a seafront with an approximate extent of 50 km (Fig. 2). According to its dominant topographical features, it is possible to recognize three defined zones with different hydrogeological behavior: mountain ranges (aquifuge rocks), hills (recharge zone) and plain (transit and discharge zones).

The piezometric level contour map analysis shows that streams are mainly gaining streams (Glok Galli et al., in press; Lima, 2012; Sala, 1975). Regarding the hydrogeochemical characteristics in the study area, despite surface water and groundwater correspond to the same hydrogeochemical facies (sodium bicarbonate type); differences in the chemical composition are generally observed (Glok Galli et al., in press). The most notable change is a marked increase in streamwater alkalinity with respect to the discharging groundwater. The electrical conductivity (EC) average value of groundwater is $1514.5 \pm 102.5 \mu\text{S/cm}$, ranging between 419 $\mu\text{S/cm}$ and 8180 $\mu\text{S/cm}$. Its pH and temperature mean values are 7.4 ± 0.7 and $16.5 \pm 0.1 \text{ }^\circ\text{C}$, respectively. On the other hand, streamwater has an EC mean value of $1121 \pm 67.6 \mu\text{S/cm}$, with a minimum of 795 $\mu\text{S/cm}$, reaching a maximum of 2020 $\mu\text{S/cm}$. The average temperature value is $18.7 \pm 1.1 \text{ }^\circ\text{C}$ and the mean value of pH is 8.3 ± 1.8 , showing its higher alkalinity (Glok Galli et al., in press).

The climate is “temperate-humid” according to the Köppen classification, or “sub-humid mesothermal, without deficiency of water” according

to the Thornthwaite method (Kruse, 1986). Over the last 40 years, annual mean rainfall was 936.5 mm, December and January being the rainiest months, while August and June had the lowest values. In the last 15 years, the annual average temperature was 13.6 $^\circ\text{C}$, July being the coldest month and January the warmest (Glok Galli et al., in press).

Based on field work and the description of drilling debris, it is possible to recognize the presence of impermeable basement in the study area, including Precambrian Basement rocks and Eopaleozoic orthoquartzites of the Balcarce Formation (Dalla Salda and Iñiguez, 1979). A thick clastic sequence of silt and silt-sandy loess-like sediments is also present, being the most important section from a hydrogeological point of view because it is part of the principal aquifer of the region, the Pampeano aquifer (Martínez and Bocanegra, 2002; Sala, 1975, 1977).

The Pampeano aquifer is an “unconfined and multi-layer” detritic aquifer, which lies sometimes directly over the very compact orthoquartzites, although fractured, and others over a Miocene deposit of marine green clays (Paraná Formation). This consists of Pampeano sediments “sensu strictu” (Pleistocene–Holocene) and Holocene loessic sediments known as Post-Pampeano sediments. Its thickness can vary from a few meters to more than 100 m and its grain size is variable, between sand and silt and with clay intercalations. Levels of “tosca” or powdered CaCO₃ and volcanic ash appear sporadically (Teruggi, 1954). The aquifer's recharge occurs due to the rain water excess of the hydrological cycle in the region, and its natural discharge takes place mostly as deep groundwater flows to the Atlantic Ocean (Glok Galli et al., in press). The shallow groundwater discharge occurs into the Mar Chiquita lagoon, either through streams or direct discharge (Glok Galli et al., in press; Lima et al., 2013).

3. Materials and methods

Sampling campaigns were carried out between October 2010 and November 2012. A total of one hundred and fifty-four groundwater samples and twenty-one streamwater sampling points were collected

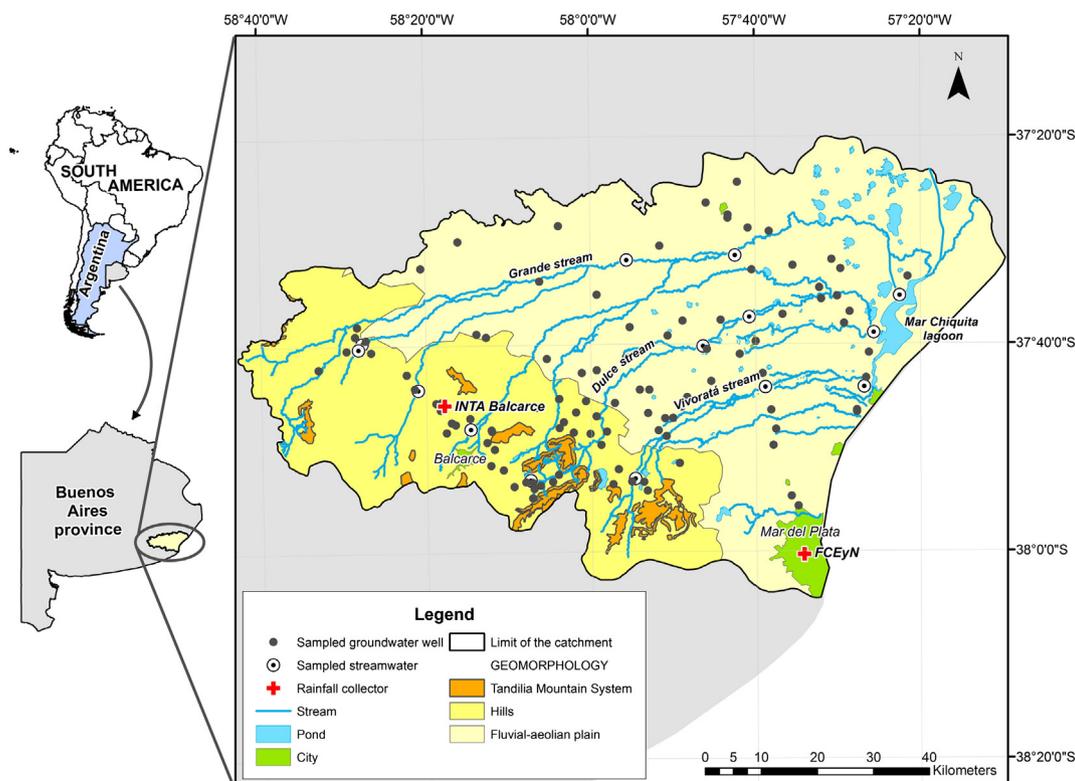


Fig. 2. Location map, geomorphology, sampling sites and rainfall stations.

(Fig. 2). From these, fifteen groundwater samples and fourteen streamwater sampling points were chosen to form the fifteen pairs of water samples used to perform hydrogeochemical modeling through PHREEQC software (Parkhurst and Appelo, 1999) (Fig. 3). These pairs were selected considering that streams are mainly gaining creeks in the Mar Chiquita lagoon's catchment (Glok Galli et al., in press; Lima, 2012; Sala, 1975). Every pair of water is in a groundwater flow line and consists of a groundwater sampling point and a sample of the stream where this groundwater is discharging (Fig. 3). Groundwater sampling points 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).

Alkalinity (as HCO_3^-), pH and electrical conductivity were determined in situ at each sampling location. Sampling points were located through a global positioning system (Garmin eTrex Vista GPS). Chemical analyses were carried out at the Hydrogeochemistry and Isotope Hydrology Laboratory of the "Instituto de Geología de Costas y del Cuaternario", Mar del Plata University (Mar del Plata city, Argentina). Total hardness and major ion concentrations were determined in all samples. The standard methods used were: chloride following Mohr method, sulfate by turbidimetry, calcium and magnesium by complexometric titrations with EDTA, sodium and potassium by flame spectrometry, silica by means of the silicomolibdate method, nitrate by the brucine method and bicarbonate-carbonate by potentiometric titration. Furthermore, fluorine by the zirconyl chloride method and total iron by spectrophotometry (Hach Drel2800 Ferrover1 method) were done. Chemical determinations were performed following detailed methodology in APHA (1992) (see "Supplementary Table 4" for further details).

3.1. Hydrogeochemical modeling

3.1.1. Direct models

Firstly, calcite saturation index (SI_{cal}) values were calculated for all water samples using PHREEQC (columns 3 and 4, Table 1). For each groundwater sampling point, the corresponding logarithm of carbon dioxide partial pressure, $\log P_{\text{CO}_2}$ (atm), was obtained from Eq. (2) (Appelo and Postma, 1993) (column 7, Table 1), at a temperature in average equal to 16.3 ± 0.3 °C (see "Supplementary Table 4"). Field measurements of alkalinity and pH were used for this purpose:

$$\log P_{\text{CO}_2}(\text{atm}) = \log[\text{HCO}_3^-] + 7.8 - \text{pH} \quad (2)$$

Then, fifteen direct hydrogeochemical models were carried out. Each groundwater sample used as the initial solution (column 1, Table 1) was constrained to calcite equilibrium under two different P_{CO_2} conditions: atmospheric conditions ($\log P_{\text{CO}_2}$ (atm) = -3.5) and a P_{CO_2} value of $\log P_{\text{CO}_2}$ (atm) = -3 , considering some variation due to algal activity in stream bodies. The SI_{cal} (columns 8 and 10, Table 1) and pH values (columns 9 and 11, Table 1) modeled for streamwater samples were taken into account in the final analysis of these direct models.

Direct models try to represent the changes produced when groundwater, typically saturated with respect to calcite and with $\log P_{\text{CO}_2}$ (atm) values of around -1.5 , due to recharge through the non-saturated zone, discharges into streams. As a result, this discharging groundwater is equilibrated to atmospheric $\log P_{\text{CO}_2}$ (atm) conditions (-3.5) or similar.

3.1.2. Inverse models

Fifteen inverse hydrogeochemical models were performed using PHREEQC (Table 2). An analytical error varying between 5% and 14%

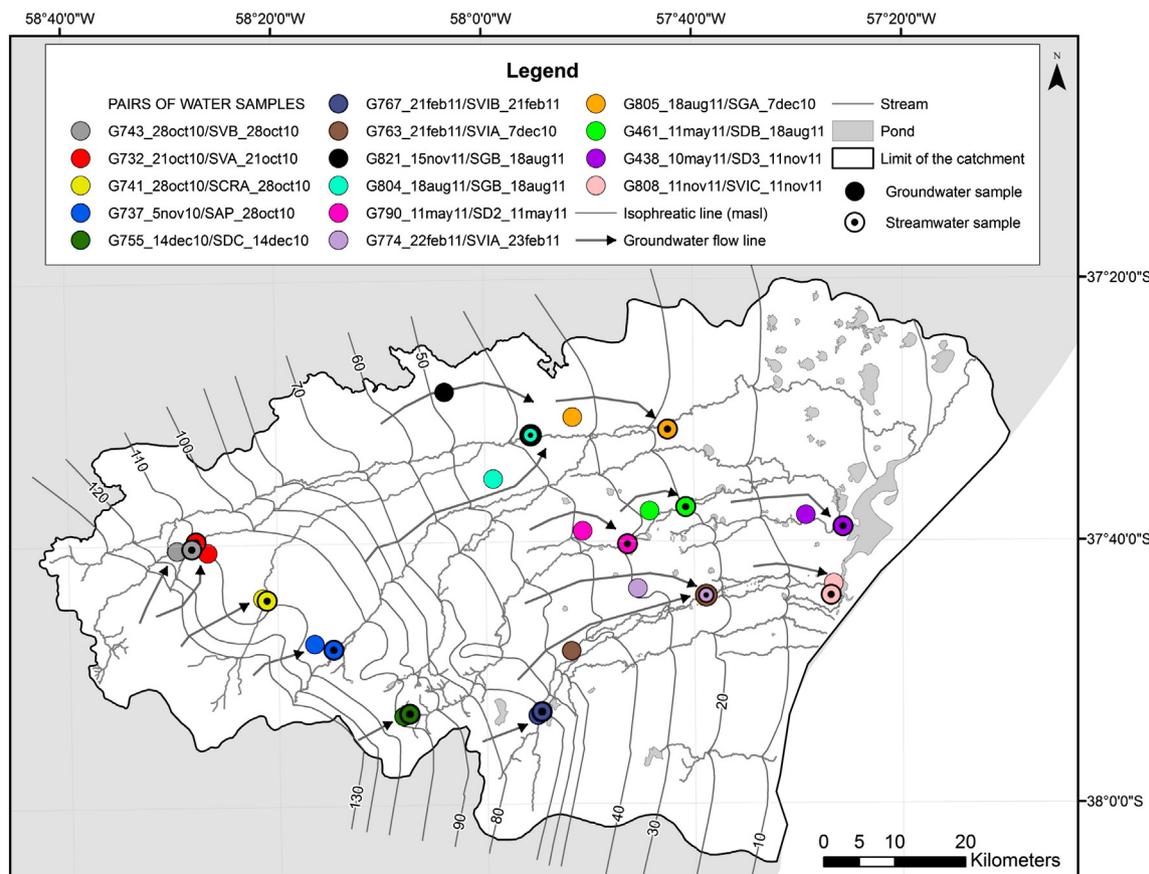


Fig. 3. Location of the fifteen pairs of water samples used to perform hydrogeochemical modeling through PHREEQC software.

Table 1

Direct hydrogeochemical modeling. Values of calculated and modeled parameters for groundwater and streamwater samples. (1) $\log P_{\text{CO}_2}$ (atm) = -3 ; (2) $\log P_{\text{CO}_2}$ (atm) = -3.5 (see explanation below the table).

Column	1	2	3	4	5	6	7	8	9	10	11
	Groundwater (GW) samples	Streamwater (SW) samples	GW SI_{cal}	SW SI_{cal}	GW pH	SW pH	GW $\log P_{\text{CO}_2}$ (atm)	SW modeled $SI_{\text{cal}}^{(1)}$	SW modeled pH ⁽¹⁾	SW modeled $SI_{\text{cal}}^{(2)}$	SW modeled pH ⁽²⁾
G743_28oct10	SVB_28oct10	−0.38	0.76	7.1	8.1	−1.2	1.19	8.7	1.48	9.2	
G732_21oct10	SVA_21oct10	0.27	1.51	7.9	9.5	−1.9	1.09	8.8	1.36	9.3	
G741_28oct10	SCRA_28oct10	0.09	0.84	7.6	8.3	−1.7	1.13	8.8	1.44	9.2	
G737_5nov10	SAP_28oct10	−0.16	1.52	7.4	8.8	−1.5	1.14	8.8	1.44	9.2	
G755_14dec10	SDC_14dec10	0.34	1.49	7.6	8.8	−1.5	1.47	8.9	1.71	9.3	
G767_21feb11	SVIB_21feb11	0.24	0.75	7.8	8.3	−2.0	1.04	8.7	1.37	9.1	
G763_21feb11	SVIA_7dec10	0.25	1.23	7.7	8.5	−1.7	1.27	8.9	1.50	9.3	
G821_15nov11	SGB_18aug11	0.08	0.82	7.4	8.3	−1.5	1.35	8.8	1.64	9.2	
G804_18aug11	SGB_18aug11	0.33	0.82	7.4	8.3	−1.5	1.55	8.7	1.85	9.2	
G790_11may11	SD2_11may11	−0.61	1.36	7.0	8.5	−1.5	0.76	8.4	1.15	8.9	
G774_22feb11	SVIA_23feb11	0.41	0.83	8.0	8.3	−2.1	1.08	8.8	1.38	9.1	
G805_18aug11	SGA_7dec10	0.35	1.46	7.1	8.9	−1.0	1.93	8.9	2.17	9.3	
G461_11may11	SDB_18aug11	0.04	1.13	7.3	8.6	−1.4	1.42	8.8	1.71	9.2	
G438_10may11	SD3_11nov11	0.19	1.34	7.5	8.5	−1.6	1.34	8.7	1.65	9.1	
G808_11nov11	SVIC_11nov11	0.60	0.79	7.2	8.2	−1.4	1.80	8.5	2.08	8.9	
Average		0.14	1.11	7.5	8.5	−1.6	1.30	8.7	1.59	9.2	

Column 1: groundwater samples taken as initial solutions.

Column 2: streamwater samples taken as reference solutions for models validation.

Column 3: calcite saturation indexes calculated by PHREEQC for groundwater samples.

Column 4: calcite saturation indexes calculated by PHREEQC for streamwater samples.

Column 5: pH values of groundwater samples determined "in situ" in the sampling campaigns.

Column 6: pH values of streamwater samples determined "in situ" in the sampling campaigns.

Column 7: $\log P_{\text{CO}_2}$ (atm) of groundwater samples calculated from equation: $\log P_{\text{CO}_2}$ (atm) = $\log [\text{HCO}_3^-] + 7.8 - \text{pH}$.

Column 8: calcite saturation indexes modeled through PHREEQC software for streamwater samples with a $\log P_{\text{CO}_2}$ (atm) = -3 .

Column 9: pH values of streamwater samples modeled through PHREEQC software with a $\log P_{\text{CO}_2}$ (atm) = -3 .

Column 10: calcite saturation indexes modeled through PHREEQC software for streamwater samples with a $\log P_{\text{CO}_2}$ (atm) = -3.5 .

Column 11: pH values of streamwater samples modeled through PHREEQC software with a $\log P_{\text{CO}_2}$ (atm) = -3.5 .

was accepted. Calcite, $\text{CO}_{2(\text{g})}$, gypsum, halite and ionic exchange of Ca^{2+} , Mg^{2+} and Na^+ were taken into account as reactant phases. These were selected considering that: 1) the Pampeano aquifer is a phreatic aquifer, which means that it is open to the atmosphere; 2) the texture of the sediments includes clay size, which provokes higher exchange capacity; 3) the CaCO_3 in outcropping sections is abundant; and 4) former detailed studies were performed in the area by Martínez and Bocanegra (2002). For halite, this mineral is not present in the aquifer's matrix. It precipitates in the non-saturated zone by evaporation and is incorporated to groundwater during recharge. This

phase involves the continuous input from the non-saturated zone when infiltration leaches the precipitated salts (Glok Galli et al., in press).

Inverse models give the amount of transferred carbon occurred in each reaction when groundwater discharges into streamwater. The simplified mass balance Eq. (1) of Cole et al. (2007) was considered as the basis to perform carbon net flux estimations between the hydrological cycle components and the atmosphere/lithosphere in the region under study.

In order to obtain the annual value of carbon that enters from the terrestrial landscape into the hydrological system of the study area (I), the following pre-existing data were used: the Mar Chiquita lagoon's catchment area of 10,000 km^2 (Fasano, 1980), the recharge mean value for the region under study of 152.6 mm/yr (Glok Galli et al., in press), and the average value of HCO_3^- in precipitation of 77.98 ± 13 mg/L . This latter was calculated from the HCO_3^- concentrations of twelve samples that were taken from the rainfall collectors located at the "INTA Balcarce" (National Institute of Agricultural Technology in Balcarce city; 121.5 m above sea level—masl) and "Facultad de Ciencias Exactas y Naturales (FCEyN)", Mar del Plata University (Mar del Plata city; 15.1 masl) (Fig. 2). Thus, the resulting equation is:

$$I = [\text{HCO}_3^-]_{\text{precipitation}} \times \text{recharge} \times \text{catchment's area} \quad (3)$$

For the estimation of the annual carbon delivered to the atmosphere as CO_2 and buried in sediments in the study area (G and S, respectively), the calculated annual mean streams' discharge value of 108×10^6 m^3/yr was used. This was obtained considering the Dulce stream's flow of 1.142 ± 0.03 m^3/s (Lima, 2012) as a mean value between the Vivoratá and Grande streams (Fig. 2), then using a total discharge of 3.426 m^3/s . Reactant phases including inorganic carbon transfer were also used, whether as released $\text{CO}_{2(\text{g})}$ or precipitated calcite, for the calculation of "G" or "S", respectively (Table 2). The organic carbon fraction was

Table 2

Inverse hydrogeochemical modeling. Values in millimoles per litre (mmol/L) of precipitated (−)/dissolved (+) Calcite and released (−)/dissolved (+) CO_2 obtained as result through PHREEQC software.

Initial solution	Final solution	Model results	
		$\Delta\text{Calcite}$ (mmol/L)	ΔCO_2 (mmol/L)
G743_28oct10	SVB_28oct10	1.35	−1.06
G732_21oct10	SVA_21oct10	−0.007	−3.02
G741_28oct10	SCRA_28oct10	0.37	−1.39
G737_5nov10	SAP_28oct10	4.18	1.77
G755_14dec10	SDC_14dec10	−0.004	−1.79
G767_21feb11	SVIB_21feb11	−0.37	−0.82
G763_21feb11	SVIA_7dec10	−1.17	−2.22
G821_15nov11	SGB_18aug11	0.52	−0.58
G804_18aug11	SGB_18aug11	−0.88	−2.1
G790_11may11	SD2_11may11	4.12	2.47
G774_22feb11	SVIA_23feb11	0.28	−0.051
G805_18aug11	SGA_7dec10	−3.22	−7.65
G461_11may11	SDB_18aug11	−2.4	−4.28
G438_10may11	SD3_11nov11	−1.62	−2.65
G808_11nov11	SVIC_11nov11	0.59	−0.35

Pair "A": G737_5nov10/SAP_28oct10.

Pair "B": G790_11may11/SD2_11may11.

excluded because its levels are normally low, ranging between 0.1 mg/L and 4 mg/L, while inorganic carbon may exceed 100 mg/L and 200 mg/L (Barcelona, 1984). Moreover, the organic fraction consideration exceeds the capabilities of PHREEQC, but using this program has been preferred to develop a simple methodology, because it is widely known and free software. Otherwise, there are two pairs of water samples that were not used in the “G” and “S” calculations, because these have calcite and $\text{CO}_{2(g)}$ values that indicate conditions to be considered separately from the other sampling points. Thus, the resulting equations are:

$$G = \Delta\text{CO}_{2 \text{ released}} \times \text{streamwater}' \text{ discharge} \quad (4)$$

and

$$S = \Delta\text{Calcite}_{\text{precipitated}} \times \text{streamwater}' \text{ discharge} \quad (5)$$

Finally, knowing I, G and S values, the remaining carbon exported in surface water and groundwater (E) for the Mar Chiquita lagoon's catchment can be estimated following the equation:

$$E = I - (G + S) \quad (6)$$

4. Results and discussion

The hydrogeochemical modeling results are shown in Tables 1 and 2, where the selected pairs of samples are sorted from W to E of the study area (Fig. 3).

For the direct hydrogeochemical modeling, groundwater and streamwater samples are shown in Table 1, in columns 1 and 2, respectively. Calcite is generally close to equilibrium in groundwater sampling points, with an average SI_{cal} of 0.14 ± 0.1 (column 3), but supersaturated in streamwater samples, with a mean SI_{cal} of 1.11 ± 0.1 (column 4). This latter SI_{cal} mean value is increased if the groundwater $\log P_{\text{CO}_2}$ (atm) value (average value: -1.6 ± 0.1 ; column 7) is decreased. Therefore, the streamwater average SI_{cal} value is 1.30 ± 0.1 when $\log P_{\text{CO}_2}$ (atm) = -3 (column 8) and 1.59 ± 0.1 when there is a change toward atmospheric conditions ($\log P_{\text{CO}_2}$ (atm) = -3.5 ; column 10).

On the other hand, a pH average value for groundwater samples of 7.5 ± 0.1 (column 5) and a mean value of 8.5 ± 0.1 (column 6) for streamwater sampling points were obtained. The modeled values of pH for streamwater samples are 8.7 ± 0.03 when $\log P_{\text{CO}_2}$ (atm) = -3 (column 9) and 9.2 ± 0.03 when $\log P_{\text{CO}_2}$ (atm) = -3.5 (column 11). Taking into account these two pH modeled mean values and the average value of this parameter for groundwater samples (7.5), a pH increase of about two units was observed as a general result, with values higher than 7 to values of around 9 (Table 1).

As can be seen in Table 2 for inverse hydrogeochemical modeling, two highlighted pairs of water samples have high positive (+) values for $\Delta\text{Calcite}$, indicating an important dissolution process for this mineral. That is, for pair “A” (see explanation below Table 2), which has a $\Delta\text{Calcite} = 4.18$ mmol/L, because this pair of samples is located in the recharge zone of the study area. However, pair “B” (see explanation below Table 2), with a $\Delta\text{Calcite} = 4.12$ mmol/L, is situated in the transit zone, but these samples having low EC values (419 $\mu\text{S}/\text{cm}$ and 906 $\mu\text{S}/\text{cm}$ for groundwater and streamwater, respectively), suggesting a local recharge process. In turn, the highlighted positive (+) ΔCO_2 values

corresponding to these pairs of samples, being equal to 1.77 mmol/L for pair “A” and 2.47 mmol/L for pair “B”, are also indicating the $\text{CO}_{2(g)}$ dissolution in waters of regional and local recharge zones, respectively.

Regarding the rest of the 13 sample pairs, in five of them, positive (+) values for $\Delta\text{Calcite}$ indicating dissolution (mean value: 0.62 ± 0.2 mmol/L) were found, while negative (–) values in eight samples suggested a larger amount of calcite precipitation (average value: -1.21 ± 0.4 mmol/L). The ΔCO_2 values were negative in the 13 cases (mean value: -2.15 ± 0.6 mmol/L), manifesting CO_2 outgassing processes. These obtained values of released carbon dioxide (2.15 mmol/L) and precipitated calcite (1.21 mmol/L) were used for the “G” and “S” calculation, respectively (Eqs. (4) and (5)).

As a result, the estimated annual value of carbon imported from the terrestrial landscape to the hydrological system of the study area, obtained from Eq. (3), is of about 2.35×10^{-5} Pg C/yr. Of these, around 2.79×10^{-6} Pg C/yr is emitted to the atmosphere as $\text{CO}_{2(g)}$ (Eq. (4)) and approximately 1.57×10^{-6} Pg C/yr is stored in sediments when calcite precipitation occurs (Eq. (5)). The remaining 1.91×10^{-5} Pg C/yr is retained in equilibrium within the system or discharged into the Mar Chiquita lagoon and/or directly to the ocean through regional flows (Eq. (6)).

Table 3 shows carbon budgets at different scales estimated by previously named authors (Cole et al., 2007; Regnier et al., 2013) and Rasera et al. (2008), together with the present study results. The petagrams of carbon per year obtained as results in each work were represented following the simplified mass balance formulated by Cole et al. (2007) (Eq. (1)). Work scales used in each paper were different and consequently, the superficial water bodies' discharge values that were compared are very diverse.

A comparison between estimates performed by this current study and the publication of Rasera et al. (2008) could be made (Table 3). In this latter, the authors elucidated the small rivers' role, which compounds the largest extension (92%) of the Amazon River network, in air–water CO_2 exchange. They estimated CO_2 outgassing rates (term G) at the Ji-Paraná River Basin, in the western Amazon. For the total drainage area of the Ji-Paraná Basin, a G value of $3.08 \times 10^{-4} \pm 1.88 \times 10^{-4}$ Pg C/yr was obtained, which is correlated with the lower G value of 2.79×10^{-6} Pg C/yr estimated for the Mar Chiquita lagoon's catchment. In the first basin, its area of 75,400 km^2 and river discharge's mean values varying between 54×10^9 m^3/yr (high water stage: 15 January–15 April) and 7×10^9 m^3/yr (low water stage: July–October), are higher than the area of the catchment under study of 10,000 km^2 and its streamwater discharge's annual value of 108×10^6 m^3/yr . Taking into account the typical small discharge of the Depressed Pampa' streams, it can be explained why the carbon contribution to the atmosphere in the Mar Chiquita lagoon's catchment is lower than that in the Ji-Paraná Basin. Thereby, an increase in the carbon export to the lagoon and/or to the ocean through groundwater direct discharge (term E) is produced in the study area.

Extrapolating this medium size catchment behavior to the entire geographic region, which covers an area of 90,000 km^2 , the simplified mass balance result—from Eq. (1) $I = G + S + E$ —for the Argentine Depressed Pampa plain would be equal to:

$$2.11 \times 10^{-4} \text{Pg C/yr} = 2.51 \times 10^{-5} \text{Pg C/yr} + 1.41 \times 10^{-5} \text{Pg C/yr} + 1.72 \times 10^{-4} \text{Pg C/yr} \quad (7)$$

Table 3
Carbon budgets at different scales estimated by different authors and this study. Terms I, G, S and E taken from Cole et al. (2007).

Study region/area	Authors	I	G	S	E
Pg (10^{15} g) C/yr					
Global scale	Cole et al.(2007)	1.9	0.75	0.23	0.9
	Regnier et al. (2013)	2.9	1.35	0.6	1.0
Total drainage area of the Ji-Paraná Basin (~75,400 km^2)	Rasera et al. (2008)		$3.08 \times 10^{-4} \pm 1.88 \times 10^{-4}$		
Mar Chiquita lagoon's catchment (10,000 km^2)	This study	2.35×10^{-5}	2.79×10^{-6}	1.57×10^{-6}	1.91×10^{-5}

The obtained amount of carbon released to the atmosphere from inland waters is smaller (2.51×10^{-5} Pg C/yr) than the previous “G” estimation performed by Rasera et al. (2008) (Table 3). This is because in the Depressed Pampa environment extremely low slopes impede the development of a well defined drainage network, dominating stream's courses which are smaller than big rivers as those present in the Ji-Paraná Basin.

5. Conclusions

For the Mar Chiquita lagoon's catchment, the obtained results from direct hydrogeochemical models fit better to the measured parameter values by exposing the groundwater log P_{CO_2} (atm) value of -1.6 to a log P_{CO_2} (atm) = -3 . This could be due to the activity of organisms inhabiting streams of the study area allowing the maintenance of a CO_2 partial pressure somewhat higher than that in the atmosphere (log P_{CO_2} (atm) = -3.5). Groundwater samples in the study area 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 the P_{CO_2} decrease.

The corresponding local carbon budget was performed by analyzing the obtained inverse hydrogeochemical models in order to estimate the annual contribution of inland waters to the carbon cycle in the catchment under study. It can be concluded that from the 100% of carbon annually entering into the hydrological cycle from the terrestrial landscape of the Mar Chiquita lagoon's catchment (I), about 11.9% is delivered to the atmosphere as CO_2 (G) and 6.7% is buried in sediments (S). The remaining 81.4% of carbon is retained in equilibrium within the system or discharged into the lagoon and/or directly to the ocean through deep groundwater flows (E) (Fig. 1c).

The extremely flat landscape of the study area minimizes the surface runoff to about just 1% of the total precipitation, increasing the importance of groundwater flows. This reduces the streamwater discharge into the lagoon and consequently, the mass transference to the atmosphere and the storage in sediments. Moreover, it can be observed that when superficial water bodies' discharge values are smaller, the CO_2 outgassing and the carbon burial in sediments are lower.

The catchment of the Mar Chiquita lagoon was studied as representative of typical watersheds in humid climate plains. Usually, most of the carbon balances in hydrological systems are focused on big rivers, but the contribution of large areas drained by small streams is not evaluated. About 8 million km^2 are occupied by this kind of landscapes in South America, including thousands of small catchments in which the hydrogeochemical modeling can be applied to obtain the partial carbon contribution of great basins' components. In this way, this simple methodology is a useful tool to get more detailed values of the amounts of carbon transferred to possible sinks.

Conflict of interest

All the authors have no conflicts of interest.

Acknowledgments

The authors would like to thank the financial support of CONICET (National Council of Scientific and Technical Research—Argentina) for the period 2009–2011, through PIP 112 200801 01318 KE1

“EVOLUCIÓN Y DINÁMICA DE LA PLANICIE COSTERA DE MAR CHIQUITA”, and to the ANPCyT that also contributes through the project PICT 2011 0768. We are also thankful to Ferrante A., Tec., who collaborated in the sampling; and Bernava G.V., Tec., who performed the chemical analyses.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2014.06.032>.

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