Exchanges of Carbon in the Coastal Seas

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Despite their moderately-sized surface areas, coastal seas and continental marginal zones play a crucial role in the biogeochemical cycles of carbon. Carbon is transported there by onwelling of inorganic carbon from the open ocean as well as by additions of riverine inputs. Estuaries and proximal coastal seas are believed to be sources of CO_2 because of the decay of terrestrial organic carbon. However, since the riverine flux of nutrients has continually been on the rise over the past few decades, these areas may now actually have enhanced biological productivity, and hence, be releasing less CO_2. The much wider open shelves, on the other hand, are believed to serve as sinks for atmospheric carbon. A recent overview suggests that the global coastal waters (extending to a water depth of 200 m) are now absorbing about 30×10^{12} mol C y^{-1} (0.36 Gt C y^{-1}) from the atmosphere. The shelves also transport 50×10^{12} mol y^{-1} dissolved organic carbon, 45×10^{12} mol y^{-1} particulate organic carbon and 21×10^{12} mol y^{-1}

particulate inorganic carbon to the open oceans. These transports represent an important, albeit often neglected, link in the global carbon cycle. Shelves and estuaries are also important sources of other greenhouse or reactive gases, such as CH_4 and dimethyl sulfide (DMS), by making up a total net flux of 0.1×10^{12} mol y^{-1} CH_4 and 0.07×10^{12} mol y^{-1} DMS into the atmosphere. The coastal seas may respond in a complex manner to future changes associated with climate and other human perturbations. On the one hand, rising CO_2 concentrations in the atmosphere will lead to an increase of the air-to-sea flux of CO_2. On the other hand, it is important to note that the biological pump may well be reduced in the future as additional dams are continually being constructed and freshwater consumption on land increases at an alarming rate. Dwindling freshwater outflow may very likely reduce the buoyancy effect on the shelves, giving way to sharp decreases in the upwelling of nutrient-rich subsurface waters, primary productivity and fish catch. The cycles of water, carbon and food are, intricately linked.

Introduction

In the natural carbon cycle, the time period for the atmosphere-biosphere exchange is the shortest, ranging from only a few months to more than a few decades. The exchange of CO_2 between the atmosphere and the hydrosphere, by contrast, takes several hundred years if the interior of the oceans is taken into consideration. However, the exchange is much more rapid, over a time period of only a few years or even less, when only the terrestrial hydrosphere and the surface mixed layer of the oceans are considered. The length of time for the atmospheric-lithospheric exchange is the longest, requiring a geological period of many thousands of years, if not more. Understandably then, sediments on the continental shelves, being at shallow depths, interact with the atmosphere more readily. Some terrestrial material even crosses the shelves, which have a mean width of 70 km and a total area of 26×10^6 km^2, and efficiently reaches the slopes, which start at an average depth of 130 m (Gattuso *et al.*, 1998). The dissolved form may also be swiftly carried to the interior of the oceans with intermediate water formation in certain areas, such as in the Arctic, Okhotsk, Mediterranean and Red Seas (Walsh, 1995; Chen *et al*., 2003). Further, the specific rates of productivity, biogeochemical cycling and sequestration of CO_2 are higher in the continental margins than in the open oceans. The end result is that it may take only years, as opposed to hundreds of years, for the atmosphere, lithosphere, biosphere and hydrosphere to interact in the continental marginal zones; accordingly, these zones may also act as essential conveyor belts in transporting carbon to the interior of the oceans.

From a qualitative perspective the cooling of water, notably in winter, along with various biological processes, notably in spring, tend to absorb CO_2 from the atmosphere, but conversely, the processes of warming, respiration of marine organisms and decomposition of organic matter release CO_2 back into the atmosphere. Bacterial processes involved in the production of CH_4 (methanogenesis) as well as in the biological production of dimethyl sulfide (DMS) on the shelves also release these important greenhouse or reactive gases into the atmosphere. Finally, direct and indirect human perturbations vis-à-vis the continental margins (e.g. pollution, eutrophication, etc.) are large and have dire consequences on marine ecosystems. Unfortunately, owing to the diversity—and therefore complexity—of the shelf systems, their precise roles in the carbon cycle have yet to be quantified with any degree of certainty. There has not even been, in fact, a consensus when it comes to the simple question posted by the Land-Ocean Interaction in the Coastal Zone project (LOICZ) in its very first report: “Are continental shelves carbon sources or sinks?” (Kempe, 1995).

Basing their argument on the imbalance between the total river transport of about 0.4 Gt C y^{-1} and the oceanic organic carbon burial rate of around 0.14 Gt C y^{-1}, Smith and Mackenzie (1987) and Smith and Hollibaugh (1993) noted that the ocean must be heterotrophic and hence must releases more CO_2 into the atmosphere than it takes up in the absence of the anthropogenic perturbation of atmospheric CO_2. Over the long term, the difference of 0.26 Gt C y^{-1} is most likely returned to the atmosphere. Ver *et al.* (1999 a, b) and Mackenzie *et al.* (2000) have recently evaluated changes in the carbon cycle in the continental margins over the past three centuries and conclude that, in spite of an increased invasion of CO_2 from the atmosphere to the continental margins driven by the rise in atmospheric CO_2, continental margin waters are still a source of CO_2 to the atmosphere. Fasham et al. (2001) adopts the same view and reports a net sea-to-air flux of 0.5 Gt C y^{-1} for continental margins.

The Mass Balances

A striking fact, however, is that the most recent JGOFS synthesis suggests that the marginal seas are actually sinks of CO_2 (Chen *et al.*, 2003). Slightly modified in light of some recent developments, the results of Chen *et al.* (2003) are wrapped up in Fig. 1 and Table 1 with the mass flow (fluxes) among various compartments balancing out. The results show that the global average new production of phytoplankton on the shelf is 65×10^{12} mol (0.78 Gt) particulate organic carbon (POC) and 21×10^{12} mol (0.25 Gt) particulate inorganic carbon (PIC) per year, which makes up only 13% of the average primary production rate and is mostly a result of upwelling (Chavez and Toggweiler, 1995; Liu *et al.*, 2000; Chen, 2000, 2003a). It is important to note that although net community productivity is rather high on global shelves (Lee, 2001), only about 0.2 Gt y^{-1} of

PIC and the same amount of POC out of the 0.48 Gt y^{-1} PIC and 6.2 Gt y^{-1} POC produced is buried and stored on the shelf, and the downslope transport of modern particulate carbon is 0.5 Gt C y^{-1}, 58% of which is organic (Chen et al., 2003). Results from major programs on the eastern US, western European, East China Sea and Mediterranean continental shelves all indicate that most of the biogenic particulate matter is remineralized over the shelves. Only a small proportion (< 8%) is exported to the adjacent slopes (Wollast and Chou, 2001; de Haas *et al.*, 2002; Chen, 2003b) but higher export ratios have occasionally been reported.

The downslope transport of POC is estimated to be only 23% of the offshore dissolved organic carbon (DOC) transport. Recent studies based on ^{13}C, ^{14}C and ^{15}N indicate that a large portion of the off-shelf transport of POC may be old terrestrial or relic matter. There have been reports of high PIC contents on the slopes (e.g. Epping *et al.*, 2002), but whether or not these are relic is unknown (Bauer *et al.*, 2001). Figure 1 indicates that there is a net offshelf transport of 50×10^{12} mol y^{-1} DOC, which compares with a terrestrial input of 27×10^{12} mol y^{-1}. The remaining 23×10^{12} mol y^{-1} DOC is produced on the shelves and represents 35% of the new organic carbon production or 27% of the total new carbon production, values which are consistent with the results of Hansell and Carlson (1998).

Interestingly, marginal seas are also sources of CH_4 and DMS (Sharma *et al.*, 1999; Marty *et al.*, 2001). In the case of CH_4, shelf sediments are likely to be the principal source, whereas in the case of DMS, biological production in the water column is probably the main source. Admittedly, these fluxes are small (Fig. 1) compared to the very large CO_2 fluxes, but they still do play an important role since they are more effective in absorbing solar energy and are more reactive in the atmosphere.

The pCO_2 of the Continental Margins

The above discussion has only dealt with carbon balances rather than with the actual CO_2 partial pressure (pCO_2) of surface waters. Yet, for surface waters to become either a source or sink for atmospheric CO_2, its pCO_2 must respectively be larger or smaller than atmospheric pCO_2. Estuaries are generally supersaturated with respect to CO_2 largely on account of the respiration of organic carbon input from rivers (Frankignoulle *et al.*, 1998; Abril *et al.*, 2002). The shelf systems have not been studied as thoroughly; in fact, the first comprehensive study of pCO_2 on a large shelf was perhaps the one carried out in the North Sea in May/June, 1986 (Kempe and Pegler, 1991). According to that, the North Sea gained 1.4 m C m^{-2} y^{-1}. Since that study, much more pCO_2 data have become available; Frankignoule and Borges (2001), for instance, measured pCO_2 during

18 cruises in the surface waters of many northwest European shelves. Their results show that these shelves are a sink of 0.09-0.17 Gt C per year which is an additional, and appreciable fraction (45%) of the presently proposed flux for the open North Atlantic Ocean (Keir *et al.*, 2001, Takahashi et al., 2002).

Data have also been collected over all four seasons in the Yellow Sea and the East China Sea (ECS) where investigators have been able to correlate surface water pCO_2 with either salinity or temperature. Indications are that much more abundant S and T data could be used to generate pCO_2 in most of these seas. The results also demonstrate that these seas are a CO_2 sink all year round (Tsunogai *et al.*, 1999; Chen and Wang, 1999). Not unlike those for the Yellow Sea and the East China Sea (ECS), other findings of low pCO_2 have been found in the Bering and Mediterranean Seas, along the Californian coast, in the Bay of Bengal, among many others (tables compiled by Chen *et al.*, 2003 and Chen, 2003b). Of interest is that the average sea surface pCO_2 could be super-saturated, and the net annual flux could still very well be from the atmosphere to the sea. This is because the highest fluxes generally occur in winter and spring during periods of undersaturation when the winds are strong. By contrast, a lower exchange rate is noted in summer and fall when surface waters are generally more supersaturated and the winds are weaker (Memery *et al.*, 2002). Gattuso *et al.* (1998) have recently compiled all of the available data for coastal ecosystems and concluded that the proximal shelf regions that are directly influenced by the input of terrestrial organic matter are net heterotrophic. That is, they release CO_2 into the atmosphere since respiration is greater than biological production. In an opposing fashion, the distal shelves are net autotrophic due to the smaller influence of terrestrial inputs and to the larger export of carbon to the sediments and across the continental shelf break.

It has frequently been considered that an autotrophic system absorbs CO_2 from the atmosphere (e.g. Smith and Hollibaugh, 1993), but intensive upwelling regions may be autotrophic and still release CO_2 to the atmosphere. It should be emphasized that the ECS and northwestern European shelves represent 9.4% of the total surface area worldwide. These results and those compiled by Chen *et al.* (2002) and Chen (2003b) confirm the findings of Gattuso *et al.* (1998) and indicate that the global shelves are CO_2 sinks.

In a recent study of the East China Sea continental shelf, Tsunogai et al. (1998) suggested that since the shallow seafloor restricts the convection of cooling water, cooling is greater for waters on the continental shelf than for waters in neighboring open oceans. This leads to the production of relatively cold and dense water, which in combination with biological production, results in a greater absorption of CO_2 in the continental shelf zone. Such a process was termed a “continental shelf pump”. Yool and Fashman (2001) looked at 33 shelves and marginal seas globally and determined that the contietal shelf pump accounts for a net oceanic uptake of 0.6 Gt C y^{-1}. Besides this, Mackenzie and colleagues also recently state, "Before anthropogenic activities, the global coastal ocean was a net autotrophic system with a net export flux to sediments and the open ocean of 20 T mol organic C/yr" (Rabouille *et al.*, 2001). These results, as shown in Fig. 2, support the conclusions of Gattuso *et al.* (1998) that the proximal coastal oceans are CO_2 sources (8.4×10^{12} mol y^{-1}), in contrast to the distal coastal oceans which are CO_2 sinks (28.4×10^{12} mol y^{-1}).

Response to Future Forcing

Granted they are small in area, but the continental margins are where the land, sea and atmosphere meet and interact. This area of the global compartment is of special significance, not only for biogeochemical cycling and processes but increasingly for human habitation. In comparison with the relatively uiform environment of the open oceans, or the rapidly mixing atmosphere, the spatial and temporal heterogeneity of the world' s coastal zone is considerable. These relatively small area so close to humans makes it disproportionately more affected by human activities when compared to the open oceans (Pacyna et al., 2000). Ver *et al.* (1999a, b) and Mackenzie *et al.* (2000) calculated that there was a sea-to-air flux of 0.2 Gt C y^{-1} in the pre-industrial era and that the flux has shrunk since

1800 because of an ever-increasing amount of nutrient discharge. The most recent estimates of Mackenzie and co-workers (Rabouille *et al.*, 2001) report a new direction of the flux by stating the continental margins as net sinks of 0.24 Gt C y^{-1} in the pre-anthropogenic state (Fig. 2). Assuming that the earlier works of these authors were all consistently low by 0.44 Gt C y^{-1}, when this error is corrected, the continental margins should have been reported as sinks of 0.34 Gt C y^{-1} for the year 2000. Needless to say, the land/ocean/atmospheric system is far more complicated than the above simple-minded algebra would suggest**,** but it is nevertheless worth underscoring the fact that the corrected air-sea flux of Ver *et al.* (1999a, b) and Mackenzie *et al.* (2000), shown in Fig. 3, now perfectly agrees with the results of 0.36 Gt C y^{-1} of the present author (Fig. 1). This is a significant amount when compared to the recently reported “global” air-to-sea flux of 2.2 Gt C y^{-1} (Takahashi *et al.*, 2002). Past trends, obviously, need to be confirmed before any attempts to predict the future can be meaningful.

One, however, cannot ignore the longer-term changes in regional weather patterns and climate that result in altered flow regimes of rivers that enter the coastal oceans. Rivers are the major conduits for the passage of water, nutrients, organic material and particulate matter from land to sea, and naturally the input of nutrients and organic matter nurtures fish-breeding in the estuaries. Changes in hydrology are an immediate consequence of dam construction and large-scale water diversion for irrigation. Most central to dramatic reductions in fish stocks in connecting estuaries, as well documented, is the completion of a large dam, such as the Nile River's Aswan Dam in Upper Egypt. Briefly put, dams block the down-stream transport of particulate matter which is an important source of nutrients and food for aquatic biota. However, the major nutrients supply actually originates from the on-shore advection of subsurface waters (Chen, 2000). Simply cutting back the river out flow will not only reduce the cross-shelf water exchange because of a reduced buoyancy effect, but also at the same time, it will diminish the onshore nutrient supply. It thus clearly follows and should come as no surprise whatsoever that primary production and fish catch on the shelf will decrease proportionately.

From a global perspective, approximately 40% of the fresh water and particulate matter entering the oceans are transported by the ten largest rivers by means of a buoyant plume on the open shelves. Hence, these shelves also, of course, face diminished biological pump and fish production when damming reduces freshwater outflow. However, how much of the riverine particulate carbon is deposited in the deltas or beaches, or converted to the ever-increasing DOC pool need to be investigated. Further, p CO_2 of shelf waters may be reduced because the total CO_2/alkalinity ratio is reduced due to dissolution of relic carbonate deposits and/or increased alkalinity due to sulfate reduction in the sediments (Chen, 2002). As a result, the coastal oceans may be heterotrophic but nevertheless absorb CO_2.

Conclusions

The first LOICZ report (Kempe, 1995) asserted that whether coastal seas are net sinks or sources of CO_2 for the atmosphere cannot be determined. Now, based on mass balance calculations as well as direct pCO_2 measurements, it is suggested that although many estuaries, coastal waters and intensive upwelling areas are supersaturated with respect to CO_2, most open shelf areas are probably undersaturated. Taken together, continental shelves are significant sinks for atmospheric CO_2 and absorb 0.36 Gt C a year. This “continental shelf pump” is primarily fueled by the cross-shelf transport of nutrients from nutrient-rich subsurface waters offshore. This compares to the shelves which release 0.1×10^{12} mol CH_4 and 0.07×10^{12} mol DMS into the atmosphere per year.

New production supported by the external sources of nutrients represents only about 13% of primary production, while the rest is respired and recycled on the shelf. Some of the organic material that is not recycled accumulates in the sediments, but most of the detrital organic matter, mainly in its dissolved form, is exported to the slopes and open oceans.

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Figure Captions

Fig. 1 Schematic diagram for the annual carbon budget (in 10^{12} mol y^{-1}) for the continental margins of the world (modified from Chen *et al.*, 2003).

Fig. 2 Organic carbon cycle in global coastal oceans in its pre-anthropogenic state. The boxes represent the reservoirs and the arrows represent the fluxes between them. The air-sea fluxes do not include the net flux of CO_2 because the carbonate system is not included in the budget (data taken from Rabouille *et al.*, 2001).

Fig. 3 Organic carbon balance (dashed line) and net exchange flux of CO_2 across the air-seawater interface (solid line) for the coastal margin system, in units of 10^{12} moles C y^{-1} and Gt y^{-1}. Positive values indicate the CO_2 flux is directed toward the surface waters (modified from Vet *et al.*, 1999a by adding 36.7×10^{12} mol y^{-1} or 0.44 Gt y^{-1} to their results).

Table 1. Fluxes relevant to continental margins (All values except f-ratio are in 10^{12} mol yr^{-1} ; numbers in parentheses are reference numbers)

	C
Rivers plus ground water and ice	32 (1, 6, DIC), 30 (1, DOC), 15 (1, 6, PIC), 20 (1, POC), 34 (2, OC), 27 (6, DOC), 18 (6, POC), 30 (7, OC), 37 (7, IC), 31 (8, OC), 13 (9, IC)
Air-to-Sea (gaseous)	25 (1), 20 (2), 49 (3), 46-75 (4), 30 (6), 8.3 (7), 62 (10), 83 (11), -0.1 (6, CH_4), -0.07 (6, DMS)
Precipitation plus dust	0.3 (1, 6, PIC), 0.2 (8, OC)
Net burial plus fish catch	15 (1, 6, 9, PIC), 15 (1, 6, 9, POC), 14 (2, POC), 12.5 (7, total), 14.5 (9, PIC)
Gross upwelling plus surface inflow	2800 (1, DIC), 80 (1, DOC), 4 (1, 6, POC), 27 (6, POC), 2827 (6, DIC), 70 (6, DOC)
Down-slope export of particulates	20 (1, 6, 9, PIC), 20 (1, 9, POC), 27 (6, POC), 167 (7, total)
Gross surface water outflow	2800 (1,6, DIC), 120 (1, 6, DOC), 1.0 (1, 6, PIC), 12 (1, POC), 22 (6, POC), 58 (7, net)
Gross offshelf export (down-slope+surface outflow)	2800 (1, 6, DIC), 120 (1, 6, DOC), 21 (1, 6, PIC), 32 (1, POC), 49 (6, POC), 225 (7, net)
Net offshore export (down-slope+surface outflow-upwelling plus surface inflow)	0 (1, DIC), 40 (1, DOC), 21 (1, 6, PIC), 28 (1, POC), 40 (2, OC), -27 (6, DIC), 50 (6, DOC), 45 (6, POC), 58 (7, total), 38 (12, OC), 33 (13, DOC), 4 (9, IC)
Primary productivity	40 (1, 6, 9, PIC), 516 (1, 6,9, POC), 368 (2, OC), 789 (5, OC), 830 (7, total), 24.5 (9, PIC),
New productivity	6 (1, PIC), 75 (1, POC), 43 (2, OC), 231 (5, OC), 167 (7, total), 158 (13, OC), 23 (6, DOC), 21 (6, PIC), 42 (6, POC)
f-ratio	0.15 (1), 0.12 (2), 0.29 (5), 0.2 (7), 0.13 (6)

Taken from**:** 1.Table 9 of Chen *et al.*, 2003 and the 27 references therein; 2. Rabouille *et al.*, 2001; 3. Yool and Fasham, 2001; 4. extrapolated from data on the European shelves by Frankignoulle and Borges, 2001; 5. Gattuso *et al.* (1998); 6. this study; 7. Liu *et al.* (2000); 8. Smith *et al.* (2001); 9. Milliman (1993) and Wollast (1994); 10. Walsh and Dieterle (1994); 11. Tsunogai *et al.* (1999); 12. Alvarez-Salgado *et al.* (2001a) and 13. Hansell and Carlson (1998).

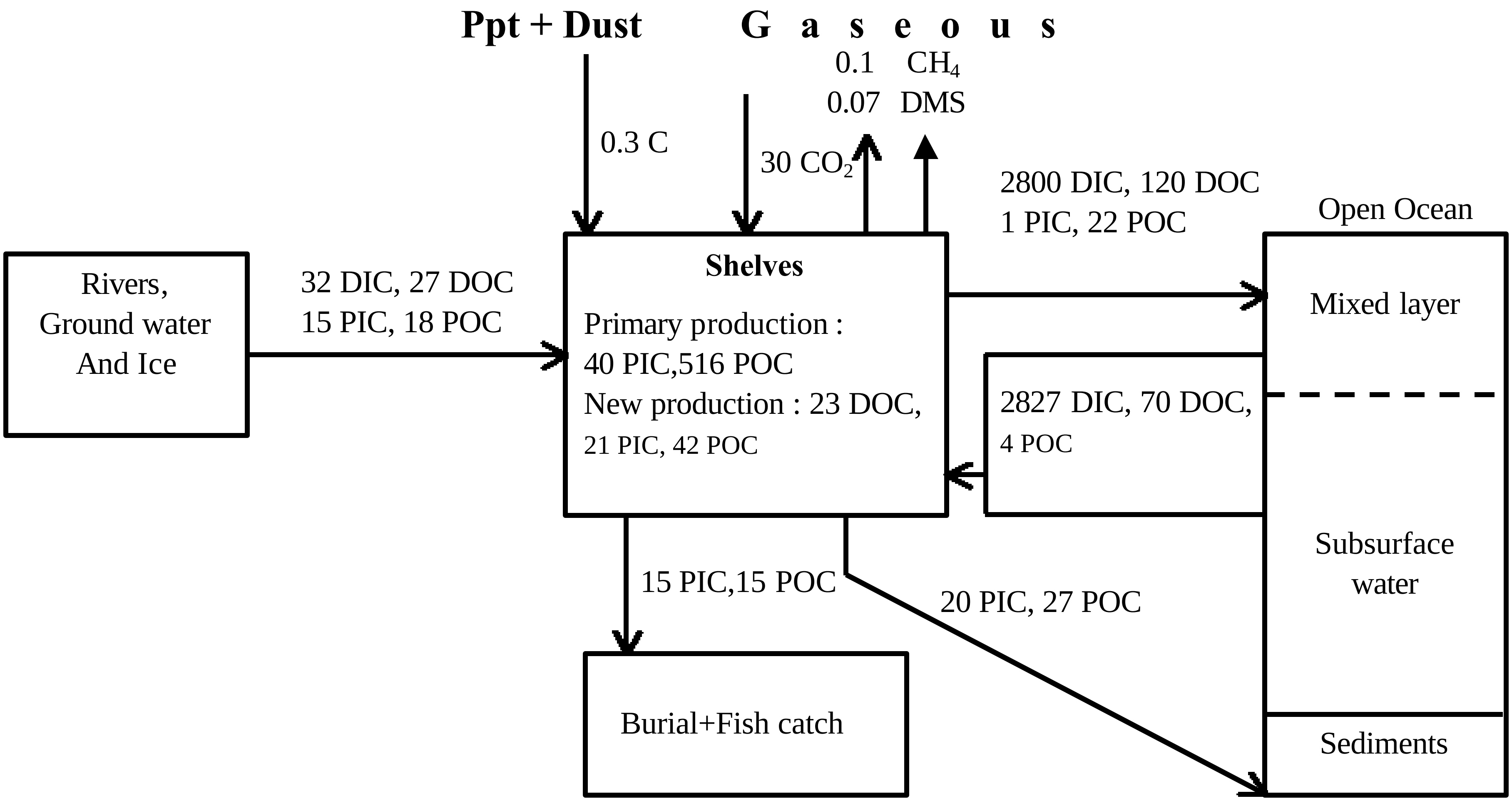

Fig. 1 Schematic diagram for the annual carbon budget (in 10^{12} mol y^{-1}) for the continental margins of the world (modified from Chen *et al*., 2003).

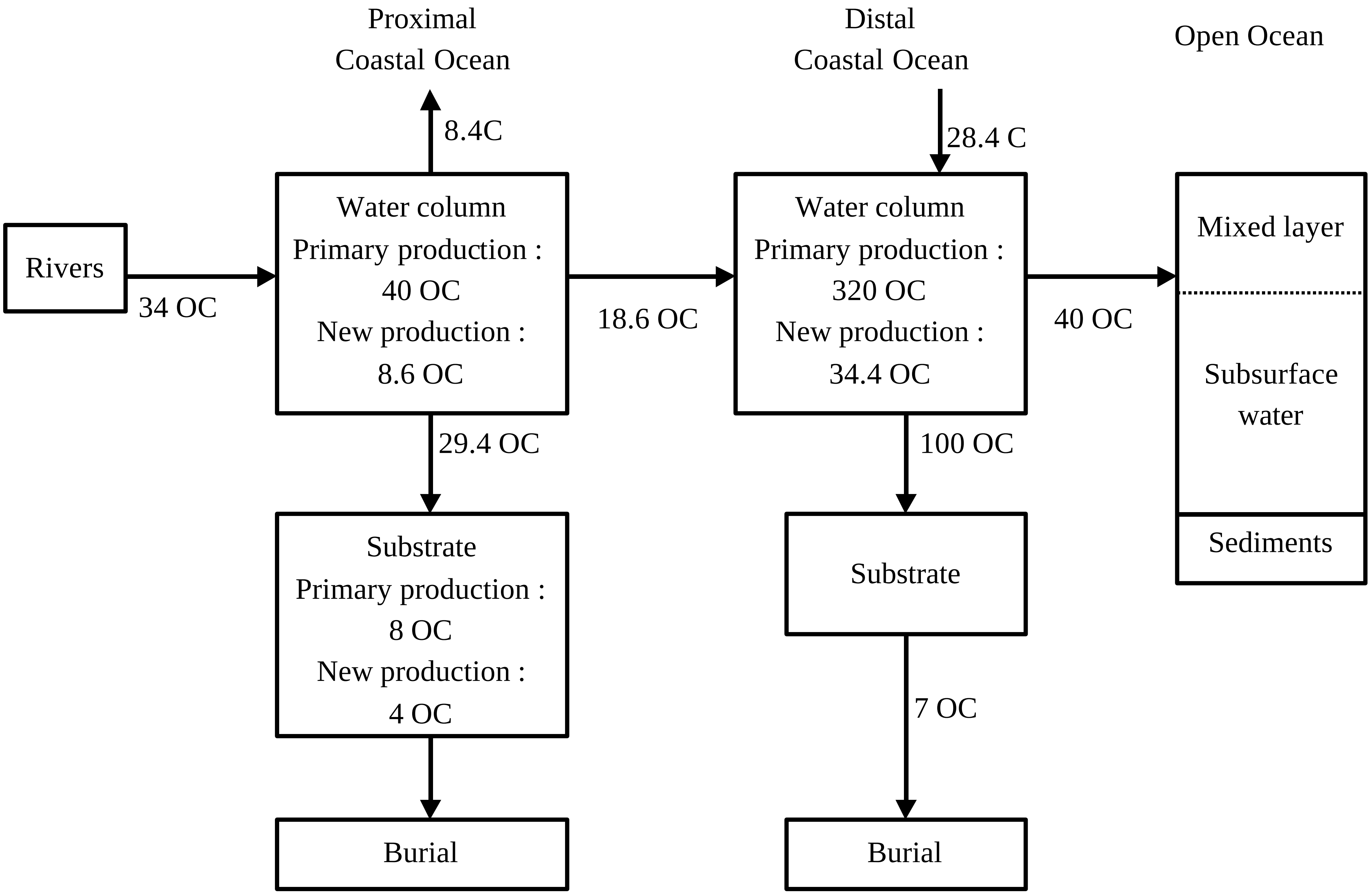

Fig. 2 Organic carbon cycle in global coastal oceans in its pre-anthropogenic state. The boxes represent the reservoirs and the arrows represent the fluxes between them. The air-sea fluxes do not include the net flux of CO_2 because the carbonate system is not included in the budget (data taken from Rabouille *et al.*, 2001).

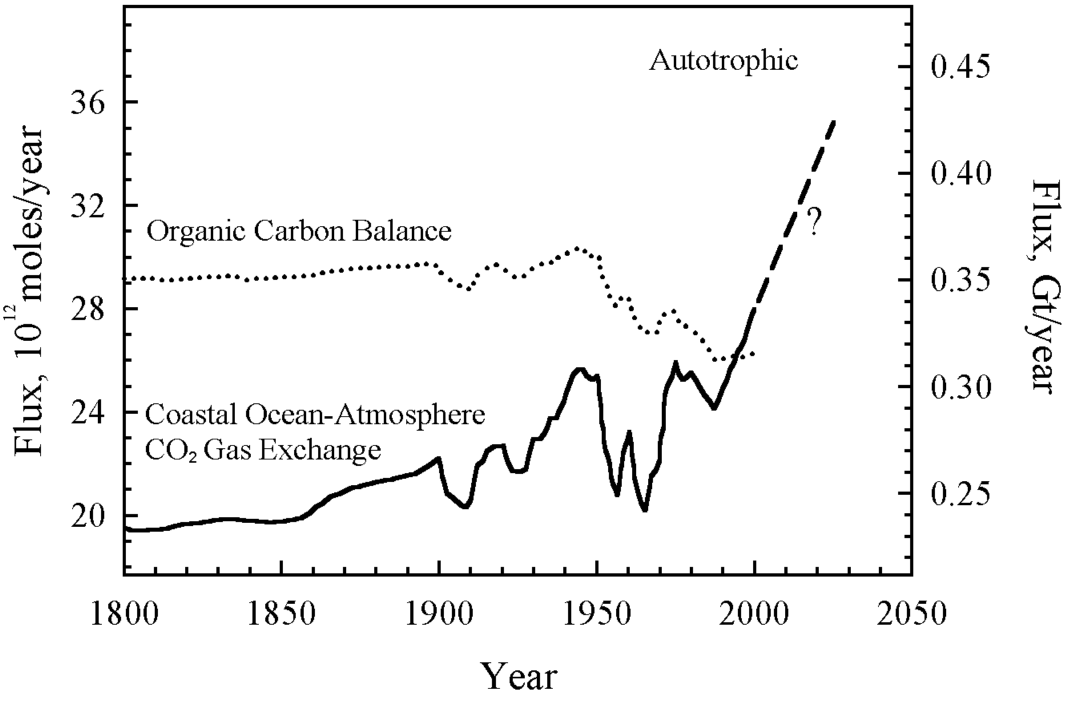

Fig. 3 Organic carbon balance (dashed line) and net exchange flux of CO_2 across the air-seawater interface (solid line) for the coastal margin system, in units of 10^{12} moles C y^{-1} and Gt y^{-1}. Positive values indicate the CO_2 flux is directed toward the surface waters (modified from Vet *et al.*, 1999a by adding 36.7×10^{12} mol y^{-1} or 0.44 Gt y^{-1} to their results).