CHAPTER 9
BIOGEOCHEMICAL CYCLING IN SEMI-ENCLOSED MARINE SYSTEMS AND CONTINENTAL MARGINS

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1: Introduction

The cycling of bioactive elements in semi-enclosed marine systems (SEMS) is controlled by a variety of physical, biological, chemical, and anthropogenic factors. Bottom topography and exchange of water with the continent (via estuaries) and the ocean are the physical drivers of this cycling. External factors, such as temperature, precipitation and wind, may be active on time scales from days to months, producing seasonal, or permanent, stratification or mixing. Exchange of matter between SEMS and interfacing reservoirs (i.e., the atmosphere, land and rivers, ocean and sediments) governs the biogeochemistry and ecosystem structure of SEMS, which are coupled through feedback loops. Many of the processes relevant to biogeochemical cycling have been affected by human activities either directly or through climate change. The extent to which these processes control system biogeochemistry varies by region; thus it is these processes that characterize a system.

This overview will outline selected fundamental processes that contribute to the complex patterns of biogeochemical cycling in SEMS. First, we briefly illustrate the main biogeochemical processes relevant for the carbon, nitrogen and phosphorus cycles. We then discuss, by way of selected examples (Figure 9-1), processes at the interfaces that link SEMS to adjacent reservoirs. We close with a brief perspective on the carbon cycle in SEMS and continental margins, and on the role these systems play in the global carbon cycle.

Figure 9-1: The SEMS and river systems addressed in this chapter.

2: Fundamental processes of the Key Elements Carbon, Nitrogen and Phosphorus

SEMS constitute highly diverse ecosystems (e.g., Gattuso et al., 1998), which may assimilate, regenerate, transform and/or remove carbon and nutrient elements to varying extents, depending on local characteristics. Carbon, nitrogen and phosphorus cycles are subject to biogeochemical processes involving both reduction-oxidation (redox) and multi-phase reactions.

2.1: The Carbon cycle—The biogeochemical cycle of carbon is very complex; only those pathways involving the major compounds (Garrels et al., 1975; Morel and Hering, 1993) in the Earth surface environment will be discussed (these are depicted in Figure 9-2). Photosynthesis is carried out primarily by phytoplankton, although macro-algae, seagrass and benthic micro-algae may also make significant contributions to ecosystem production in SEMS. Mangroves and
symbiotic algae in corals play a particularly important role in tropical margins. The direct product of photosynthesis—glucose—provides essential energy to organisms and is also used in building other biochemical compounds. A major fraction of photosynthetic production is eventually degraded and respired back to CO2 and water by marine organisms. In contrast to the strong seasonality of primary production, respiration shows a less pronounced, but still significant, seasonal variability.

**Figure 9-2:** Biogeochemical pathways of the carbon cycle. Pathways of bio-synthesis and bio-degradation are shown as schematics to represent the complex biochemical pathways. Only the most common compounds are shown [redrawn from Liu et al., 2008 and used with permission from Springer].

Often coupled to photosynthesis is the formation by organisms of calcium carbonate shells and skeletons. Calcareous plankton includes both the autotrophic coccolithophores, and the heterotrophic pteropods and foraminifera, which are the major producers of calcium carbonate shells in the water column. Another form of calcium carbonate formation takes place in coral reefs, where coral polyps and coralline macro-algae produce massive carbonate deposits. Calcium carbonate exists in two major forms: calcite and aragonite. Of the two, aragonite is more soluble and may be transformed into calcite. As particulate organic matter deposits on the seafloor in continental margins, a major fraction is recycled in the sediment, resulting in a strong benthic-pelagic coupling (Middelburg and Soetaert, 2004; Liu et al., 2007). In shallower parts of the continental shelf and in semi-enclosed seas, 20-50% of primary production may be consumed on the seafloor (Rabouille et al., 2001). Without sufficient oxygen, or other compounds functioning as oxidants, organic matter may be split into compounds with higher and lower oxidation states during fermentation reactions by anaerobic microbes (Figure 9-2). The end products of these fermentation reactions are CO2 and methane. CO2 is very soluble in seawater, but methane is less so and therefore tends to escape to the atmosphere as gas.

The distributions of nitrogen and phosphorus in marine environments are often closely related, however, their biogeochemical pathways are quite different.

**2.2: The Nitrogen cycle**—Nitrogen compounds span oxidation states from -3 to +5 and, are therefore sensitive to redox conditions. The redox pathways of the nitrogen cycle are depicted in Figure 9-3. In the center of the diagram is organic nitrogen, indicated by RNH2, which represents the nitrogenous organic matter that is produced by organisms, and also the organic nitrogen compounds that are discharged from human activities.

**Figure 9-3:** The biogeochemical pathways of the nitrogen cycle (modified after Liu and Kaplan, 1982; Codispoti et al., 2001) [redrawn from Liu et al., 2008 and used with permission from Springer].
• Phytoplankton, bacteria and archaea compete for ammonium (NH₄⁺). In a mainly light-dependent process, phytoplankton, bacteria and archaea assimilate ammonium to form organic matter. During nitrification, bacteria and archaea oxidize ammonium to nitrite (NO₂⁻) and in a second step to nitrate (NO₃⁻).

• Under low oxygen or anoxic conditions, ammonium may be lost from the environment due to its conversion to nitrogen gas (N₂) during anaerobic oxidation of ammonium, also known as anammox (Jetten et al., 2003; Kuypers et al., 2003).

• Under low oxygen conditions, nitrate may be consumed during nitrate respiration (also called denitrification) by heterotrophic bacteria (Delwiche and Bryan, 1976). Nitrite is an intermediate product of nitrate respiration which can be further reduced to nitrous oxide (N₂O) or dinitrogen gas during denitrification.

• Nitrogen fixation can serve as a source of bioavailable nitrogen in SEMS (see section 5) and counteracts the loss of fixed nitrogen from the environment through the above-mentioned processes.

• Conversion of fixed nitrogen to nitrogen gas, which will then escape to the atmosphere, is a major pathway for removal of fixed nitrogen in the coastal zone. Nitrous oxide (N₂O) may also escape from the coastal environment to the atmosphere. N₂O is a potent greenhouse gas that makes a potentially significant contribution to global warming (Forster et al., 2007). The conversion of dissolved inorganic nitrogen (DIN) to N₂ during denitrification, or anammox, in SEMS and continental margins represents the most important nitrogen sink in the ocean. Consequently, this sink may regulate the global carbon cycle (Altabet et al., 2002).

2.3: The Phosphorus cycle—In contrast to nitrogen, phosphorus remains constantly at an oxidation state of +5. However, its speciation and availability are still sensitive to redox conditions due to its chemical affiliates. Particulate phosphorus is primarily introduced to the marine environment by rivers, with primary production playing a minor role in the supply of particulate phosphorus (Meybeck, 1982; Beusen et al., 2005). As particulate organic matter sinks to the seafloor (Figure 9-4a), a major fraction of it may be decomposed. This decomposition consumes oxygen, resulting in significantly reduced oxygen concentrations in the lower water column.

**Figure 9-4:** Biogeochemical cycles in SEMS and shallow marine environments. The compounds marked with asterisks are significantly influenced by human activities. (a) Carbon cycle, (b) Nitrogen cycle and (c) Phosphorus cycle [redrawn from Liu et al., 2008].

Within the oxygenated surface layer of seafloor sediments, particulate organic phosphorous is efficiently remineralized (Figure 9-4c) and converted to dissolved inorganic phosphorus (DIP). A major fraction of this DIP may diffuse out of the sediments re-entering the water column phosphorus cycle. On the other hand, phosphorus-containing minerals may be formed authigenically from the build-up of DIP in the pore waters of the sediments. Burial of these minerals represents a major sink of phosphorus in the ocean (Berner et al., 1993). Low oxygen conditions may occur near the sediment surface on the seafloor, or even in the bottom water in
contact with the seafloor, favoring the reduction and dissolution of phosphorus-containing ferric hydroxides (Canfield, 1993). These reduction and dissolution processes act to release DIP to the pore water. If the oxygenated layer is thin, the DIP released in this layer may escape back into the water column. Conversely, if the oxic layer is thick, most of the DIP released will form authigenic minerals as mentioned above.

3: The Semi-Enclosed Marine System – River Interface:
SEMS are very often influenced by enhanced river inputs. This river input establishes the linkage of the marine system to natural processes and human activities occurring on land. Rivers supply not only large amounts of water, but also particulate and dissolved constituents to the marine system. As a result, riverine influence affects both the base-line conditions, as well as the temporal variability, of SEMS. As these dissolved and particulate constituents are discharged to the coastal zone, they pass through the estuarine system undergoing significant modifications due to changes in both salinity and pH. Hydrodynamics ultimately determine whether, and where, this riverine sediment is deposited.

Natural variability of river input on monthly to interannual time scales (e.g., caused by the variability of precipitation), as well as variability stimulated by human activities, including climate change, will affect the biogeochemical characteristics of SEMS on interannual and decadal time scales (Rabalais et al., 2002; Vicchi et al., 2004; Gypens and Lancelot, 2006). The more closed the system is, or the more river input it receives, the higher the potential impact of altered riverine inputs on a semi-enclosed marine system. Thus, systems receiving large riverine inputs are more vulnerable to human forcing. Unfortunately, interannual variability of river runoff may hamper the identification of long-term trends during the early phase of change, making it difficult to recognize and respond to alterations before ecosystems have been significantly affected.

Abiotic processes such as aggregation, flocculation and desorption, play an important role in the sedimentation and release of dissolved and colloidal organic constituents (Figure 9-4). However, dissolved inorganic constituents remain rather unaffected by these processes (Hollibaugh et al., 1991). An important exception to this is the interaction of trace metals with particles or colloids. Particles can serve as sources of trace metals through desorption or dissolution (e.g., Watson et al., 2000). However, particularly in estuarine mixing zones, particles and colloids can also act as a sink for trace metals, removing them from the water column (e.g., Sañudo-Wilhelmy et al., 1996; Pan and Liss, 1998). Photochemical reactions can break down dissolved organic matter (Amon and Benner, 1996), making otherwise resistant constituents available for further microbial consumption (Bushaw et al., 1996).

Biotic processes, on the other hand, determine the distribution of dissolved inorganic constituents. For example, autotrophic organisms may assimilate materials at the river-ocean interface, while heterotrophic organisms play a role in the regeneration and consumption of organic matter at this interface (Dagg et al., 2004). Autotrophic organisms fuel food webs by producing organic matter and releasing oxygen. In a reverse process, the supply of organic matter to SEMS stimulates heterotrophic activity and respiration, which leads to the consumption of oxygen.
The increased delivery of dissolved nutrients to SEMS as a consequence of fertilizer use, municipal sewage or manure disposal results in enhanced productivity in these regions. This can be considered one of the most obvious threats to SEMS over recent decades (Turner and Rabalais, 1991; Humborg et al., 1997; Vicchi et al., 2004; Seitzinger et al., 2005). Anthropogenic nitrogen (Figure 9-4b) may enter SEMS as organic nitrogen and inorganic fixed nitrogen, namely as, ammonium, nitrate or nitrite.

Enhanced nutrient input and eutrophication—which results in the internal production of “excess” organic matter—have either led to, or exacerbated, hypoxic or anoxic conditions in many ocean regions. The Gulf of Mexico is the best-known example of this phenomenon (e.g., Rabalais et al., 2000; Justic et al., 2002). Another example is the East China Sea, where the riverine nutrient load, (e.g., 77-123 Gmol N yr⁻¹ for DIN, Chapter 8, this volume), sustains the high productivity occurring on the shelf. In the region of 20-50 m isobaths, near-bottom hypoxia has been observed, with dissolved oxygen concentrations as low as 1-2 mg/l (Tong and Zhang, 2007).

Effective management in these areas, such as wastewater treatment and more efficient use of fertilizer, could work to mitigate human pressure on coastal ocean regions. Recently implemented policies designed to reduce riverine nutrient loads have helped to prevent the onset of anoxic conditions in the southern bight of the North Sea (OSPARCOM, 2000).

In SEMS influenced by large rivers, the effects of riverine inputs can extend appreciably into the basin. The summer plume from the Changjiang (Yangtze River), for example, spreads as far as 300-400 km from the river mouth. The Bay of Bengal is almost entirely influenced by freshwater input, as evident from reduced salinities over the whole region. The area of a semi-enclosed marine system affected by river plumes, however, can shrink drastically as water discharge is reduced. For example, in the Bohai (North China), the annual freshwater influx from the Huanghe (Yellow River) and other rivers has been dramatically decreased (i.e., 50-60%) as a result of human activities (e.g., irrigation) in the catchment areas over last two decades (Zhang et al., 2004). Associated changes in circulation, vertical mixing and nutrient supply have the potential to alter the entire system.

Many processes in SEMS are related to the input of particulate matter. Drainage basin characteristics (e.g., relief, geology, erosion and runoff) determine the sediment yield for a region. This may result in significant differences in suspended matter concentration in rivers with high relief and erosion rates, such as the Ganges-Brahmaputra and the Huanghe in Asia, versus low relief and erosion in high-latitude rivers such as Ob, Yenisei and Lena (Milliman and Meade, 1983). Suspended matter plays a major role in biogeochemical processes because particulates are important sites both for microbial activity (Herman and Heip, 1999) and enhanced adsorption of colloidal matter. Unless particles settle or are removed from the water column by suspension feeders (e.g., Dagg et al., 1996), turbidity (at suspended particulate matter concentration >10 mg/L) may inhibit the autotrophic uptake of nutrients due to light limitation (DeMaster and Pope, 1996). However, suspended matter of riverine origin represents a major source of bioavailable nutrients. Nitrogen from particulate matter, for example, can make a significant contribution to total nitrogen, especially in turbid river systems. Mayer et al. (1998) estimated the contribution from particulate nitrogen at between 40-90% for rivers such as the Mississippi and the Huanghe.
The majority of the phosphorus delivered to most SEMS by rivers is also in particulate form (Chapter 8, this volume). River-borne particulate organic phosphorus may originate from terrestrial ecosystems as well as from waste from human activities. However, of greater significance is the particulate inorganic phosphorus (Figure 9-4c), which prevails as iron-bound phosphorus (Fe-P), and is often associated with coatings on mineral grains (Berner et al., 1993). Reduced sediment input from rivers because of damming affects the total amount of P delivered to the estuary (Dagg et al., 2004). This is significant, for example, in the Huanghe and the Bohai, where the sediment load has decreased by 60-80% during recent decades due to damming (Yang et al., 1998; Wang et al., 2007). Another factor worth noting is that phosphorus, like dissolved silica (Humborg et al., 1997), can be retained in reservoirs up-stream, while the watersheds down stream supply extra nitrogen to the river as a result of agricultural activities. Depending on the regional conditions, a reduction of phosphorus input may counteract overall eutrophication, but this reduction may also cause P-limitation, enhancing the obvious shifts in nutrient ratios (e.g., N/P) and consequently contributing to environmental problems.

4: The Semi-Enclosed Marine System – Open Ocean Interface

The open ocean exerts further control on nutrient conditions in SEMS. In open shelf seas that are well ventilated, ocean waters constitute a major and, in some cases, dominant, source for nutrients (Figure 9-4). For example, oceanic nutrients dominate in the open shelves of the Mid-Atlantic Bight (Fennel et al., 2006). The competition between riverine and oceanic inputs can be exemplified in the North Sea. Its southern part receives most of the freshwater and thus riverine nutrients, whereas its northern part is primarily under oceanic control, with riverine nutrients playing a negligible role (Thomas et al., 2005; Bozec et al., 2006). The enormous input of nutrients from the Atlantic Ocean (Thomas et al., 2008) make the North Sea one of the most productive ocean areas in the world. This productivity is further enhanced by riverine nutrient inputs in the southern regions.

The East China Sea provides another example of the importance of oceanic circulation on the nutrient dynamics of SEMS. The seasonal flow pattern of the Kuroshio Current and its branches (e.g., Taiwan Warm Current) over the East China Sea Shelf has an important effect on circulation in this region (Zhang and Su, 2006; Chapter 6, this volume). In summer, effluents from the Changjiang disperse over the broad East China Sea, inducing a strong gradient from eutrophic coastal waters to off-shore oligotrophic waters (Gong et al., 1996); Kuroshio waters can be distinguished at water depths of 50-100m. In winter, the river plumes spread southward, while the Taiwan Current Warm Water occupies the broader shelf. The surface waters of the Kuroshio are devoid of nutrients, whereas nutrient concentrations in its deep water are higher than in shelf waters of the East China Sea. Furthermore, river and oceanic waters have distinct nutrient compositions. Open ocean waters act as the primary source for phosphorus, and to a lesser extent for nitrogen, while river input is phosphorus deficient relative to nitrogen (Chen and Wang, 1999). Given the short residence time (a few months) for waters on the East China Sea Shelf, circulation is of great importance in the biogeochemical cycling of nutrients there (Zhang et al., 2007a).
5: The Semi-Enclosed Marine System – Atmosphere Interface

The atmosphere constitutes another significant source of nutrients to SEMS, particularly for the delivery of nitrogen to systems surrounded by densely populated areas. Atmospheric nutrient input can exceed riverine input, and can thus make a significant contribution to the annual nutrient availability and related productivity of coastal areas (Thomas et al., 1999, 2003; Bozec et al., 2006). In the Yellow Sea and East China Sea, atmospheric deposition accounts for 40-50% of total DIN input from land sources (i.e., river plus atmosphere), 10-40% of total phosphate and 1-5% of dissolved silicate, respectively (Zhang et al., 2007b). In the Bay of Bengal, despite the enormous riverine input received, atmospheric N deposition is estimated to be three times greater than the DIN input by rivers (Naqvi et al., 2006).

In some areas, nitrogen fixation serves as a further source of reactive nitrogen. Fixation of atmospheric nitrogen appears to supply significant amounts of bioavailable nitrogen to oligotrophic subtropical areas, but can also play a role in higher latitude systems. For example, in the Baltic Sea input by N-fixation is of comparable magnitude to that input by rivers. It has been reported that some river plumes provide favorable conditions for nitrogen fixation, possibly due to the physical stabilization of the water column (Ohlendiek et al., 2000; Voss et al., 2006). On the other hand, the atmosphere serves as a sink for elemental nitrogen and nitrous oxide produced by denitrification in anoxic water columns or surface sediments (Fennel et al., 2006).

SEMS play a significant role in exchanging CO2 between the ocean and atmosphere (Thomas et al., 2004; Borges, 2005; Borges et al., 2005). Particularly relevant for carbon cycling and air-sea exchange in SEMS is the river supply of dissolved inorganic carbon (DIC) and alkalinity (AT). The characteristics of river DIC inputs are established by the soil conditions of the drainage area; rivers draining lime-rich soil carry higher inorganic carbon loads than rivers draining siliceous soils (e.g., Thomas and Schneider 1999, Thomas et al. 2003). Land-use changes and water management activities such as damming and irrigation also affect the riverine alkalinity concentrations (Raymond and Cole, 2003). On geological time scales, the enhanced weathering caused by rising atmospheric CO2 conditions will eventually affect alkalinity in SEMS and the open ocean.

The DIC/AT ratio influences air-sea fluxes of carbon in the estuarine mixing zone. In the case of large rivers, this ratio may also influence fluxes downstream in the plume (Körtzinger, 2003). DIC/AT ratios set the conditions for CO2 super- or undersaturation, thus defining thermodynamically driven CO2 fluxes, which then are modulated by biological processes. Inorganic nutrients stimulate uptake of atmospheric CO2 from the atmosphere to replenish biologically fixed carbon, while the input of organic nutrients supports heterotrophic activity, which causes a net CO2 release to the atmosphere. Estuarine zones appear to act predominately as CO2 sources (Frankignouille et al., 1998; Borges, 2005), but CO2 uptake in river plumes is observed in some regions, for example, in the East China Sea (Chen and Wang, 1999) and in the Bay of Bengal (Kumar et al., 1996). Some semi-enclosed basins are thought to act as “continental shelf pumps” that transfer carbon from the atmosphere into the deeper ocean (Tsunogai et al., 1999; Thomas et al., 2004). Biological and physical mechanisms have been inferred; however, the individual physical, chemical and biological characteristics of specific SEMS require case-by-case studies and up-scaling tools have yet to be developed (Borges, 2005).
6: The Semi-Enclosed Marine System – Sediment Interface:
Sediments in the shallow waters of SEMS play an important role in mediating the concentrations of nutrients (Figure 9-4) and $A_T$ in bottom waters. On the seasonal time scale, sedimentation delays water-column remineralization of organic matter and consequently supplies recycled nutrients to the pelagic environment. Sedimentary particulate organic phosphorus, for example, is efficiently remineralized and converted to DIP within the oxygenated surface layer of the sediments. A major fraction of DIP may then diffuse out of the sediments and re-enter the phosphorus cycle in the water column. If sediments accumulate over time, they buffer eutrophication by temporarily storing nutrients. In this way, sediments also “buffer” mitigation strategies for nutrient reduction by slowly releasing temporarily stored nutrients back to the water column, effectively delaying the response of SEMS to these measures.

Nutrient retention has been examined using numerical simulations, for example, in the Gulf of Thailand (Liu et al., 2007). The Gulf receives nutrients mainly from the Chao Phraya River, which discharges an estimated 1.8 Gmol of DIN annually into the northern end of the Gulf. Decreasing nutrient concentrations in the southern Gulf have been reported and effectively simulated by a numerical model of this area (Liu et al., 2007). However, the modest influx of nutrients from the Chao Phraya River can account for less than 1% of the total primary production, which is estimated to be 399 mg C m$^{-2}$ d$^{-1}$ (Liu et al., 2007). Additional input of nutrients may come from the nearby Mekong River and from upwelling of nutrient-rich water from the deep South China Sea. However, numerical simulations have demonstrated that the total input of nutrients can only account for a quarter of the estimated primary production, while the other three-quarters must be sustained by nutrients regenerated from the sediments. It has been further demonstrated that benthic regeneration provides nutrients not only to the overlying water column in the Gulf of Thailand, but also to the euphotic zone in the South China Sea proper, enhancing primary production there by 15% (Liu et al., 2007).

Based on numerical simulations of the South China Sea, the particulate organic matter reaching the seafloor on the shelves represents 21% of the primary production, which compares well with the estimated global averages of 15-36% (Smith and Hollibaugh, 1993; Wollast, 1998; Mackenzie et al., 2004). Sedimentary denitrification may remove 14% of the particulate organic nitrogen reaching the seafloor, which corresponds to an average nitrogen removal of 67 mmol N m$^{-2}$ yr$^{-1}$. This estimate is considerably smaller than that for the Mid-Atlantic Bight (400 mmol N m$^{-2}$ yr$^{-1}$) (Fennel et al., 2006), but closer to the global average of 167-245 mmol N m$^{-2}$ yr$^{-1}$ (Wollast, 1993). In the Yellow Sea, Liu et al. (2003) found that nutrient inputs through the sediment–water interface can be 5 times higher than river inputs for nitrate and dissolved silicate, but represent only 10% of the riverine input of phosphorus. In the East China Sea, the burial of organic matter is $7.4\times10^6$ tC yr$^{-1}$, which is about one order of magnitude higher than the outflow of particulate organic carbon (POC) (i.e., $0.25\times10^6$ tC yr$^{-1}$) into the Northwest Pacific Ocean (Deng et al., 2006).

Furthermore, bottom sediments in SEMS affect nutrient ratios in the water column through sediment–porewater–water column exchange (Figure 9-4b,c), because burial efficiencies and regeneration rates differ among different nutrients. Redox conditions play a major role in releasing and retaining phosphorus in sediments. In the case of nitrogen, sediments can be a major site for denitrification, removing combined nitrogen at a rate close to, or exceeding, the
rate of riverine or oceanic nitrogen supply (Vicchi et al., 2004; Fennel et al., 2006).

Seepage of groundwater through unconsolidated sediments constitutes a significant source of nutrients and fresh water to SEMS, particularly in nearshore areas. Estimates of nutrient and water inputs via groundwater cover a wide range and these inputs may be comparable to or even exceed those from rivers. Accordingly, groundwater-borne nutrients likely exert significant control on the productivity of SEMS. Nutrients in groundwater originate from point sources such as septic devices or larger scale urban or agricultural sources. Similar to riverine inputs, the effects of groundwater nutrient inputs on the ecosystems of SEMS are complex and depend strongly on the particular setting of the system. For example, denitrification may significantly decrease nitrogen inputs when groundwater is released into a denitrifying layer. Moreover, nutrients may be intensively exchanged across the groundwater–SEMS interface in both directions, which makes the quantification of this “new” nutrient input difficult. There is, however, much evidence to suggest that groundwater inputs play a major, and likely underestimated, role in the ecosystems of SEMS (e.g., Valiela et al., 1990; Giblin and Gaines, 1990; Moore, 1996; Crusius et al., 2005; Niencheski et al., 2007). Future research should further improve our understanding of the role of groundwater discharge in coastal ecosystems.

7: A global perspective:
SEMS and continental margins provide an important link between the land and the ocean interior, and also between the atmosphere and the deep ocean (Liu et al., 2000). Here we summarize the role of SEMS and continental margins as both a major conduit and a supplementary carbon repository in global biogeochemical cycles (Figure 9-5).

Figure 9-5: The present-day global carbon cycle (after Denman et al., 2007) and shallow marine environments: a comparison. The inventories are in units of Pg C; the fluxes are in units of Pg C yr\(^{-1}\). The dotted arrows indicate terrigenous carbon flux discharged to the ocean and its fate. The dashed curves represent anthropogenic carbon fluxes. The values in parentheses indicate the increase rate (Pg C yr\(^{-1}\)) of carbon inventory. For clarity, only net trans-boundary fluxes are shown [redrawn from Liu et al., 2008 and used with permission from Springer].

According to the latest IPCC assessment (Denman et al., 2007), fossil fuel burning and deforestation contributed 384 Pg C and 140 Pg C, respectively, to anthropogenic CO\(_2\) in the atmosphere (up until 1994). Of this 524 Pg C contribution, 165 Pg C remains in the atmosphere. Rising atmospheric CO\(_2\) concentrations have led to an undersaturation (with respect to CO\(_2\)), of ocean surface waters at the global scale, rendering the ocean a net sink for CO\(_2\), and increasing the carbon content of the ocean over time.

The current production rate of anthropogenic CO\(_2\) is 8 Pg C yr\(^{-1}\), of which 5.4 Pg C yr\(^{-1}\) is from fossil fuel burning and the remainder from deforestation. Forty percent of the emitted anthropogenic CO\(_2\) remains in the atmosphere and 27.5% is taken up by the ocean, while the balance is presumably taken up by the land biota, likely by temperate forests. However, the net rate of oceanic uptake of atmospheric CO\(_2\) has been reduced to 1.6 Pg C yr\(^{-1}\) due to the outgassing of river-borne carbon. On the other hand, the net carbon flux into the open ocean is
offset by 0.6 Pg C yr\(^{-1}\) introduced from land. This yields an increase in the rate of oceanic carbon uptake of 2.2 Pg C yr\(^{-1}\). The surface ocean stores 0.6 Pg C yr\(^{-1}\), while the intermediate and deep waters store 1.6 Pg C yr\(^{-1}\) of this ‘extra’ carbon.

Based on the IPCC 2007 report (Denman et al., 2007) and a recent synthesis of the biogeochemistry of semi-enclosed seas and continental margins (Liu et al., 2008), we will illustrate the role of continental margin carbon fluxes in the global ocean carbon budget (Figure 9-5). First, the fate of terrigenous carbon, which is discharged by rivers to SEMS, and continental margins, is described (Table 9-1).

<table>
<thead>
<tr>
<th>Table 9-1: Fate of terrestrial carbon inputs in SEMS and marginal seas</th>
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<tbody>
<tr>
<td><strong>Riverine carbon inputs</strong></td>
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<tr>
<td><strong>Burial as organic or carbonate carbon</strong></td>
</tr>
<tr>
<td><strong>Release to atmosphere</strong></td>
</tr>
<tr>
<td><strong>Export to open ocean:</strong></td>
</tr>
<tr>
<td>-Deep sea burial</td>
</tr>
<tr>
<td>-Release to atmosphere in open ocean</td>
</tr>
</tbody>
</table>

Present-day release of terrestrial carbon from continental margins and semi-enclosed seas to the atmosphere is within the range of estimated values of preindustrial CO\(_2\) release (0.14-0.36 Pg C yr\(^{-1}\)) (Mackenzie et al., 2004). The partitioning of (terrestrial) carbon deposition between the margins (0.15 Pg yr\(^{-1}\)) and the interior (0.05 Pg yr\(^{-1}\)) approximates the proportions suggested by Sabine et al. (2004). 55% of riverine carbon inputs are exported to the open ocean, which is similar to the proportion suggested by Smith and Hollibaugh (1993).

Secondly, the contribution of export production from SEMS and marginal seas to global ocean export production is considered (Table 9-2):

<table>
<thead>
<tr>
<th>Table 9-2: Export production from SEMS and marginal seas</th>
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<tbody>
<tr>
<td><strong>World Ocean:</strong></td>
</tr>
<tr>
<td>-Primary Production</td>
</tr>
<tr>
<td>-Export production</td>
</tr>
<tr>
<td><strong>SEMS and marginal seas:</strong></td>
</tr>
<tr>
<td>-Primary Production</td>
</tr>
<tr>
<td>-Export production</td>
</tr>
<tr>
<td>-POC burial on continental slopes</td>
</tr>
</tbody>
</table>

We assume here that the export efficiency of the open oceans applies to the semi-enclosed and marginal seas as well. This assumption is based on the idea that shelf-dominated margins may have lower export efficiency, but that this is partially compensated for by the higher export efficiency of slope-dominated margins. Therefore, it is reasonable to assume that the export production of margins is \(\sim 2\) Pg C yr\(^{-1}\). The estimated flux of (marine) particulate organic carbon
(POC) of 0.19 Pg C yr\(^{-1}\), deposited on the continental slope and rise, thus reflects 9.5% of the export production of semi-enclosed and marginal seas. This delivery efficiency agrees well with the recent observations during the OMEX project that suggest that 8-10% of POC exported from the continental margin reaches the seafloor (Wollast and Chou, 2001). Similar burial rates have been obtained for SEMS and marginal seas by Duarte et al. (2005) and Dunne et al. (2007), for example. In particular, Duarte et al. (2005) provide an exhaustive discussion on the strengths and limitations of the above estimates, consideration of which appears to be crucial when discussing the carbon budget of SEMS and marginal seas at a global scale.

Third, the fate of anthropogenic CO\(_2\) taken up by semi-enclosed seas and continental margins is assessed (Table 9-3). As anthropogenic CO\(_2\) builds up in the atmosphere, there is additional uptake by ocean surface waters. This uptake is counteracted by the release of CO\(_2\), from terrestrial origins, to the atmosphere, yielding an estimated net CO\(_2\) uptake by the ocean of approximately 0.3 Pg C yr\(^{-1}\).

**Table 9-3: Anthrropogenic CO\(_2\) uptake in SEMS and marginal seas**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Net CO(_2) uptake from the atmosphere:</td>
<td>0.29-0.36 PgC yr(^{-1})</td>
</tr>
<tr>
<td>Release to atmosphere (terrestrial carbon)</td>
<td>0.2 PgC yr(^{-1})</td>
</tr>
<tr>
<td>Uptake of anthropogenic CO(_2):</td>
<td>0.5 PgC yr(^{-1})</td>
</tr>
<tr>
<td>-Accumulation in SEMS and marginal seas</td>
<td>0.05 PgC yr(^{-1})</td>
</tr>
<tr>
<td>-Export to open ocean</td>
<td>0.45 PgC yr(^{-1})</td>
</tr>
</tbody>
</table>

Validation of the proposed scenario requires a quantitative understanding of the function of the continental shelf pump, which has yet to be achieved. This exercise is intended to demonstrate that carbon fluxes in continental margins have important implications for the ocean carbon cycle at the global scale. If the proposed scenario is valid, the uptake of anthropogenic CO\(_2\) in semi-enclosed and marginal seas contributes 0.5 Pg C yr\(^{-1}\) of the total oceanic uptake of 2.2 Pg C yr\(^{-1}\). This would attribute an uptake of 1.7 Pg C yr\(^{-1}\) of anthropogenic CO\(_2\) to the open oceans. This line of argument is based on the assumption that the estimated open ocean uptake of 2.2 Pg C yr\(^{-1}\) is representative of the world ocean’s uptake of anthropogenic CO\(_2\).

Alternatively, it has been argued that the uptake of anthropogenic CO\(_2\) in semi-enclosed and marginal seas constitutes a complement, rather than a fraction, of the open ocean uptake (Tsunogai et al., 1999; Thomas et al., 2004). In this case a fraction of the 0.5 Pg C yr\(^{-1}\) taken up by SEMS and marginal seas would complement the total open ocean uptake of 2.2 Pg C yr\(^{-1}\). It is clear that a proper assessment and understanding of the continental shelf pump (Tsunogai, 1999; Thomas et al., 2004) and its sensitivity to climate change is thus of critical relevance to reliably assessing the global ocean uptake of anthropogenic CO\(_2\).

References


Wollast, R., and L. Chou. 2001. The carbon cycle at the ocean margin in the northern Gulf of


Figure 9-4