



A new direction in effective accounting for the atmospheric CO₂ budget: Considering the combined action of carbonate dissolution, the global water cycle and photosynthetic uptake of DIC by aquatic organisms

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ABSTRACT

The magnitudes, variations, locations and mechanisms responsible for the global atmospheric CO₂ sink are uncertain and under continuing debate. Previous studies have focused mainly on the sinks in the oceans, and soil and vegetation on the continents. Here, we show, based on theoretical calculations and field monitoring evidence, that there is an important but previously underestimated sink for atmospheric CO₂ as DIC-dissolved inorganic carbon that results from the combined action of carbonate dissolution, the global water cycle and the photosynthetic uptake of DIC by aquatic organisms in ocean and land. The sink constitutes up to 0.8242 Pg C/a, amounting to 29.4% of the terrestrial CO₂ sink, or 10.4% of the total anthropogenic CO₂ emission. 0.244 Pg C/a are transferred to the sea via continental rivers and 0.2278 Pg C/a by meteoric precipitation over the seas. 0.119 Pg C/a is released back to the atmosphere again, and 0.2334 Pg C/a is stored in the continental aquatic ecosystem. Therefore, the net sink is estimated as 0.7052 Pg C/a. This sink may increase with an intensification of the global water cycle as a consequence of global warming, rising anthropogenic emissions of CO₂ and carbonate dust in atmosphere, and afforestation, which increases the soil pCO₂ and thus the carbonate dissolution. Fertilization with the elements N, P, C, Fe, Zn, and Si increases the organic matter storage/burial by aquatic organisms and thus decreases the CO₂ return to the atmosphere. Based on the ensemble mean projection of global warming for the year 2100 by IPCC, it is estimated that the atmospheric CO₂ sink will increase by 21%, or about 0.18 Pg C/a. However, the uncertainty in the estimation of this sink needs further exploration.

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1. Introduction

One of the most important challenges in the science of global change is effective accounting of the global budget for atmospheric CO₂ (Broecker et al., 1979; Tans et al., 1990; Sundquist, 1993; Joos, 1994; Schindler, 1999; Melnikov and O'Neill, 2006). Anthropogenic activities have clearly altered the global carbon cycle and significant gaps exist in our understanding of this cycle. Roughly half of the CO₂ emitted by burning fossil fuels remains in the atmosphere, and the other half is absorbed by the oceans and the terrestrial biosphere (Tans et al., 1990; Siegenthaler and Sarmiento, 1993; Raven and Falkowski, 1999; Sabine et al., 2004; Reay et al., 2007). The partitioning between these two sinks is the subject of considerable debate (Tans et al., 1990; Sabine et al., 2004). Without robust accounting for the fate of CO₂ leaving the atmosphere predictions of future CO₂ concentrations will remain uncertain (Siegenthaler and Oeschger, 1978; Jones et al., 2003).

As defined by Melnikov and O'Neill (2006), increase in atmospheric CO₂ concentration (N_a) is a function of emissions from fossil fuels (E_{ff}) together with net emissions from changes in land use (E_{lu}) minus the uptake in oceans (F_{oc}) and the residual (terrestrial) sink (F_{res}).

$$N_a(t) = E_{ff}(t) + E_{lu}(t) - F_{oc}(t) - F_{res} \quad (1)$$

Current estimates suggest that $E_{ff} = 6.3$ Pg C/a, $E_{lu} = 1.6$ Pg C/a, $F_{oc} = 1.9$ Pg C/a, and $N_a = 3.2$ Pg C/a. Therefore, the terrestrial sink is $F_{res} = 2.8$ Pg C/a.

Previous studies have focused mainly on sinks in the oceans and soil/vegetation on the continent (Detwiler and Hall, 1988; Sarmiento and Sundquist, 1992; Hudson et al., 1994; Davidson et al., 1995; Friedlingstein et al., 1995; Khashgi et al., 1996; Nabuurs et al., 1997; Fan et al., 1998; Schulze et al., 1999; Lal, 2004; Woodbury et al., 2007). Here, we show, based on theoretical calculations and evidence from field monitoring results, that there is an important but previously underestimated sink (Meybeck, 1993; Liu and Zhao, 2000; Gombert, 2002) for atmospheric CO₂ by the combined action of carbonate dissolution (Dreybrodt, 1988), the global water cycle (Shiklomanov, 1993), and the photosynthetic uptake of DIC (dissolved inorganic carbon) by aquatic organisms (Yang et al., 1996; Einsele et al., 2001; Lerman and Mackenzie, 2005; Iglesias-Rodriguez et al., 2008). This sink is much larger than previous estimations where only riverine transport of atmospheric carbon was considered (Meybeck, 1993). It is also larger than the sink that arises from dissolution of carbonate rocks in the world's karst areas (Liu and Zhao, 2000; Gombert, 2002). The sink is caused by CO₂ uptake in rainwater and soil water. Dissolution of carbonates by these waters consumes their enhanced CO₂ concentrations worldwide and not only in the karst areas.

2. Methods and data

The atmospheric CO₂ sink in rainfall is given by:

$$\text{Rainwater flux} \times \text{observed mean DIC concentration in rainwater.} \quad (2)$$

The CO₂ sink in the continental runoff is computed as:

$$\text{Runoff flux} \times \text{calculated equilibrium DIC concentration with respect to the world's mean soil CO}_2 \text{ and calcite.} \quad (3)$$

The rainwater flux and runoff flux were taken from the work of Shiklomanov (1993). To estimate the mean DIC of rainwater, 16 references (Munger, 1982; Panettiere et al., 2000; Lara et al., 2001; Zhang et al., 2003; Al-Khashman, 2005a; Kulshrestha et al., 2005; Liu et al., 2005; Rastogi and Sarin, 2005; Jawad Al Obaidy and Joshi, 2006;

Arsene et al., 2007; Báez et al., 2007; Singh et al., 2007; Özsoy et al., 2008; Anatolaki and Tsitouridou, 2009; Celle-jeanton et al., 2009; Ladouche et al., 2009) were used, which report representative DIC or HCO₃⁻ data of the rainwater from various locations around the globe (Fig. 1). The carbon flux calculated from these data is considered only for rainwater falling into the oceans. The CO₂ from rainfall on land contributes to the soil pCO₂ and must therefore be excluded from this balance; otherwise it would be counted twice. To obtain the sink of CO₂ due to continental runoff we assume that the groundwater is in equilibrium with the soil pCO₂ and also with calcite in carbonate terrains. The corresponding equilibrium values of DIC are listed in Table 1. The runoff fluxes were calculated separately for carbonate and non-carbonate regions, the former having a much higher DIC for the same pCO₂ because of the presence of dissolved carbonate.

Global mean soil pCO₂ was calculated by use of the equation by Brook et al. (1983) as:

$$\log(\text{pCO}_2) = -3.47 + 2.09 \left(1 - e^{-0.00172 \text{ AET}}\right), \quad (4)$$

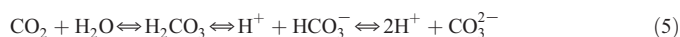
where AET is the annual evapotranspiration in mm.

The equilibrium DIC concentration in calculating the CO₂ sink via continental runoff is based on both theoretical and field observational evidences (Dreybrodt, 1988; Ford and Williams, 1989, 2007; White, 1997; Liu et al., 2007), which are given in the Sections 3 and 4.

The net CO₂ sink is calculated as: (the total CO₂ sink by dissolution of carbonate and CO₂) – (CO₂ release flux from runoff waters). The latter depends on the difference in pCO₂ between water and the atmosphere, which depends again on the balance of carbonate deposition and organic matter storage/burial in the water (Einsele et al., 2001; Lerman and Mackenzie, 2005).

3. Solubility of CO₂ in the systems of CO₂–H₂O and CaCO₃–CO₂–H₂O and calculation of equilibrium DIC concentration

CO₂ is readily soluble in water. The reaction:



establishes an equilibrium mixture of carbonic acid, bicarbonate and carbonate ions, which make up the “dissolved inorganic carbon” (DIC) fraction. The proportion of each species depends on pH. At high pH the reaction shifts to the right hand side of Eq. (5). At pH between 7 and 9, about 95% of the carbon in the water is in the form of bicarbonate (HCO₃⁻). At high pH > 10.5, carbonate predominates (Dreybrodt, 1988).

At a global mean annual surface temperature of 15 °C and global mean atmospheric CO₂ partial pressure (pCO₂) of 380 ppmv, the equilibrium value of the DIC for the CO₂–H₂O system is calculated to be 20 μmol/l according to Dreybrodt (1988). However, in the CaCO₃–CO₂–H₂O system, uptake of CO₂ by water is enhanced remarkably by carbonate dissolution, which can be presented as:



For each Ca²⁺ dissolved one CO₂ molecule is converted to HCO₃⁻. For example, at 15 °C and a pCO₂ of 380 ppmv, the equilibrium concentration of the DIC for the CaCO₃–CO₂–H₂O system is 1231 μmol/l, or about 66 times larger than that in the CO₂–H₂O system (Table 1). If carbonate dissolution proceeds in soil water or in groundwater recharged by soil water with higher pCO₂, the amount of the CO₂-uptake by water is even larger (Table 1). For example, according to Brook et al.'s (1983) Eq. (4) using global mean annual evapotranspiration of 548 mm in the continents (Shiklomanov, 1993), world soil pCO₂ may reach up to ~6400 ppmv. In this case,

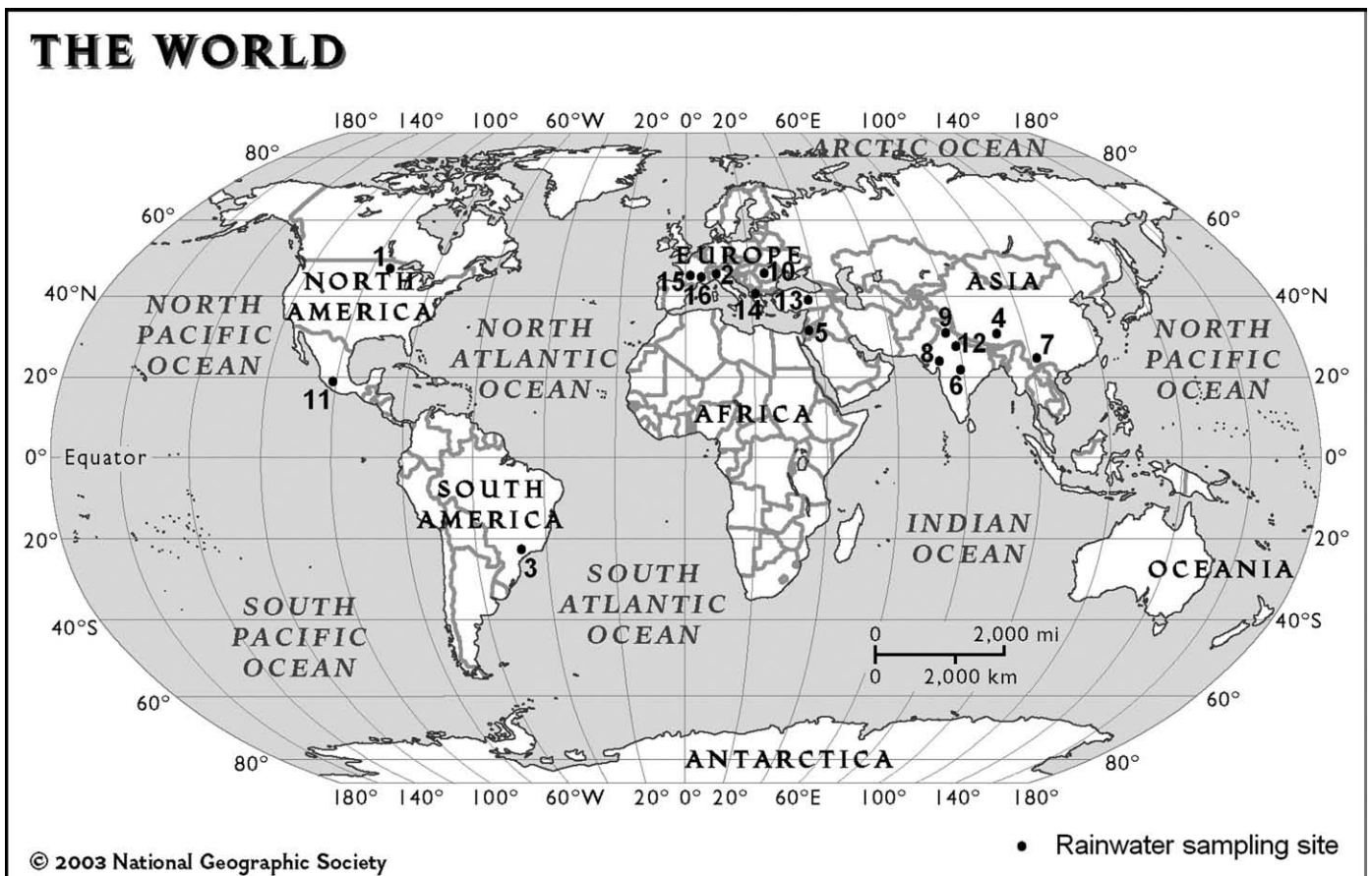


Fig. 1. The geographic location of each source of rainwater data on the globe. The world map is from <http://www.nationalgeographic.com/resources/ngo/education/xpeditions/atlas/>. 1: North-Central United States (Munger, 1982); 2: Bologna, Italy (Panettiere et al., 2000); 3: Piracicaba River Basin, Southeast Brazil (Lara et al., 2001); 4: Lhasa, Tibet (Zhang et al., 2003); 5: Eshidiya area, Jordan (Al-Khashman, 2005a); 6: Hyderabad, south-central India (Kulshrestha et al., 2005); 7: Xishuangbanna, Southwest China (Liu et al., 2005); 8: Ahmedabad, NW India (Rastogi and Sarin, 2005); 9: Roorkee, North India (Jawad Al Obaidy and Joshi, 2006); 10: the northeastern Romania, Iasi region (Arsene et al., 2007); 11: Mexico City, Mexico (Báez et al., 2007); 12: Northern Indo-Gangetic Plains (Singh et al., 2007); 13: Mersin, North-Eastern Mediterranean Region (Özsoy et al., 2008); 14: Thessaloniki, Greece (Anatolaki and Tsitouridou, 2009); 15: Hérault region, France (Celle-Jeanton et al., 2009); 16: Gard region, France (Ladouche et al., 2009).

equilibrium values of the DIC for $\text{CO}_2\text{-H}_2\text{O}$ and $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ systems are 302 and 3643 $\mu\text{mol/l}$, respectively (Table 1).

DIC can be also derived from the weathering and dissolution of silicate minerals. The weathering process also involves consumption of CO_2 (Ludwig et al., 1998; Dupré et al., 2003; Mortatti and Probst, 2003). In a simplified form it can be presented as:



The CO_2 is supplied either directly from the atmosphere or from soils.

The above reactions are important in the sequestration of atmospheric CO_2 because all of the HCO_3^- for silicate weathering and half in the case of carbonate dissolution are of atmospheric origin. Although the soil CO_2 comes from the decay of organic matter, and not directly from the atmosphere, the uptake of this CO_2 by weathering decreases soil CO_2 release to the atmosphere. Therefore, the uptake of soil CO_2 by rock weathering must be regarded as a sink of atmospheric CO_2 (Yuan, 1997; Ludwig et al., 1998; Liu and Zhao, 2000; Gombert, 2002; Dupré et al., 2003; Mortatti and Probst, 2003). The weathering products are transported to rivers, and lakes, and to the oceans, where they are used by plankton organisms to build their skeletons and tissues. When the plankton dies and falls to riverbeds, lake floors and seafloors, it is buried in fluvial, lake and marine sediments as a

Table 1
Calculated equilibrium values ($\mu\text{mol/l}$) of dissolved inorganic carbon (DIC) in systems of $\text{CO}_2\text{-H}_2\text{O}$ and $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ under different pCO_2 and temperature according to Dreybrodt (1988).

pCO_2 (ppmv)	380 ^a (15 °C) ^a	700 ^b (18 °C) ^b	6400 ^c (15 °C)	7940 ^d (18 °C)	210,000 ^e (15 °C)
$\text{CO}_2\text{-H}_2\text{O}$ system	20	33	302	342	9640
$\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ system	1231	1440	3643	3775	26950
Ratio of DIC of $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ to $\text{CO}_2\text{-H}_2\text{O}$ system	66.55	43.64	12.06	11.04	2.80

^a World mean values for present atmosphere (Longinelli et al., 2005).

^b Projected atmospheric values in 2100 (IPCC, 1996).

^c Present global mean soil pCO_2 calculated according to Brook et al. (1983).

^d Estimated global mean soil pCO_2 in 2100 according to Brook et al. (1983).

^e Upper limit for soil air pCO_2 (Drake, 1980).

Table 2
Carbonate compositions of rainwaters around the world.

Location	Type	Rainfall (mm/a)	pH	DIC ($\mu\text{mol/l}$)	Ca^{2+} ($\mu\text{eq/l}$)	Mg^{2+} ($\mu\text{eq/l}$)	Ref.
NUS	Rural	495	5.27 (4.27–7.42)	48.6 (0.4–137)	80 (32–169)	26 (21–35)	1
NUS	Mixed	580	5.00 (4.33–6.88)	60 (0–226)	49 (24–119)	19 (8–29)	1
NUS	Urban	730	4.67 (3.61–6.77)	4 (0–8)	23 (14–34)	7 (6–8)	1
BI	City	880	–	94 ^a (27.86–800.16)	154 (39–1190.5)	24 (9.17–116.67)	2
PRB	Rural	1350	4.5 (4.4–4.5)	49 (31–67)	5.0 (2.3–7.7)	1.9 (1.2–3.7)	3
LT	Rural	375	7.60 (7.45–8.78)	213 ^a (137–288.9)	146.3 (93.2–197.4)	8.1 (5.66–10.9)	4
EAJ	Mine area	50	6.62±0.68	151.30±37.28 ^a	192.10±40.42	133.60±17.71	5
HSI	City	800	6.4 (5.5–7.2)	29.2 ^a (21.7–36.6)	80 (40.1–119.2)	14.5 (8.7–20.4)	6
XSC	Rain forest	1487	6.13 (5.69–7.25)	37.3 ^a (16.4–79.6)	18.6 (4.4–113.7)	8.3 (3.8–92.5)	7
ANWI	City	565	6.7 (5.2–8.2)	71 ^a (8–836)	78 (5.5–1057)	15 (1.5–251)	8
RNI	Urban area	1100	7.03 (6.85–7.21)	88 ^a (67–108)	145 (123–160)	23 (18–29)	9
NRI	Urban area	420	5.92 (4.26–7.42)	32.40 ^a (0.75–287.73)	107.46 (1.77–644.58)	16.74 (0.79–142.18)	10
MCM	City	635	5.08 (4.11–6.92)	27.36 ^a (0–485.7)	26.44 (0.25–437.90)	2.46 (0.07–23.69)	11
NIGP	Urban area	852	7.23 (6.51–8.71)	168.55 ^a (40.00–512.13)	264.39 (89.30–653.50)	81.02 (34.58–187.50)	12
MNMR	Urban area	588	6.22 (6.15–6.37)	180.7 ^a (64.5–263.7)	192.8 (152.5–252.7)	30.9 (21.7–36.9)	13
TG	Urban area	494	–	26.5 ^a (0.06–363)	153 (10.5–1788)	15.9 (2.33–562)	14
AF	Urban area	500	–	13 ^a (0.00–524.6)	51.7 (5–1047)	10 (0.00–85.6)	15
HRF	Rural (H1–H5)	1008 (553–1761)	6.0 (5.0–6.9)	109.5 ^a (3.1–361.2)	88.0 (39.8–163.3)	41.0 (15.6–103.6)	16
GRF	Rural (G1–G4)	727 (360–1057)	6.1 (5.4–6.8)	161.9 ^a (23.1–590.5)	117.8 (28.1–338.7)	18.5 (7.4–43.8)	16
RWWM	–	719	–	82.88 ^a	99.59	21.51	–

NUS: North-Central United States; BI: Bologna, Italy; PRB: Piracicaba River Basin, Southeast Brazil; LT: Lhasa, Tibet; EAJ: Eshidiya area, Jordan; HSI: Hyderabad, south-central India; XSC: Xishuangbanna, Southwest China; ANWI: Ahmedabad, NW India; RNI: Roorkee, North India; NRI: the northeastern Romania, Iasi region; MCM: Mexico City, Mexico; NIGP: Northern Indo-Gangetic Plains; MNMR: Mersin, North-Eastern Mediterranean Region; TG: Thessaloniki, Greece; AF: Avignon, France; HRF: Hérault region, France; GRF: Gard region, France; RWWM: rainfall weighed world mean.

1: Munger, 1982; 2: Panettiere et al., 2000; 3: Lara et al., 2001; 4: Zhang et al., 2003; 5: Al-Khashman, 2005a; 6: Kulshrestha et al., 2005; 7: Liu et al., 2005; 8: Rastogi and Sarin, 2005; 9: Jawad Al Obaidy and Joshi, 2006; 10: Arsene et al., 2007; 11: Báez et al., 2007; 12: Singh et al., 2007; 13: Özsoy et al., 2008; 14: Anatolaki and Tsitouridou, 2009; 15: Celle-Jeanton et al., 2009; 16: Ladouche et al., 2009.

^a As HCO_3^- .

relatively long-term carbon sink (Dean and Gorham, 1998; Einsele et al., 2001; Lerman and Mackenzie, 2005; Iglesias-Rodriguez et al., 2008).

Because of the very low solubility and slow weathering kinetics of silicate minerals, over an order of magnitude lower than that of carbonate (Ludwig et al., 1998; Roy et al., 1999; Dalai et al., 2002; Dupré et al., 2003; Millot et al., 2003; Mortatti and Probst, 2003; Singh et al., 2005; West et al., 2005; Wu et al., 2005; Tipper et al., 2006; Moon et al., 2007; Zakharova et al., 2007; Wu et al., 2008), we concentrate on the CO_2 uptake by carbonate dissolution in this study.

4. DIC of rainwaters and runoffs

In this section, we summarize the general characteristics of DIC of the rainwater and runoff in the world, and examine whether the waters are in equilibrium with surrounding CO_2 and calcite. These results will be used in the following section to calculate the CO_2 sink by carbonate dissolution in the global water cycle.

4.1. DIC of world rainwaters

Table 2 summarizes the carbonate compositions of rainwater around the world. It shows large variations in DIC from values as low as $0 \mu\text{mol/l}$, up to a maximum of $836 \mu\text{mol/l}$.

Munger (1982) studied the chemistry of atmospheric precipitation in the north-central United States to learn the influence of sulfate, nitrate, ammonia and calcareous soil particulates. The author found that the supply of alkaline soil dust and gaseous NH_3 available to neutralize anthropogenic acids in the atmosphere controls the acidity of precipitation in the north-central United States. Acidity increased 4-fold from west to east as the effect of alkaline dust and NH_3 decreased with increasing distance from the cultivated prairie; Ca^{2+} and Mg^{2+} decreased 2 to 3-fold across the transect. Lara et al. (2001) found that the sources of composition of rainwater at Piracicaba River

Basin (Southeast Brazil) differ among sites and appear to be correlated to different land-uses. They are controlled mostly by three sources: soil dust, sugar cane burning and industrial emissions. Zhang et al. (2003) studied the chemistry of precipitation waters in Lhasa and other remote towns in Tibet. They found that Lhasa's precipitation events were consistently alkaline with weighted averages of pH 8.36 for the 1987–1988 period, and 7.5 for 1997 to 1999. Only one event was weakly acidic during 1997–1999. They showed that although CO_2 partial pressure decreases with increasing elevation, this change can only raise pH by 0.1 units in the sampling areas. Chemical analysis indicated that the major contributor to alkaline precipitation is continental dust rich in calcium carbonate. The analyses also showed that Tibet is still one of the cleanest areas in the world though the decline of pH from the 1980s to 1990s, which was reflected by an increase of NO_3^- and SO_4^{2-} in precipitation, had shown some air pollution generated by the global and regional atmospheric circulations (Zhang et al., 2003).

A systematic study (Rastogi and Sarin, 2005) of individual precipitation events, collected for three years (2000–2002) during the period of SW-monsoon (June–September) from a semi-arid region (Ahmedabad) in India, showed that the rainwater is characteristically alkaline in nature. The measured abundances of Ca^{2+} , Mg^{2+} and HCO_3^- , and linear regression parameters among ($\text{Ca}^{2+} + \text{Mg}^{2+}$) and HCO_3^- all tend to suggest that crustal sources (like carbonate dust) dominate the chemical composition of precipitation in this region (Rastogi and Sarin, 2005). Al-Khashman (2005a, 2005b) also showed that the high values of pH, HCO_3^- , Ca^{2+} and Mg^{2+} in the rainwater of the Petra Region and Eshidiya area, Jordan, originates from dust in the atmosphere that contains a large fraction of calcite and dolomite.

Based on these descriptions, we conclude that the world's rainwater chemistry is influenced more strongly by natural sources than by anthropogenic ones, and that DIC in rainwater results mainly from the dissolution of carbonate dust in the CO_2 – H_2O system of the atmosphere though local importance of anthropogenic DIC loadings

from cement plants are possible. This assertion is supported by the linear relation between the molar concentrations of HCO_3^- and $(\text{Ca}^{2+} + \text{Mg}^{2+})$, which exhibits a slope close to 2 (the theoretical value for carbonate dissolution in $\text{CO}_2\text{-H}_2\text{O}$ system) for the rainwaters of Table 2 as shown in Fig. 2. The higher pH (generally greater than 5.60, Table 2) confirms this conclusion further though we noticed that many field studies have shown acid to very acid rain falling in abundance downwind of heavy industrial locations (Table 2). However, the world's mean rainwater DIC concentration ($82.88 \mu\text{mol/l}$, Table 2) and even the maximum of $836 \mu\text{mol/l}$ in Table 2 are much lower than the equilibrium value of $1231 \mu\text{mol/l}$ for the system of $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}$ at $T = 15^\circ\text{C}$, and the present atmospheric $p\text{CO}_2$ of 380 ppmv (Table 1). This is most likely due to the short rainwater–dust interaction time, less than 10^4 s, the time to reach equilibrium with respect to calcite (Dreybrodt, 1988), the low carbonate dust content, and the low $p\text{CO}_2$ in the atmosphere, all contributing to the lower non-equilibrium value.

Therefore the Table 2 global mean rainwater DIC concentration of $82.88 \mu\text{mol/l}$ will be used in the next section to calculate the CO_2 sink in the world rainwaters.

4.2. DIC of runoffs

Fig. 3 depicts the global water cycle after Shiklomanov (1993) and, in italics, its CO_2 sinks in Pg C/a as estimated in this work. In this context we refer to runoffs of river- and groundwater on the continents.

The relationship between DIC in karst (carbonate) groundwater (chiefly as HCO_3^- at $7 < \text{pH} < 9$) and soil CO_2 has been confirmed by sample field observations in the karst areas of North China and Southwest China (Liu and Zhao, 2000; Liu et al., 2007) and also in the karst area of USA (Macpherson et al., 2008). For example, at the Guilin Karst Experimental Site in Guangxi, SW China, reforestation and temperature increase induced an average annual soil CO_2 increase of about 131% from 6573 ppmv to 15213 ppmv in 6 years. Seasonal increases in $p\text{CO}_2$ in summer enhanced carbonate rock dissolution, and thus increased the HCO_3^- concentrations of the epikarst spring S25 (Fig. 4).

Fig. 5 shows an example of storm-scale variations in water stage (discharge), pH, $[\text{HCO}_3^-]$, calculated CO_2 partial pressure ($p\text{CO}_2$), and the calcite saturation index (SI_{calcite}) for a similar epikarst spring at the Maolan Karst Experimental Site in Guizhou, SW China at 15-minute intervals, July 19–20, 2004. Each storm event causes a decrease in pH,

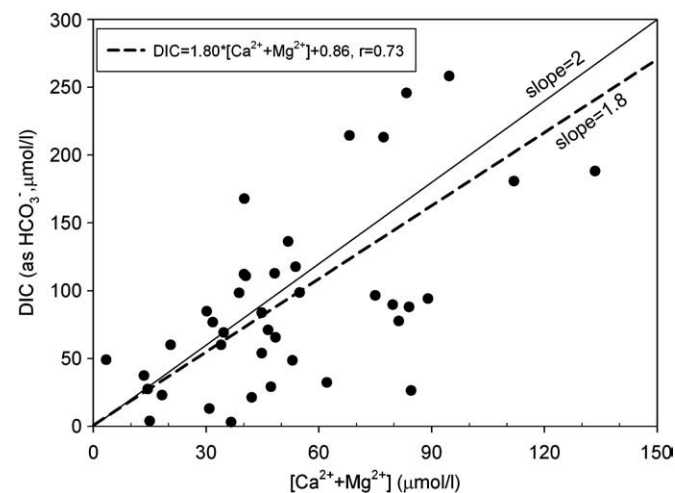


Fig. 2. The linear relationship between molar concentrations of HCO_3^- and $\text{Ca}^{2+} + \text{Mg}^{2+}$ in the world's rainwaters. Solid line is for pure carbonate dust dissolution in $\text{CO}_2\text{-H}_2\text{O}$ system, and dashed line is the actual one for the world's rainwaters; Data points on the graph are from the locations listed in Table 2.

and consequently an increase in the HCO_3^- concentration. This shift results most likely from uptake of soil CO_2 by the rainwater on its way to the spring (Liu et al., 2007).

Macpherson et al. (2008) report that the long-term increase in shallow groundwater CO_2 in the karst area of Konza Prairie, USA is similar to, but greater than the increase of atmospheric CO_2 . They found that the groundwater $p\text{CO}_2$ increased by about 20% between 1991 and 2005; alkalinity increased by about 13%, Ca about 5%, and Mg by about 29% over the 15-year study period. This indicates clearly that groundwater is a CO_2 sink through weathering of limestone, i.e., soil-generated CO_2 is transformed to alkalinity through dissolution of calcite and dolomite (Macpherson et al., 2008).

In addition, Fig. 5 shows that outside of storm surges, the calcite saturation index of the karst waters is close to zero (Liu et al., 2007). At the annual scale this is true for most published cases in the world karst areas reviewed by Dreybrodt (1988), Ford and Williams (1989, 2007), and White (1997). This is valid for most of the karst ground waters in the world because of the fast dissolution kinetics of calcite, which establishes equilibrium with respect to calcite in the time of about 10^4 s (Dreybrodt, 1988). Therefore, in our calculation of CO_2 sinks in the global water cycle, the equilibrium DIC values of carbonate dissolution with respect to a given soil $p\text{CO}_2$ are used for carbonate ground waters and the river waters supplied by them.

For the ground waters and river waters in non-carbonate areas, the saturation index of calcite is generally much lower than zero, and the DIC of these waters is close to the equilibrium value of the $\text{CO}_2\text{-H}_2\text{O}$ system, and far below the equilibrium value of the $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ system (Cameron et al., 1995; Markich and Brown, 1998; Telmer and Veizer, 1999; Millot et al., 2003; Mortatti and Probst, 2003). For example, Cameron et al. (1995) reported that the Fraser River, a major river system in Canada that is mainly in non-carbonate areas has a saturation index of calcite as low as -1.4 to -2.1 , while its DIC varied between 450 and $2220 \mu\text{mol/l}$ (mean: 1310). This DIC value is much lower than the equilibrium value ($5000 \mu\text{mol/l}$) of $\text{CaCO}_3\text{-CO}_2\text{-H}_2\text{O}$ system, but close to the equilibrium value ($640 \mu\text{mol/l}$) of $\text{CO}_2\text{-H}_2\text{O}$ system, both at $p\text{CO}_2 = 15,000$ ppmv and $T = 18^\circ\text{C}$ (Dreybrodt, 1988). Therefore, in the following calculation of CO_2 sinks in the global water cycle, the equilibrium DIC values of the pure $\text{CO}_2\text{-H}_2\text{O}$ system are used for non-carbonate ground waters and the river waters supplied by these ground waters.

5. Calculation of CO_2 sinks by the global water cycle

To calculate the CO_2 sink, as DIC, by the global water cycle, we use the various fluxes among atmosphere, ocean and continent provided by Shiklomanov (1993) in the global water cycle model (Fig. 3). In this model, precipitation fluxes between the atmosphere and internal continental drainage, between the atmosphere and external continental drainage, and between the atmosphere and the oceans are 9000 , $110,000$ and $458,000 \text{ km}^3$, respectively. From Section 4.1, it is known that the mean DIC for the global precipitation is $82.88 \mu\text{mol/l}$. However, only half of this ($41.44 \mu\text{mol/l}$) is of atmospheric origin because the carbonate chemistry of world rainwater comes mainly from the dissolution of carbonate dust. Adopting this latter value, then the atmospheric CO_2 sinks by drawdown of these precipitation fluxes are found to be 0.0045 , 0.0547 and 0.2278 Pg C/a , respectively (Fig. 3 and Table 3). The total sum of these (0.287 Pg C/a) is close to the value obtained by Liu et al. (2004), who estimated the rainout of atmospheric CO_2 as 0.27 Pg C/a .

In Table 3 we list that part of total DIC, which is due to atmospheric CO_2 and contributes to the sink as (DIC). The corresponding carbon sink is given by $\text{flux} \times (\text{DIC}) \times 12 \times 10^6 \text{ g/a}$ and is listed in Table 3 and Fig. 3.

According to Baumgartner and Reichel (1975) and Shiklomanov (1993) the annual global internal runoff and external runoff are 2000 and $44,800 \text{ km}^3$, respectively. For the global mean surface temperature

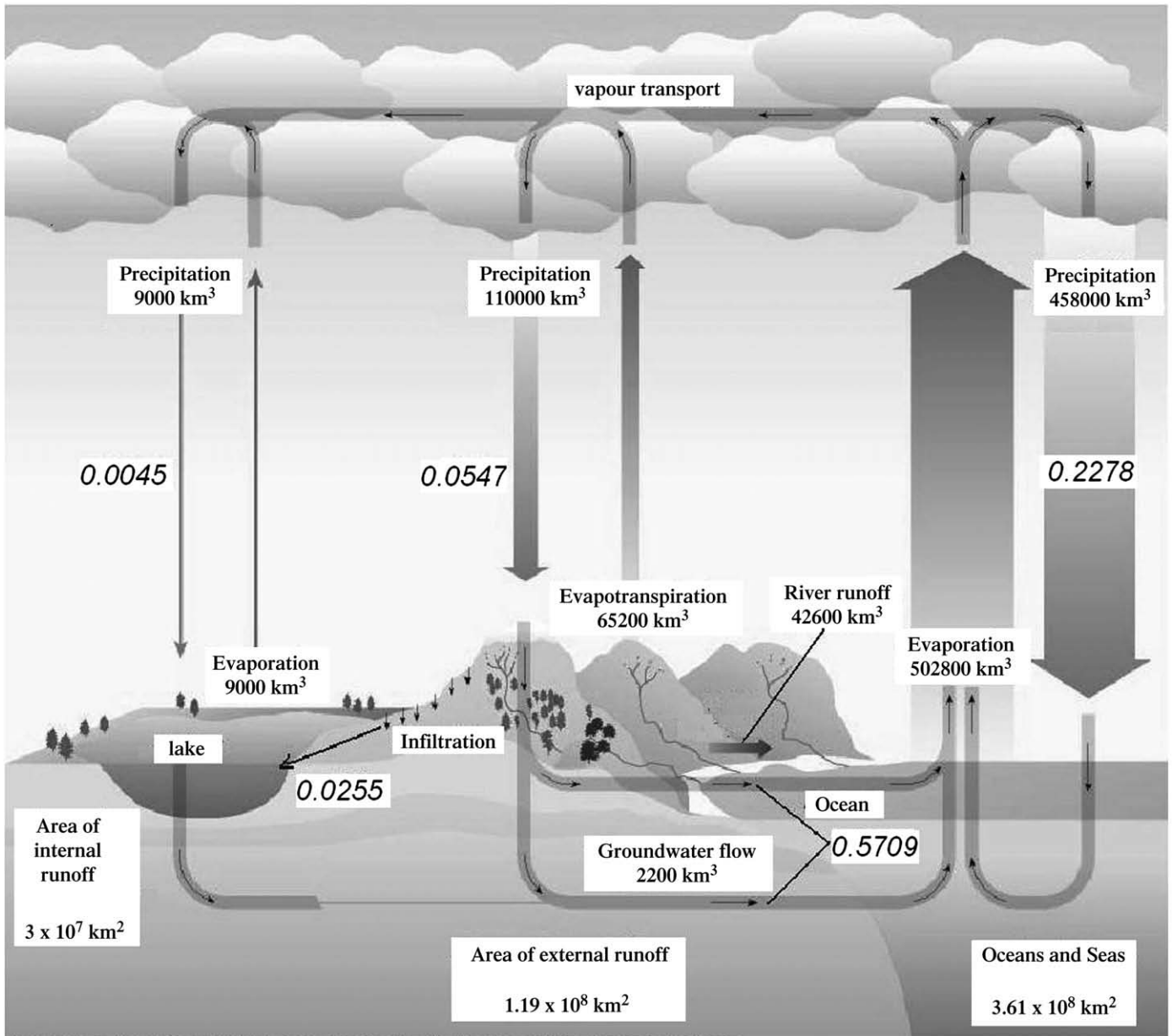


Fig. 3. The global water cycle and its CO₂ sinks (italic numbers, in Pg C/a; water fluxes from Shiklomanov (1993)).

of 15 °C and the global mean soil pCO₂ of 6400 ppmv we obtain the following equilibrium values of DIC; in non-carbonate areas the mean is 302 μmol/l for dissolution of CO₂ in the system H₂O–CO₂ (Table 1). In carbonate areas the equilibrium value of DIC by calcite dissolution is 3643 μmol/l. For carbonate dissolution only half of the DIC is taken from the atmosphere and (DIC) = 0.5 × DIC = 1822 μmol/l. About 15% of the land area has carbonate rocks outcropping at the surface (Ford and Williams, 1989, 2007; Yuan, 1997; Gombert, 2002). Consequently it is presumed that 15% of the continental runoff will exhibit the high (DIC) values of carbonate dissolution. If we assume that the remaining 85% of the land surface is completely devoid of carbonates its runoff has the low value (DIC) = 302 μmol/l. In this case we find an average (DIC) = (0.15 × 1822 + 0.85 × 302) = 530 μmol/l, which yields a carbon sink of 0.0127 Pg C/a for interior runoff and a sink of 0.2849 Pg C/a for the exterior discharge (Table 3).

However, calcite and dolomite are common minerals in other sedimentary rocks and in the C horizons of many soils in humid regions. In addition, there is huge area of soil, rich in pedogenic carbonate (≥3 kg C/m² as calcrite) that is present in the arid–

semiarid climates, that prevail over 48% of the continental area (Adams, 1993; Adams and Post, 1999). Therefore, the CO₂ sinks in continental runoff will be much larger. Combined with the findings of Ford and Williams (1989, 2007) and Adams and Post (1999), the total area of regions with carbonate (including carbonate rock and pedogenic carbonate) could be larger than 50% of the continents. We adopted 50% in our conservative estimate as carbonate dissolution and 50% as dissolution of atmospheric CO₂ in the system H₂O–CO₂. Then, the CO₂ sinks by internal runoff and external runoff are estimated to be 0.0255 and 0.5709 Pg C/a, respectively (Fig. 3 and Table 3).

Therefore, the total atmospheric CO₂ sink resulting from DIC in the global water cycle could be approximately 0.8242 Pg C/a (Table 3).

6. Photosynthetic uptake of DIC by aquatic organisms

DIC in waters is mainly consumed by aquatic photosynthesis in the ocean and on the continents. Some of it, however, will return to the atmosphere due to the CO₂ pressure difference between water and

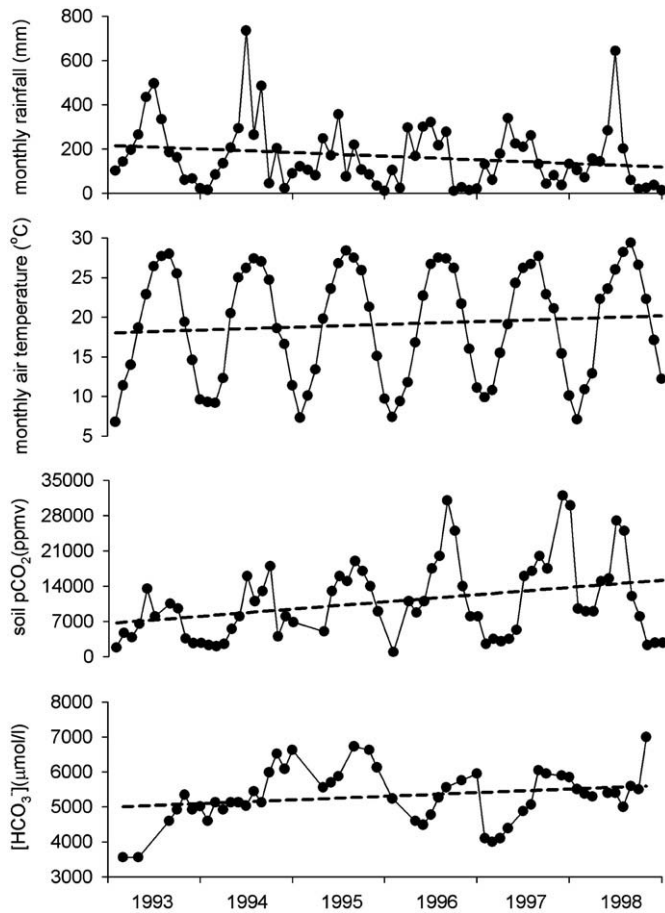


Fig. 4. Variations of monthly mean air temperature, soil $p\text{CO}_2$ and $[\text{HCO}_3^-]$ of the epikarst spring S25, showing the annual and seasonal variations of $[\text{HCO}_3^-]$ with soil $p\text{CO}_2$, at the Guilin Karst Experimental Site, Guangxi, SW China (modified after Liu and Zhao (2000)).

the atmosphere (Ritschard, 1992; Maier-Reimer, 1993; Yang et al., 1996; Raven and Falkowski, 1999; Invers et al., 2001; Kahara and Vermaat, 2003; Van Oijen et al., 2005; Kanduč et al., 2007). Aquatic ecosystems, such as rivers, lakes, and the oceans, play an important role in the carbon cycle by means of the so-called “biological pump” (Wagener and Rebello, 1987; Longhurst and Harrison, 1989; Maier-Reimer, 1993; Dean and Gorham, 1998; Cassar et al., 2004; Tortell et al., 2008). Organisms occupy the well-mixed surface layers of a given river/lake/ocean and grow by photosynthesis at a rate which varies according to the nutritional state of the water. Dead biota and feces fall down through the water column thus removing carbon from the surface layers and hence reducing the partial pressure of CO_2 there. This reduction enables uptake of new CO_2 from the atmosphere and of new DIC from the rivers and rainwaters.

Our argument that carbonate dissolution serves as an important atmospheric CO_2 sink, depending on the uptake rate of CO_2 and/or HCO_3^- by aquatic organisms, differs from the generally accepted position that the consumption of atmospheric CO_2 resulting from carbonate weathering on the continents is balanced over relatively short time scales by carbonate precipitation in the oceans and that all CO_2 is released back to the ocean–atmosphere system. This widely held supposition is at least partly wrong, because it does not consider the large uptake of CO_2 by the photosynthesis that produces organic carbon in the aquatic systems of both oceans and the continent. For example, Ternon et al. (2000) found that the fertilization of oceanic waters by the Amazon River around its outflow enhances the biological pump of CO_2 , which contributing up to 30% to lowering of $p\text{CO}_2$ in these areas, and so increasing the atmospheric CO_2 sink in the

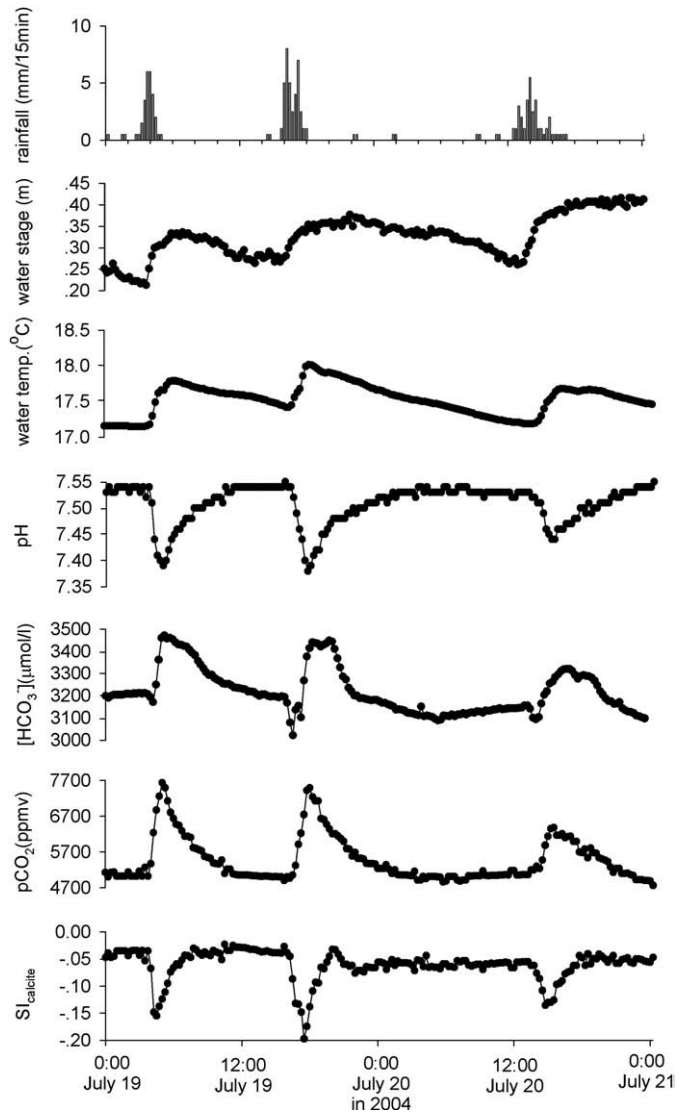


Fig. 5. Storm-scale variations in water stage, pH, $[\text{HCO}_3^-]$, calculated CO_2 partial pressure ($p\text{CO}_2$), and calcite saturation index ($\text{SI}_{\text{calcite}}$) for Maolan epikarst spring (Guizhou, SW China) at 15-minute intervals, on July 19–20, 2004, showing an increase in CO_2 sink after rainfall by soil CO_2 drawdown by rainwater and subsequent uptake by carbonate rock dissolution (modified after Liu et al. (2007)).

Atlantic Ocean. Einsele et al. (2001) studied atmospheric carbon burial in modern lake basins and its significance for the global carbon budget. They found that although area of lake basins is only about 0.8% of the ocean surface or 2% of the land surface, a surprisingly high amount of atmospheric carbon is buried, which amounts to 0.07 Pg C/a, more than one fourth of the annual atmospheric carbon burial in the modern oceans. This burial is mainly accomplished by rapid accumulation of lacustrine sediments and a very high preservation factor on average 50 times higher than that in the oceans. Lerman and Mackenzie (2005) found that primary production and net storage of organic carbon counteract CO_2 production by carbonate precipitation, and cause lower CO_2 emissions from the surface layer through the reaction: $\text{Ca}^{2+} + 2\text{HCO}_3^- \rightleftharpoons \text{CaCO}_3 + \text{CH}_2\text{O} + \text{O}_2$. Ridgwell and Zeebe (2005) conclude that biologically driven carbonate deposition by calcareous plankton provides a significant buffering of ocean chemistry and of atmospheric CO_2 in the modern system. Wang et al. (2007) found that the flux of CO_2 diffusing to the atmosphere from the Changjiang (Yangtze River) decreased dramatically (~75%) during the past several decades (1960s–2000) due to the marked increase in nutrient (e.g. NO_3^-) concentrations. This shows the

Table 3
Calculation of carbon sinks by precipitation and runoff in the global water cycle.

Item	Flux (km ³ /a)	DIC (μmol/l)	Carbon sink ^a (Pg C/a)
Precipitation in internal runoff area	9000 ^b	82.88 × 0.5 ^c	0.0045
Precipitation in external runoff area	110,000 ^b	82.88 × 0.5 ^c	0.0547
Precipitation over sea	458,000 ^b	82.88 × 0.5 ^c	0.2278
Internal runoff	2000 ^d	530 ^e	0.0127
		1062 ^f	0.0255
External runoff	44,800 ^b	530 ^e	0.2849
		1062 ^f	0.5709
Total	–	–	0.8242

^a Carbon sink = (DIC) × flux × 12 × 10⁶ (g/a), where the factor 12 is the atomic weight of carbon. Total carbon sink by the global water cycle is 0.8242 (0.2278 + 0.0255 + 0.5709 = 0.8242 Pg C/a, or 10¹⁵ g C/a, where the sinks by the precipitation in internal and external runoff areas have been excluded from this balance because the CO₂ from rainfall on land contributes to the soil pCO₂. Otherwise it would be counted twice.)

^b Shiklomanov (1993).

^c 82.88 is the world mean value of rainwater DIC calculated based on the 16 representative references (see Table 2 and the text), and the factor 0.5 results from the fact that only half of the world rainwater (HCO₃⁻) is of atmospheric origin because the carbonate chemistry of world rainwater comes mainly from carbonate dissolution in the CO₂-H₂O system of atmosphere (CaCO₃ + CO₂ + H₂O = Ca²⁺ + 2HCO₃⁻, CaMg(CO₃)₂ + 2CO₂ + 2H₂O = Ca²⁺ + Mg²⁺ + 4HCO₃⁻) (see Fig. 2).

^d Baumgartner and Reichel (1975).

^e Calculated value on account of the mixing of karst water and non-karst water on the land as: 3643 × 15% × 0.5 + 302 × 85% = 530, where 302 and 3643 are calculated equilibrium concentrations (μmol/l) of dissolved inorganic carbon (DIC) in open CO₂-H₂O and CaCO₃-CO₂-H₂O systems under global mean soil CO₂ partial pressure of pCO₂ = 6400 ppmv and global mean surface temperature of 15 °C respectively (Table 1), 15% and 85% are percentage of karst area and non-karst area in the continent respectively (Ford and Williams, 1989), and the factor 0.5 results from the fact that in the case of carbonate dissolution only half of the (HCO₃⁻) is of atmospheric origin.

^f Calculated value on account of the mixing of water from carbonate area (karst area + soil area with pedogenic carbonate in dryland areas except karst areas) and water from non-carbonate areas on the land as: 3643 × 50% × 0.5 + 302 × 50% = 1062, where 302 and 3643 are calculated equilibrium concentrations (μmol/l) of dissolved inorganic carbon (DIC) in open CO₂-H₂O and CaCO₃-CO₂-H₂O systems under global mean soil CO₂ partial pressure of pCO₂ = 6400 ppmv and global mean surface temperature of 15 °C respectively (Table 1), both 50% are percentage of carbonate area and non-carbonate area in the continent respectively (Ford and Williams, 1989; Adams and Post, 1999), and the factor 0.5 results from the fact that in the case of carbonate dissolution only half of the (HCO₃⁻) is of atmospheric origin.

importance of CO₂ uptake by plankton in river systems, and also the importance of elemental fertilization to the plankton growth. Yang et al. (2008) determined the carbon source/sink of a subtropical, eutrophic lake by an overall mass balance and a gas exchange and carbon burial balance. They found that the ratio of carbon emission into the atmosphere to carbon burial into the sediment was only 0.08, indicating that this lake is an effective carbon sink. More recently, Iglesias-Rodriguez et al. (2008) studied the phytoplankton calcification in a high-CO₂ world both in the laboratory and from field evidence. They found that the calcification and net primary production in the coccolithophore species *Emiliania huxleyi* are significantly increased by high CO₂ partial pressures. This indicates that over the past 220 years there has been a 40% increase in average coccolith mass. The authors conclude that coccolithophores are already responding and will probably continue to respond to rising atmospheric CO₂ partial pressures.

All of these findings show the significance of carbonate dissolution in both the atmospheric CO₂ sink and the DIC fertilization in the aquatic ecosystems of the oceans and continents. On account of this and the low solubility and slow weathering kinetics of silicates, carbonate dissolution is more important than silicate weathering in contributing to the atmospheric CO₂ sink.

The surface areas of rivers and internal lakes are not very large compared with those of exterior drainage or with the oceans. Therefore the direct exchange of carbon between rivers/lakes and atmosphere is possibly less important (Kling et al., 1991; Telmer and Veizer, 1999). However, the rivers of the world are conduits carrying

large amounts of carbon and nutrients to the sea and to the internal lakes (Kempe, 1984; Meybeck, 1993).

The riverine input of atmospheric CO₂ to the oceans is estimated to be 0.244 Pg C/a (Meybeck, 1993). The mean release rate of carbon from the rivers to the atmosphere is 20% of the external and internal runoff sinks (see Table 3) with large variations (2% to 30%, Kling et al., 1991; Wang et al., 2007; Zhai et al., 2007; Yang et al., 2008). This amounts to 0.119 Pg C/a. The difference between the internal and external sinks and riverine input to the oceans plus release to the atmosphere amounts to 0.2334 Pg C/a. It must have remained in the continental aquatic ecosystem, possibly in lakes, reservoirs and rivers, or it is stored in the large but slowly cycled groundwater reservoirs. This has been partly confirmed by the work of Cole et al. (2007), who estimated that about 0.2 Pg C/a is buried in aquatic sediments in the inland waters (lakes, reservoirs and rivers). This role of groundwater results from its greater carbon storage capacity due to its large reservoir volume (Trenberth et al., 2007) and from the substantially greater load of carbon compared to the global rivers (Kempe, 1979).

The return carbon flux from the oceans by evaporation can be neglected, on account of the role of the oceans as huge atmospheric CO₂ sinks due to the photosynthetic uptake of DIC by ocean organisms (the “biological pump” effect, Wagener and Rebello, 1987; Longhurst and Harrison, 1989; Maier-Reimer, 1993; Raven and Falkowski, 1999; Cassar et al., 2004; Blain et al., 2007).

To summarize, the atmospheric CO₂ sink as DIC in the global water cycle is 0.8242 Pg C/a, of which 0.4718 Pg C/a goes to the sea via continental rivers (0.244 Pg C/a) and via precipitation over sea (0.2278 Pg C/a), 0.119 Pg C/a is released to the atmosphere again, and 0.2334 Pg C/a is stored in the continental aquatic ecosystem. Therefore, the net sink should be 0.7052 Pg C/a, which is about 8.9% of total anthropogenic CO₂ emissions, or 25% of the terrestrial CO₂ sink (Melnikov and O'Neill, 2006), showing the significance of the combined action of carbonate dissolution, the global water cycle and the photosynthetic uptake of DIC by aquatic organisms in the atmospheric CO₂ sink.

7. The future of the atmospheric CO₂ sink in the global water cycle

According to Eqs. (2) and (3), the atmospheric CO₂ sink in the global water cycle may increase with global-warming-intensified global water cycling (Huntington, 2006) through an increase in rainwater DIC due to the increase in pCO₂ and carbonate dust in atmosphere. Furthermore the increase in runoff DIC due to reforestation/afforestation, which increases the soil CO₂, and thus the concentration of DIC in water (Liu and Zhao, 2000; Macpherson et al., 2008) is also important.

According to previous studies (Allen and Ingram, 2002; Wetherald and Manabe, 2002; Labat et al., 2004), the increase of global runoff related to climate warming could be 2–5% per degree. Climate model projections summarized by the IPCC indicate that the average global surface temperature will likely rise a further 1.1 to 6.4 °C during the twenty-first century depending on differing scenarios of future greenhouse gas emissions. With an ensemble mean temperature increase of 3.75 °C and an accompanying precipitation increase of 13%, the CO₂ sink by the global water cycle is estimated to increase by 13% (or 0.8242 × 13% = 0.1071 Pg C/a) if the DIC of rainwater and runoff are kept unchanged. In fact, because of the forecast increase in pCO₂ from 380 ppmv to 700 ppmv in the atmosphere (Table 1), the rainwater DIC is estimated to increase by 17% in the CaCO₃-CO₂-H₂O system and by 65% in the CO₂-H₂O system. In addition, due to the increase in evapotranspiration and reforestation/afforestation by global warming and anthropogenic activity, soil CO₂ concentrations may also increase remarkably (Liu and Zhao, 2000; Macpherson et al., 2008). If we assume that the actual evapotranspiration increases by 13%, the world mean soil pCO₂ will increase from 6400 ppmv to 7940 ppmv according to the equation of Brook et al. (1983).

We take this value for our conservative estimate in calculating the runoff equilibrium DIC. This value is highly likely, being conservative because it does not include the increase of soil CO₂ caused by the fertilization effect due to the CO₂ increase in the atmosphere (Macpherson et al., 2008) and the reforestation effect (Liu and Zhao, 2000). For example, Macpherson et al. (2008) found that groundwater pCO₂ in Konza Prairie, USA increased from 8913 ppmv to 11,482 ppmv, about a 29% increase (2569 ppmv) in only 15 years, from 1991 to 2005. Consequently runoff DIC increases by 3.62% (Table 1).

With these values, the CO₂ sink in the Global Water Cycle is then estimated to increase by about 21.27% (or 0.1753 Pg C/a) in the year 2100. This value is partly supported by the study of Raymond et al. (2008), who found that the bicarbonate flux from the Mississippi River (North America's largest river) increased from 0.01 Pg C/a to 0.0146 Pg C/a (or 46% increase) during the past 50 years, owing to land use change and management.

8. Conclusions and perspective

Based on theoretical calculations and field monitoring evidence, we have shown, that there is an important but previously underestimated sink for the atmospheric CO₂ as dissolved inorganic carbon that results from the combined action of carbonate dissolution, the global water cycle and the photosynthetic uptake of DIC by aquatic organisms. The sink constitutes up to 0.8242 Pg C/a, or 29.4% of the terrestrial CO₂ sink, or 10.4% of the total anthropogenic CO₂ emission. Of this sink, 0.4718 Pg C/a goes to the sea via continental rivers (0.244 Pg C/a) and precipitation over sea (0.2278 Pg C/a), 0.119 Pg C/a is released to the atmosphere again, and 0.2334 Pg C/a is stored in the continental aquatic ecosystem. Therefore, the net sink amounts to 0.7052 Pg C/a. This sink may increase with the global-warming-intensified water cycling, by the increase in CO₂ and carbonate dust in atmosphere caused by human activity, by reforestation/afforestation (increasing the soil pCO₂ and thus the carbonate dissolution), and by effects of the elemental (N, C, etc.) fertilizing on aquatic organisms (increasing the organic matter storage/burial and thus decreasing the CO₂ return to the atmosphere). Under the projection of global warming for the year 2100 given by the IPCC, it is estimated that the CO₂ sink will increase by 21%, or about 0.18 Pg C/a.

In summary, the combined action of carbonate weathering, the global water cycle and aquatic organisms may act as a regulator of atmospheric CO₂. These processes jointly provide a negative climate feedback mechanism that partly counteracts the anthropogenic increase of atmospheric CO₂.

However, for full understanding and more accurate assessment of these processes, the temporal and spatial variations in DIC in precipitation and runoff in the world, which are related to the temporal and spatial distribution of carbonate dust and CO₂ in the atmosphere, and pedogenic carbonate and CO₂ in the soil respectively, remain to be determined more accurately in the future. Another important topic, in order to evaluate the role of these fluxes in the global carbon cycle is the oceanic and lake response to the river carbon input (Sempere et al., 2000; Ternon et al., 2000). Though it is found that aquatic organisms both in ocean and on land can be fertilized by increased nitrate, phosphate, Si, Fe, Zn and CO₂ (DIC) (Riebesell et al., 1993; Lvov et al., 1996; Raven and Falkowski, 1999; Cai et al., 2004; Cassar et al., 2004; Pierini and Thomaz, 2004; Blain et al., 2007; Zondervan, 2007; Tortell et al., 2008), it is not very clear how much of this carbon is trapped in the lakes, estuaries and coastal zones, by organic and inorganic sedimentation and how much returns to the atmosphere through respiration processes (Barth and Veizer, 1999; Wang and Veizer, 2000; Helie et al., 2002; Cole et al., 2007; Zondervan, 2007).

Therefore, this study does not aim to give a precisely accurate estimation of the atmospheric CO₂ sink due to the combined action of

carbonate dissolution, the global water cycle and the photosynthetic uptake of DIC by aquatic organisms. Rather, it provides a new direction in research into effective accounting for the atmospheric CO₂ budget.

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