

Significance of the carbon sink produced by H₂O–carbonate–CO₂–aquatic phototroph interaction on land

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Abstract One of the most important questions in the science of global change is how to balance the atmospheric CO₂ budget. There is a large terrestrial missing carbon sink amounting to about one billion tonnes of carbon per annum. The locations, magnitudes, variations, and mechanisms responsible for this terrestrial missing carbon sink are uncertain and the focus of much continuing debate. Although the positive feedback between global change and silicate chemical weathering is used in geochemical models of atmospheric CO₂, this feedback is believed to operate over a long timescale and is therefore generally left out of the current discussion of human impact upon the carbon budget. Here, we show, by synthesizing recent findings in rock weathering research and studies into biological carbon pump effects in surface aquatic ecosystems, that the carbon sink produced by carbonate weathering based on the H₂O–carbonate–CO₂–aquatic phototroph interaction on land not only totals half a billion tonnes per annum, but also displays a significant increasing trend under the influence of global warming and land use change; thus, it needs to be included in the global carbon budget.

Keywords Carbon sink · H₂O–carbonate–CO₂–aquatic phototroph interaction · Carbonate weathering · Biological carbon pump · Land aquatic ecosystem · Global change

1 Introduction

One of the most important questions in the science of global change is how to balance the atmospheric CO₂ budget [1–4]. According to Melnikov and O’Neill [3], there is a large terrestrial missing carbon sink as follows:

The (terrestrial) missing carbon sink = sources (emissions from fossil fuels + net emissions from changes in land use) – sinks (oceanic uptake + atmospheric increase), i.e., $2.8 = 7.9 (6.3 + 1.6) - 5.1 (1.9 + 3.2)$ (all values in Pg C/a, $1 \text{ Pg} = 10^{15} \text{ g}$).

The locations, magnitudes, variations, and mechanisms responsible for the terrestrial missing carbon sink, however, are uncertain and continue to be debated. The prevailing dogma has focused on carbon sinks in soil and vegetation [5–8]. The preferred explanation for the missing carbon sink is the effect of CO₂ and/or nitrogen fertilization [5–7]. For example, Kheshgi et al. [7] found that ~25 % of CO₂ emissions are sequestered by the terrestrial biosphere. Therefore, there is still a ~0.8 Pg C/a missing sink (or net terrestrial flux) to be determined.

Although the positive feedback between global change and the silicate chemical weathering of rocks is used in geochemical models of atmospheric CO₂ [9], this effect is believed to operate over a long timescale and therefore is generally left out of the current discussion of human impact upon the carbon budget [10]. For example, current global carbon budgets assume that pre- and post-anthropogenic riverine carbon fluxes are equal [11].

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Here, we show, by synthesizing recent findings in rock weathering research and studies into biological carbon pump effects in surface aquatic ecosystems, that the carbon sink produced by carbonate weathering based on the H_2O –carbonate– CO_2 –aquatic phototroph interaction on land not only totals one half billion tonnes per year [12], but also displays a significant increasing trend under the dual influence of global warming and land use change [12–15], comparable with those in the world's forests [8]. Therefore, the atmospheric CO_2 sink produced by the H_2O –carbonate– CO_2 –aquatic phototroph interaction on land needs to be included in the global carbon budget due to both its large quantity and its changing characteristics.

2 Significance of weathering of trace carbonates in silicate rock watersheds

Although primarily known in carbonate rocks, carbonate (mainly CaCO_3) is also commonly associated with silicate rocks, such as shales, calcareous sandstones, metamorphosed gneisses and schists, hydrothermally altered granitic rocks [16], and pristine granitoids, which probably form CO_2 -rich fluids associated with the final cooling of batholiths as well as during later periods of hydrothermal activity [17, 18]. Therefore, the CO_2 consumed in silicate rock terrains does not necessarily result primarily from silicate weathering: It may be chiefly due to the contribution of rapid calcite dissolution in the silicate rocks [16–18]. For instance, Blum et al. [16] investigated the major element and strontium (Sr) isotope geochemistry of bedrocks, surface waters, and river sands in the Raikhot watershed within the High Himalayan Crystalline Series (HHCS) of northern Pakistan. Mass balance calculations of mineral-weathering contributions to the flux of dissolved ions from the watershed showed that 82 % of the HCO_3^- flux is derived from the weathering of carbonate minerals and only 18 % from silicate weathering, even if the bedrock in the watershed is predominantly silicate rocks (quartzofeldspathic gneiss and granite) with only ~1 % carbonate. This indicated the significance of small amounts of bedrock carbonate in controlling the water chemistry of silicate rock watersheds. It also suggests that the flux of Sr with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in major Himalayan rivers may be derived mainly from the weathering of small amounts of calcite within the HHCS silicates. Therefore, models using the flux of radiogenic Sr from the Himalaya as a proxy for silicate weathering rates may overestimate the amount of CO_2 consumption attributable to reactions with silicates there. Similar results were obtained by Jacobson et al. [19, 20], who showed that the conventional application of two-component Ca/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ mixing equations overestimated silicate-derived Sr^{2+} and HCO_3^- fluxes from the

Himalaya. They found that carbonate dissolution provided more than 90 % of the weathering-derived HCO_3^- , Ca^{2+} and Sr for at least 55 ka following initial exposure of rock surfaces, although carbonate may represent only ~1.0 wt% in fresh glacial till; this significantly increases the ratios of $\text{HCO}_3^-/\text{Na}^+$ and $\text{Ca}^{2+}/\text{Na}^+$ in the so-called silicate end-member reservoir. Jacobson et al. [20] also found the following: (1) Carbonate bedrock in the Himalaya has a wide range of ratios of Ca/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ that cannot be adequately defined by a single end-member in conventional mass balance equations; and (2) Ca^{2+} behaves non-conservatively during transport in Himalayan stream waters. The removal of up to 70 % of the dissolved Ca^{2+} by calcite precipitation appears to be a pervasive process in the Himalaya that drives dissolved Ca/Sr ratios toward values much lower than those measured in carbonate bedrock. Therefore, they concluded that, without taking these factors into account, stream water Ca/Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, and hence HCO_3^- , can be erroneously interpreted as representing the dominance of silicate dissolution. We think similar problems could arise with the inversion method if ratios of HCO_3^-/Na and Ca/Na are used. This may explain why Gaillardet et al. [21] obtained such high estimates of CO_2 consumption from silicate weathering despite the fact that its weathering rates are 10^2 – 10^8 times lower than those of carbonates [22, 23]. They calculated CO_2 consumption *vis-à-vis* silicate weathering by measuring the bulk chemistry of large rivers and underestimated the carbonate weathering contributions that occur in predominantly silicate areas.

In a more recent study, Moore et al. [24] tracked the relation between mountain uplift, silicate weathering, and long-term CO_2 consumption by the use of Ca isotopes in the Southern Alps, New Zealand. Although rocks in the sampled watershed contain only ~3 % hydrothermal and metamorphic calcite, these authors found that riverine Ca largely originates from carbonate weathering and that the fraction of Ca from carbonate weathering increases with increasing tectonic activity, from ~50 %–60 % in regions experiencing the lowest uplift rates to as high as >90 % in regions experiencing the highest uplift rates. Therefore, they concluded that silicate weathering in the Himalayan–Tibetan Plateau is also not a major sink for atmospheric CO_2 .

It should be noted that present results are mainly from the uplifted silicate areas, which are conventionally thought to have stimulated CO_2 consumption by silicate weathering. Research results from other areas are needed in future.

To summarize, the contribution of carbonate weathering to the atmospheric CO_2 sink may have been greatly underestimated in these previous studies [21, 25, 26] due to ignorance of the important role played by trace calcite in silicate rock areas.

3 Photosynthetic uptake of DIC by aquatic phototrophs (the biological carbon pump effect)

DIC (dissolved inorganic carbon, $\text{DIC}=\text{CO}_2(\text{aq}) + \text{HCO}_3^- + \text{CO}_3^{2-}$) in surface waters is consumed by aquatic photosynthesis on the continents and in the ocean [27–30]. Some of it, of course, will return to the atmosphere due to the CO_2 pressure difference between water and the atmosphere. Aquatic ecosystems, such as rivers, lakes, wetlands, and the oceans, play an important role in the carbon cycle by means of the so-called biological pump [31]. Aquatic phototrophs occupy the well-mixed surface layers of a given river, lake, wetlands, or 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, hence reducing the partial pressure of CO_2 there. This reduction enables the uptake of new DIC from the surface waters and/or of new CO_2 from the atmosphere.

Our argument that the H_2O –carbonate– CO_2 –aquatic phototroph interaction serves as an important atmospheric CO_2 sink that depends on the carbonate dissolution, and the uptake rate of DIC (CO_2 and/or HCO_3^-) by aquatic phototrophs differs from the generally accepted view that the consumption of atmospheric CO_2 resulting from carbonate weathering on the continents is balanced over a relatively short timescale by carbonate precipitation in the oceans and that all of the CO_2 involved is released back to the ocean–atmosphere system [10]. This latter contention is at least partly problematic because it does not consider the large uptake of DIC by the photosynthesis that produces organic carbon in the aquatic systems of both oceans and continents. For instance, Ternon et al. [32] found that the fertilization of oceanic waters by the Amazon River around its outflow enhances the biological pumping effect of CO_2 , contributing up to 30 % of the measured lowering of $p\text{CO}_2$ there, and so, increasing the atmospheric CO_2 sink in the Atlantic Ocean. Einsele et al. [33] investigated atmospheric carbon burial in modern lake basins and its significance for the global carbon budget. They found that, although the area of lake basins is only about 0.8 % of the ocean surface (or 2 % of the land surface), a surprisingly large amount of atmospheric carbon is buried in them, amounting to 0.07 Pg C/a, or more than one-fourth of the annual atmospheric carbon burial in the modern oceans. This burial is accomplished mainly by the rapid accumulation of lacustrine sediments and a very high preservation factor which is, on average, 50 times higher than that observed in the oceans. Lerman and Mackenzie [34] found that the primary production and net storage of organic carbon counteract the CO_2 released by carbonate precipitation, leading to lower CO_2 emissions from the surface layer through the reaction: $\text{Ca}^{2+} + 2\text{HCO}_3^- \Rightarrow \text{CaCO}_3 + \text{CH}_2\text{O} + \text{O}_2$. Wang et al.

[35] found that the flux of CO_2 into the atmosphere from the Changjiang (Yangtze River) has decreased dramatically (~ 75 %) during the past four decades (~ 1960 – 2000) due to a marked increase in nutrient (e.g., NO_3^-) concentrations. This may show the importance of CO_2 uptake by phototrophs in river systems due to the importance of elemental fertilization for phototroph growth. Yang et al. [36] investigated the carbon source/sink of a subtropical, eutrophic lake by investigating the overall mass balance expressed as a balance between gas exchange and carbon burial. They found that the ratio of carbon emission into the atmosphere to carbon burial in the sediment was only 0.08, indicating that this lake is an effective carbon sink.

All of these findings show the significance of photosynthetic uptake of DIC by aquatic phototrophs (the biological carbon pump effect) in stabilizing the carbon sink produced by carbonate weathering through the transformation from DIC to organic carbon.

However, most researches were done in the uncontaminated rivers or streams. For the situation in the contaminated rivers or streams (such as dark water, in which low light will limit the amount of photosynthesis), more work has to be done in future.

4 Net carbon sink produced by H_2O –carbonate– CO_2 –aquatic phototroph interaction on land

In a recent attempt to balance the atmospheric CO_2 budget, Liu et al. [12] considered the combined effects of carbonate dissolution, the global water cycle, and the photosynthetic uptake of DIC by aquatic phototrophs. They found that the net atmospheric CO_2 sink produced by the H_2O –carbonate– CO_2 –aquatic phototroph interaction on the land (for the expression of carbonate weathering based on H_2O –carbonate– CO_2 –aquatic phototroph interaction, see the new conceptual model in Fig. 1) could be as large as 0.477 Pg C/a ($\text{CFR1} + \text{CFR2} + \text{CFS-AL}$ in Fig. 2), which accounts for about 17 % of the terrestrial missing carbon sink and is comparable with the carbon sink in the world's forests [8]. This is much larger (by a factor of about three) than the estimate of 0.148 Pg C/a obtained by Gaillardet et al. [21], who underestimated the carbonate weathering sink in silicate areas and did not consider the photosynthetic uptake of DIC by land aquatic phototrophs or the burial of part of the resulting organic matter on the continents ($\text{CFR2} + \text{CFS-AL} = 0.233$ Pg C/a, Fig. 2). This latter value of 0.233 Pg C/a has been confirmed by the independent work of others [37, 38]. For instance, Waterson and Canuel [37] have shown that the contribution of autochthonous organic carbon (AOC) derived from DIC transformed by aquatic photosynthesis in the Mississippi River system (the largest river system in North America) can constitute 20 %–57 % of the

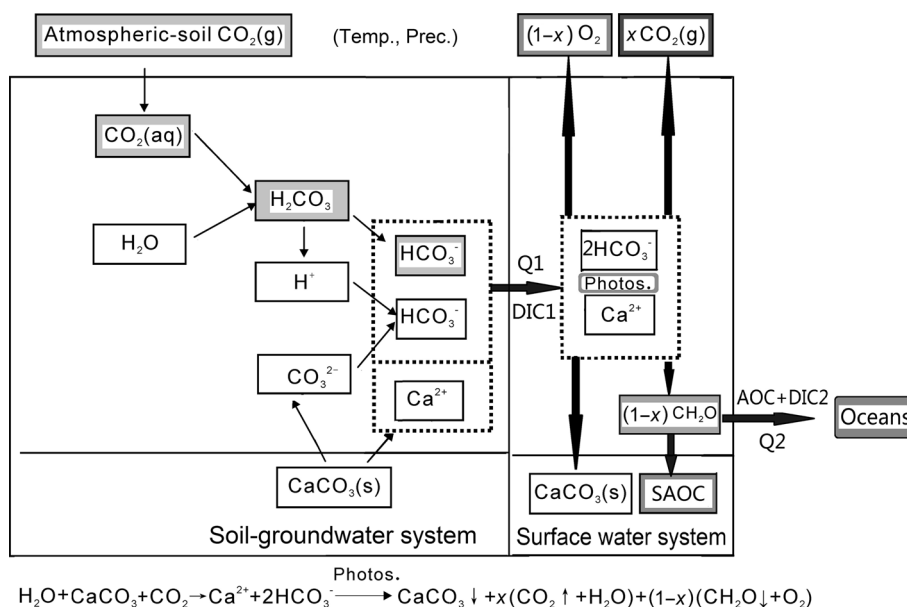


Fig. 1 Conceptual model of the carbon cycle produced by carbonate weathering (karst processes) based on H₂O–carbonate–CO₂–aquatic phototroph interaction (drawing in reference to Lerman and Mackenzie [34] and Liu et al. [12]). Notes: 1. CSF (net carbon sink flux produced by H₂O–carbonate–CO₂–aquatic phototroph interaction) = 0.5 × Q × ([DIC2] + [AOC])/A + F_{SAOC} where the ratio 0.5 indicates that only one half of the HCO₃[−] generated by carbonate dissolution is of atmospheric origin; Q is the discharge from the surface water system; [DIC2] is the concentration of dissolved inorganic carbon in the surface water system; and [AOC] is the concentration of total organic carbon in the surface water system transformed from DIC1 (dissolved inorganic carbon in the groundwater system) by submerged aquatic phototrophs via photosynthesis in the surface water system. F_{SAOC} is the sedimentary flux of autochthonous organic carbon (OC) in the surface water system over the catchment area (A). 2. Unlike the conventional carbonate weathering carbon cycle model [9, 10, 25], which considers H₂O–carbonate–CO₂ interaction and ignores organic matter formation produced by the aquatic photosynthetic uptake of DIC, this new conceptual model helps to answer important questions such as whether carbonate weathering could be contributing to the long-term carbon sink (e.g., through sedimentation, burial of autochthonous organic matter, F_{SAOC}), and thus, to a proportionate degree, controlling long-term climate change

total organic carbon (TOC). If the lower value, 20 %, is multiplied by the sedimentary deposition of organic carbon in inland waters (0.6 Pg C/a) plus riverine TOC discharge to oceans (0.5 Pg C/a) [38], a similar value of 0.22 Pg C/a AOC is obtained. Therefore, the atmospheric CO₂ sink due to carbonate weathering based on the H₂O–carbonate–CO₂–aquatic phototroph interaction on land has previously been greatly underestimated. If the result put forward by Jacobson et al. [19] (i.e., about 10 % of HCO₃[−] originates from silicate weathering) is applied to the case of Gaillardet et al. [21], then the atmospheric CO₂ sink produced by silicate weathering is diminished from 0.14 Pg C/a to about 0.014 Pg C/a and, correspondingly, the atmospheric CO₂ sink due to carbonate weathering is bound to increase from 0.148 to 0.211 Pg C/a, i.e., fifteen times greater than the silicate weathering sink [39]. In other words, carbonate reactions contribute about 94 % of the atmospheric CO₂ sink that is due to rock weathering, while only 6 % results from silicate weathering [39]. The similarity of calcium isotope ratios in the world’s largest rivers and in marine limestones [40] provides further support for the dominance of carbonate weathering in CO₂ consumption in the world’s watersheds.

5 Increase in the carbon sink under the dual influence of global warming and land use change

A substantial amount of the atmospheric carbon taken up on land through photosynthesis and chemical weathering is transported laterally along the aquatic continuum from upland terrestrial ecosystems to the ocean [38, 41, 42]. Thus far, global carbon budget estimates have implicitly assumed that the transformation and lateral transport of carbon along this aquatic continuum has remained unchanged since pre-industrial times [11]. However, a synthesis of published work reveals the magnitude of present-day lateral carbon fluxes from land to ocean and the extent to which human activities have altered these fluxes. For instance, Battin et al. [38] showed that anthropogenic perturbation (e.g., land use and land cover changes) may have increased the flux of carbon to inland waters by as much as 1.0 Pg C/a since pre-industrial times, mainly owing to an enhanced carbon export from soils. Most of this additional carbon input into upstream rivers is either emitted back into the atmosphere as carbon dioxide (~0.4 Pg C/a) or sequestered in sediments (~0.5 Pg C/a) along the continuum of freshwaters, estuaries, and coastal

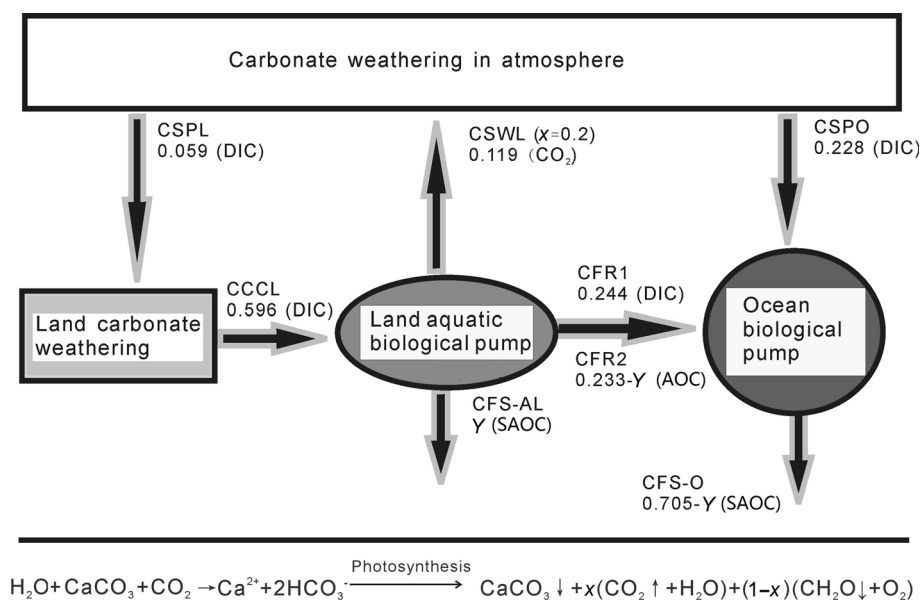


Fig. 2 Atmospheric carbon sources and sinks (Pg C/a) produced by carbonate weathering based on H_2O –carbonate– CO_2 –aquatic phototroph interaction (drawing in reference to Liu et al. [12]). CSPL: carbon sink resulting from precipitation on the land; CSPO: carbon sink resulting from precipitation in the ocean; CCCL: carbonate weathering carbon flux on the land; CSWL: carbon source flux from waters on the land; CFR1: DIC flux from rivers to the ocean; CFR2: autochthonous organic carbon (AOC) flux from rivers to the ocean; CFS-AL: autochthonous sedimentary organic carbon (SAOC) flux in surface waters on land (Y to be determined); CFS-O: autochthonous sedimentary organic carbon (SAOC) flux in the ocean; DIC: dissolved inorganic carbon; AOC: autochthonous organic carbon; SAOC: autochthonous sedimentary organic carbon. Note: The conventional carbon cycle model of carbonate weathering [9, 10, 25] (or the karst processes-related carbon cycle model) does not consider organic processes, i.e., $x = 1$, and all CO_2 gas is returned to the atmosphere. Thus, carbonate weathering does not form a net long-term carbon sink and cannot influence climate change over extended timescales

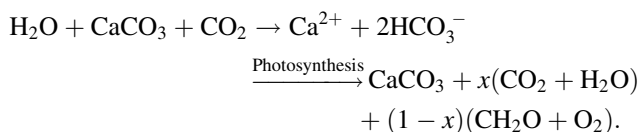
waters downstream, leaving only a perturbation carbon input of ~ 0.1 Pg C/a to the open ocean. Thus, they suggest that carbon fluxes along the land–ocean aquatic continuum need to be included in global carbon dioxide budgets.

Such overall assessments [38, 41, 42], however, do not show detailed mechanisms determining the changes. In contrast, Macpherson et al. [15] investigated an increasing trend in shallow groundwater CO_2 and limestone weathering at Konza Prairie, Kansas, USA, a mid-continental North American undisturbed grassland. This site is restricted to use for ecological research to avoid the complexities of changing land use and water management that are problematic for large river chemistry research in developed countries. The authors found that groundwater CO_2 increased by 20 % between 1991 and 2005, and that the long-term increase in shallow groundwater CO_2 was greater than the 7 % increase in atmospheric CO_2 recorded over the same time period, due to increased soil CO_2 from the microbial breakdown of vegetation and/or root respiration. The latter two factors may be synergetically enhanced in relation to increasing atmospheric CO_2 [43–46] and/or increasing atmospheric temperatures [46]. Therefore, Macpherson et al. [15] propose that

groundwater is a CO_2 sink by way of the weathering of limestone; soil-generated CO_2 is transformed to alkalinity through the dissolution of calcite or dolomite. For the surface water system detailed in Fig. 1, Raymond and Cole [13] show an increase of ~ 60 % in the export of carbonate alkalinity ($\text{HCO}_3^- + \text{CO}_3^{2-}$) from North America's largest river, the Mississippi, during the past half-century. This increase is in part the result of increased flow resulting from higher rainfall in the Mississippi Basin. Subcatchment data from the Mississippi suggest that the increase in the export of alkalinity is also linked to amount and type of land cover. In a later paper, Raymond et al. [14] further demonstrated that land use change and management have arguably been more important than changes in climate and plant CO_2 fertilization as factors contributing to the increases in riverine water and carbon export from this large region over the past 50 years. These observations have important implications for the potential management of carbon sequestration throughout the world.

On the other hand, there are also many records of long-term increases in organic carbon concentrations in the world's rivers, streams, or lakes during recent decades [47–51]. For instance, Worrall et al. [47] found an approximately 100 % increase in dissolved organic carbon (DOC)

concentrations over 30 years in the River Tees in northern England. All these increases in DOC or TOC were related to climate change and/or a decrease in acid deposition. As a result of these findings, questions about the true causes of the long-term increases in DOC and/or TOC remain open. The DOC or TOC sources in these rivers or lakes need to be determined before this problem can be solved. Are they soil derived (allochthonous) or formed in aquatic ecosystems (autochthonous) [52–54]? If autochthonous, the long-term increases in organic carbon concentrations in the world’s rivers, streams, wetlands, or lakes may also be related to the fertilization of possibly increased DIC [55–57], i.e., they may be linked to carbonate weathering by way of the H₂O–carbonate–CO₂–aquatic phototroph interaction [39]:

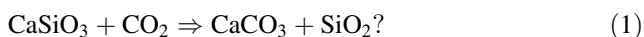


Findings by Bianchi et al. [52, 53] suggest that autochthonous production in the Mississippi River may be more important as a source of DOC and POC than previously thought, for example. Increases in nutrient loading and decreases in the suspended load in the Mississippi (because of dams), as well as in other large rivers around the world, have resulted in significant changes in the sources and overall cycling of riverine DOC and POC.

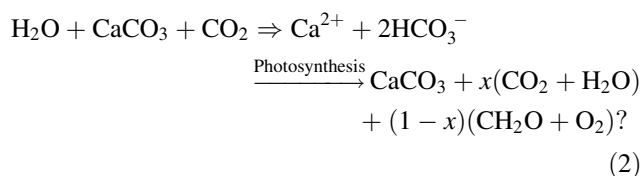
6 Implications of the new conceptual model

We have shown that the rapid kinetics of carbonate dissolution and the importance of carbonate minerals in controlling the DIC in both silicate and carbonate watersheds, coupled with aquatic photosynthetic uptake of the weathering-derived DIC and burial of a part of the resulting organic carbon, suggest that the atmospheric CO₂ sink produced by carbonate weathering based on H₂O–carbonate–CO₂–aquatic phototroph interaction [12, 39] on land may have been underestimated in much previous work by a factor of about three.

Firstly, we must question the origin of carbonates in oceans and lakes since the first appearance of aquatic phototrophs about 3.416 billion years ago [58]. Is it mainly due to the following silicate weathering reaction:



Or is it mainly due to the following carbonate weathering reaction:



Because of the much faster kinetics of carbonate weathering, the carbonates in oceans and lakes may originate mainly from (2), the carbonate-shifted reaction [34, 39, 59], though more work remains to be done to confirm this.

Secondly, we must reassess the atmospheric CO₂ sinks produced by rock weathering since the first appearance of aquatic phototrophs. It appears that the atmospheric CO₂ sink by way of rock weathering rests chiefly on carbonate dissolution and subsequent aquatic photosynthetic uptake of the resulting DIC [12]. There is a great deal of evidence to show that biological productivity may be limited by the supply of DIC from rock weathering. For example, Liu et al. [57] found that DIC utilization and induced calcium carbonate precipitation by *Oocystis solitaria* Witt were much higher (4.6- and tenfold, respectively) in karst water (with high [DIC], as an analog of the carbonate aquatic system) than in non-karst water (with low [DIC], as an analog of the silicate aquatic system). This clearly shows the greater significance of the karst water environment in DIC fertilization and its consequent effect upon the growth of *Oocystis solitaria* Witt; it is also significant for the carbonate weathering-related carbon sink in general. Iglesias-Rodriguez et al. [60] studied phytoplankton calcification in a high-CO₂ environment. Their laboratory evidence shows that calcification and net primary production in the coccolithophore species *Emiliania huxleyi* are significantly increased by high CO₂ partial pressures and HCO₃⁻. Their field evidence from the deep ocean is consistent with these laboratory conclusions, indicating that over the past 220 years, there has been a 40 % increase in average coccolith mass. The coccolithophores are already responding, and will probably continue to respond, to rising atmospheric CO₂ partial pressures and HCO₃⁻. Of course, considering inland waters are generally oversaturated in CO₂, aquatic primary production may be limited by other micronutrients, such as P [61], N [62], Zn [63], or Fe [64], and this needs to be investigated further in future studies.

In brief, the rock weathering-related carbon sink will be greatly underestimated where only DIC concentrations at river mouths are considered and the transformation of DIC to autochthonous TOC [29, 39] is neglected. In order to assess correctly the carbon sink produced by rock weathering, it is necessary to consider the concentrations of both DIC and autochthonous TOC in rivers.

Thirdly, the presence of a “biological carbon pump effect” in natural aquatic ecosystems which diverts carbon produced by the reaction $\text{Ca}^{2+} + 2\text{HCO}_3^- \xrightarrow{\text{Photosynthesis}}$

$\text{CaCO}_3 + x(\text{CO}_2 + \text{H}_2\text{O}) + (1 - x)(\text{CH}_2\text{O} + \text{O}_2)$ to the lithosphere by means of sedimentation and burial of the organic carbon [33, 59, 65–69] implies that such carbonate weathering might also be significant in controlling long-term climate change, due to the substantial production and burial of AOC, the latter being an important mechanism in the formation of lacustrine and marine petroleum source rocks [70, 71]. For example, Jarvis et al. [68] studied black shale deposition, atmospheric CO_2 drawdown, and cooling during the Cenomanian–Turonian Oceanic Anoxic Event about 93.95 Ma ago. They found that rising $p\text{CO}_2$ and sea surface temperatures (SST) during the Late Cenomanian were due to volcanic degassing; $p\text{CO}_2$ and SST maxima occurred at the onset of black shale deposition, followed by falling $p\text{CO}_2$ and cooling due to carbon sequestration by marine organic productivity and preservation, in addition to increased silicate weathering. This questions the traditional point of view [9, 10, 25] that only chemical weathering of calcium silicate rocks can potentially control long-term climate change by providing feedback interactions with atmospheric CO_2 drawdown via precipitation of carbonate. In another recent study, Bowen and Zachos [72] investigated the rapid carbon sequestration at the termination of the Paleocene–Eocene Thermal Maximum about 56 Ma ago and found that the rate of recovery is an order of magnitude more rapid than that expected for carbon drawdown by silicate weathering alone. Therefore, they concluded that the accelerated sequestration of organic carbon could reflect the regrowth of carbon stocks in the biosphere or shallow lithosphere that were released at the onset of the event. This may provide further support for our new conceptual model of a carbon sink produced by carbonate weathering based on H_2O –carbonate– CO_2 –aquatic phototroph interaction.

7 Future directions for research

There are two great problems in the study of carbon cycle of aquatic systems. One is the high degree of uncertainty present in estimating the fluxes of carbon sources and carbon sinks, and the other is a paucity of knowledge about the mechanisms determining sources and sinks. At present, oceans are regarded an important carbon sink ($2 \pm 0.4 \text{ Pg C/a}$) [73]. However, inland waters are mainly considered as an important carbon source (2.1 Pg C/a : 1.8 ± 0.25 for streams and rivers, and $0.32^{+0.52}_{-0.26}$ for lakes and reservoirs) [74]. Although two studies [38, 41] have considered inland waters as an important carbon sink through the burial of organic carbon in their aquatic systems, the sources (or forming mechanisms) of this organic carbon remain to be determined; there is also substantial

difference (0.2 versus 0.6 Pg C/a) in the carbon sink flux estimation between these two studies. It would thus appear that solid results concerning carbon sequestration in aquatic systems cannot, as yet, be provided. This review is therefore an effort to emphasize the importance of complete mechanisms (H_2O –carbonate– CO_2 –aquatic phototroph interaction on land) in understanding the terrestrial carbon cycle.

There are two major processes which sequester carbon on the continents [12, 13, 21]: (1) Photosynthesis, where plants store the atmospheric carbon in the ecological system in the form of organic carbon and (2) carbon storage in aqueous systems in the form of DIC and AOC. Inorganic carbon cycling is as important as organic carbon cycling, but current studies of terrestrial ecosystems consider mainly organic carbon cycling; the interaction between inorganic and organic carbon cycles is neglected. Elucidating the coupling relations between the inorganic and organic carbon cycles is the key to revising the carbon cycle model, especially in carbonate rock areas.

In short, we need to combine the separate studies of photosynthesis and water–rock–gas interaction into a water–rock (soil)–gas–organisms interaction study (Fig. 3). In carbonate terrains, especially in karst regions, the carbon sink produced by carbonate weathering has a similar impact on the organic carbon sink. Therefore, atmosphere, vegetation, soil, carbonate, and water have to be considered within the context of the carbon cycle as a whole (Fig. 3).

The conventional rock weathering evaluation method based on water–rock–gas interaction considers only inorganic components; the calculation can be simply expressed as

$$\text{CSF} = F_{\text{DIC}} = n \times Q \times [\text{DIC}]/A, \quad (3)$$

where CSF is the rock weathering carbon sink flux; F_{DIC} is the DIC flux via runoff; A is the watershed area; Q is the aqueous discharge; $[\text{DIC}]$ is the concentration of dissolved inorganic carbon at river mouths; and n is the rock weathering coefficient for the carbon sink. For the weathering of carbonate rocks $n = 0.5$, indicating that only one half of the HCO_3^- generated is of atmospheric origin when the rock dissolves; for pure silicate weathering, $n = 1$ because all the HCO_3^- involved is of atmospheric origin [21].

However, due to the presence of aquatic phototrophs (Fig. 4), a large proportion of the DIC in aquatic ecosystems is converted into organic carbon (Fig. 2), forming AOC. Therefore, in order to calculate the rock weathering carbon sink flux (CSF) correctly, it is necessary to consider AOC values [37, 52, 53, 75]. The CSF is thus rewritten as

$$\begin{aligned} \text{CSF} &= F_{\text{DIC}} + F_{\text{AOC}} + F_{\text{SAOC}} \\ &= n \times Q \times ([\text{DIC}] + [\text{AOC}])/A + F_{\text{SAOC}}, \end{aligned} \quad (4)$$

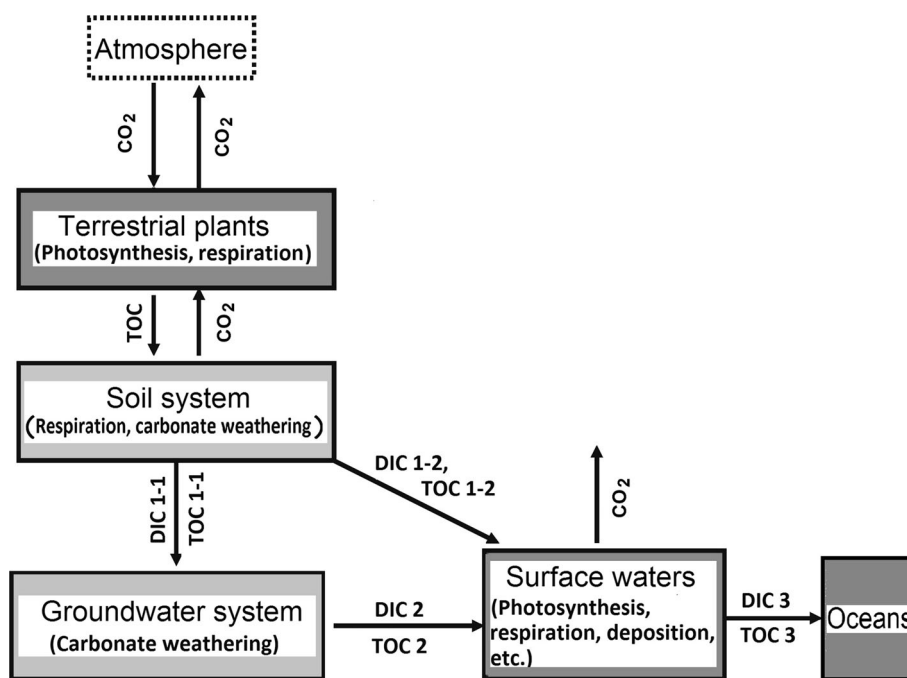


Fig. 3 Conceptual model of the carbon cycle in carbonate (rock) areas based on water–rock (soil)–gas–organism interaction (DIC: dissolved inorganic carbon; TOC: total organic carbon)



Fig. 4 (Color online) Aquatic phototrophs (dominated by *Chara fragilis*) flourishing in a karst spring-fed pond at the Maolan National Nature Reserve, Guizhou, SW China

where F_{DIC} and F_{AOC} are the dissolved inorganic carbon flux and the AOC flux via surface runoff, respectively; F_{SAOC} is the sedimentary flux of AOC in surface water system(s); and [DIC] and [AOC] are the concentrations of the DIC and autochthonous OC at river mouths, respectively.

Any prediction of the extent of the carbon sink produced by H_2O –carbonate– CO_2 –aquatic phototroph interaction under global warming and land use change needs to be enhanced and corroborated with additional evidence.

Satellite observations indicate that the water cycle will increase at a rate of 7 % per °K of surface warming [76]. Raymond et al. [14], however, argue that land use change and management have been more important than changes in climate and plant CO_2 fertilization *vis-à-vis* increases in riverine water and carbon export from the Mississippi River over the past 50 years. The vital question is how far this applies to other parts of the world.

Finally, it should be noted that, although the DIC concentration in water can be increased by rock weathering due to high concentrations of deep earth CO_2 [77, 78], this is not of atmospheric origin and so cannot be regarded as a carbon sink. Thus, this carbon must be deducted from any carbon sink calculations. In addition, other inorganic acids such as sulfuric acid formed by the oxidation of sulfide [79–83] and nitric acid due to nitrification [84, 85] can also increase the DIC concentration in water. Their roles are similar to that of deep earth CO_2 and thus should also be deducted from the calculation of carbon sinks. Nevertheless, determining the relative contributions of all these mechanisms, which will vary in importance regionally and temporally, is a critical component of future research.

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