Chapter 9. THE BIOGEOCHEMISTRY OF CARBON DIOXIDE IN THE COASTAL OCEANS

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Contents

1. Introduction

Accumulation of atmospheric CO_2 (Keeling and Whorf, 2002) and depletion of atmospheric oxygen (Keeling and Shertz, 1992) from combustion of organic matter (OM) stored over geological time provide conclusive evidence that *H. sapiens* has driven the planet into a metabolic state of net heterotrophy in the past 300 years. That is, the fossil fuel combustion, cement production, anthropogenically-stimulated and natural ecosystem metabolism of the planetary ecosystem is currently consuming more organic matter than is produced in photosynthesis by all the world's terrestrial and marine plants. Rising concentrations of atmospheric CO_2 threaten the planet with global warming and associated impacts like rising sea levels (Chapter 20). The ocean and land biospheres also serve to ameliorate these effects by absorbing CO_2 from the atmosphere (Sarmiento and Gruber, 2002). In this chapter we provide a comprehensive synthesis of observations of CO_2 uptake and release by the coastal oceans, critically evaluate arguments about their metabolic status, and discuss new findings on the sources and character of organic matter inputs that fuel coastal ocean metabolism. We conclude that the global coastal ocean as a whole is autotrophic and potentially a strong sink for atmospheric CO_2. Further we suggest that the open sea, over its full depth, is heterotrophic by ~ 200

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Tmol y^{-1}, as a consequence of organic matter exported from the coastal ocean. Yet it too is a sink for atmospheric CO_2.

Defining the area of the global coastal ocean is a difficult and important issue. Previous debate about the role of these continental margin systems in the global carbon cycle stems in part from inconsistencies in definition and in the areas considered in budgeting exercises. Here we adopt a general encompassing definition articulated recently by an international planning group (Hall et al., 2004). In their definition, the global coastal ocean includes "…the region between the land and the open ocean that is dominated by processes resulting from land—ocean boundary interactions. The exact dimensions vary depending on the research issue or chemical element of interest but draw attention to the unique aspects attributable to the boundary system and generally consist of the continental shelf, slope, rise and adjacent inland seas." (Hall et al. 2004, page 9). This concept of the coastal ocean system also includes regions impacted by boundary currents that may extend significantly offshore, such as jets and filaments. The problem of defining the area of interest is illustrated by comparing Tables 2 and 3, to which we return below. In general, adhering to the definition just articulated, we use the term "coastal ocean" or "global coastal ocean" in deference to the title of this volume, unless we are referring to a particular, more specific marine system.

However defined, the coastal ocean is the junction point in the biosphere where the land, ocean and atmospheric components of the planetary biogeochemical system meet and interact. It is 400,000–500,000 km long but just ~100 km wide (Wollast, 1998; Smith, 2000). Into this region flow annually riverine inputs including 85 Tmol carbon, 2 – 4 Tmol nitrogen and 0.7 Tmol phosphorus. Each element is supplied in both dissolved and particulate, and organic and inorganic forms from natural and anthropogenic terrestrial sources (Table 1**;** Meybeck 1993; Gattuso et al. 1998). If confined within buoyant river plumes that encompass a surface layer ~25 m deep on the inner third of the global continental shelves, this input would result in an average enhancement of *in situ* N and P concentrations of 10 and 3 μM, respectively. These levels are well above the average half-saturation constants for uptake by phytoplankton and bacteria. Of course, the actual nutrient inputs may be concentrated in smaller areas where the local impact is greater, but this simple calculation gives an idea of the intensity of the biogeochemical exchanges and transformations in coastal ocean. The coastal ocean also receives even larger inputs of nutrients from offshore, oceanic processes like upwelling (see Section 4). The global continental ocean is a powerful reactor mediating biogeochemical exchanges between the land and ocean biospheres.

K_s, the half-saturation constant for nutrient uptake by phytoplankton defines the nutrient concentration at which the utilization rate by the cell is exactly half the maximum rate at nutrient saturation. Thus when the ambient nutrient concentration is near K_s, any increase in concentration results in an increase in the uptake rate, faster growth and possibly eutrophication.

TABLE 1
Carbon nitrogen and phosphorus inputs from land to the global coastal ocean (Tmol yr^{-1}).
Data taken from summary discussion in Gattuso et al (1998). --, no data.

Input	Natural	Anthropogenic	Total	Ratio	Natural	Anthropogenic	Total
Dissolved Inorganic fluxes				Dissolved Inorganic ratios			
DIC	32	—	32	C:N	121	--	62
DIN	0.27	0.25[1]	0.52	N:P	22	17	19
DIP	0.01	0.02[2]	0.03	C:P	2667	--	1185
Dissolved Organic fluxes				Dissolved Organic ratios			
DOC	17	4[3]	21	C:N	24	16	22
DON	0.7	0.25[1]	0.95	N:P	58	17	35
DOP	0.01	0.02[2]	0.03	C:P	1417	267	778
Particulate fluxes				Particulate ratios			
PIC	14	—	14				
POC	14	4[3]	18	C:N	12	--	11
PON	2.4	0.5	2.9	N:P	4	--	5
pp4	0.6	—	0.6	C:P	23	--	30
Total Organic fluxes				Total Organic ratios			
TOC	31	8	39	C:N	10	11	10
TON	3.1	0.75	3.85	N:P	258	50	6
TOP[1]	0.01	0.02	0.63	C:P	2583	533	62
Total Input fluxes				Total Input ratios			
C	77	8	85	C:N	23	8	19
N	3.4	1.0	4.4	N:P	5	33	7
P	0.62	0.03	0.65	C:P	123	267	130

[1] anthropogenic dissolved nitrogen flux of 0.5 Tmol split evenly between DIN and DON
[2] anthropogenic dissolved phosphorus flux of 0.03 Tmol split evenly between DIP and DOP
[3] anthropogenic POC + DOC flux of 8 Tmol split evenly between fractions
[4] particulate phosphorus assumed to be inorganic

Marine biogeochemistry can trace its origins to the application of chemical methods to the study of plankton ecology by the 'Kiel School' of biological oceanography in the late 19th–early 20th centuries and its later flowering at Plymouth in the 1920's (Mills 1989). The field became global in scope following the advent of satellite-based remote sensing and deployment of a global network of deep-ocean sediment traps in the 1980's (NAS, 1984). Even so, development was concentrated in the open sea, largely as a result of the Joint Global Ocean Flux Study (JGOFS) that conducted basin-scale surveys and large process studies; and established several long-term time series observatories in the 1990's (Hanson et al., 2000). The focus on the open sea derived from the need to understand and quantify the role of the ocean as a sink for anthropogenic carbon dioxide (CO_2). CO_2 exchange is mediated by gas transfer across the ocean surface (see below), of which 93% (360 x 10^6 km^2) is over the open ocean >200 m deep. John Walsh (Walsh et al., 1981) first suggested that continental shelf systems could sequester significant amounts of atmospheric CO_2 in response to anthropogenic eutrophication (see also Walsh et al., 1985; Walsh, 1991). This idea eventually led to a new generation of coordinated research programs over the world's continental shelves. Uncertainties about the oceanic carbon balance, and great intrinsic interest in the coastal ocean stimulated the development of the Land-Ocean Interactions in the Coastal Zone (LOICZ) program (Holligan and Reiners, 1992) and a new focus on coastal ocean biogeochemistry (Liu et al., 2000ab). Of course there are many other strands and themes in marine biogeochemistry which cannot be cited here. It was the combined influence of JGOFS and LOICZ, and interest in the carbon cycle that stirred some of the developments evaluated critically below.

One focus of this research has been the balance between *in situ* net primary production of organic matter (P) and its oxidation by respiratory processes (R). This *metabolic balance* determines whether a system is a net producer or consumer of organic matter. Systems are termed net heterotrophic (R>P) or autotrophic (P>R), depending on the annual metabolic balance. The P:R balance has a venerable tradition in aquatic ecology deriving from the concept of community production (Odum, 1956). Purdy (1917, cited in Odum, 1956) demonstrated net heterotrophy in the Potomac estuary. Smith and Hollibaugh (1993) presented a budgetary approach to the carbon cycle in the global coastal ocean and open sea, arguing that the ocean as a whole is heterotrophic, with a net oxidation (respiration) rate of ~23 Tmol C yr^{-1} (0.3 PgC yr^{-1}), 30% of which is concentrated in the coastal ocean (7% of total ocean area). Thus they argue that organic metabolism in the sea is a net source of CO_2 release to the atmosphere and not a sink, as is usually understood (see below). 0.3 PgC is a small number when compared to the 48 PgC of annual net primary production in the global ocean (Field et al., 1998), but significant in relation to recent estimates of anthropogenic CO_2 uptake of 1 – 2 PgC yr^{-1} by the global ocean (Houghton et al., 2001).

Other recent reviews provide a valuable foundation for our treatment. Walsh (1988) constructed carbon budgets and numerical simulations for a variety of continental shelf systems in different circulation regimes. Wollast (1998) compared the C and N cycles of the coastal and open oceans in a preceding volume of this series, suggesting that the inner margins of the continental shelves were heterotrophic while the outer shelves had positive net community production. Gattuso et al. (1998) critically reviewed primary production and net metabolism in coastal ocean systems, concluding that only estuaries were heterotrophic, whereas the open sea as well as the shelves had positive net production (see below). Atkinson and Huthnance (2003) assess the physical mechanisms supporting primary production over the global coastal ocean. Liu et al. (2000ab) offer a new interpretation of the role of the coastal ocean as a conduit for the net transport of carbon from the land and atmosphere to the open sea. Finally Chen et al. (2003) provide a comprehensive analysis of nutrient and carbon cycling in the coastal oceans. Together these reviews conclude that the ocean as a whole consumes more organic matter than it produces internally. This problem is the subject of intense debate, and a source of considerable misunderstanding regarding the role of marine biological processes in acting as sources or sinks of atmospheric CO_2.

2. Overview

The coastal ocean is an open system, continuously exchanging materials with its several interfaces (land, open sea, sediments and atmosphere). In this chapter we are concerned mainly with the exchanges of carbon at three of these interfaces (signified by the thick arrows in Figure 9.1): transport of organic matter from land to the coastal oceans; net transport of organic matter from the coastal oceans into the open ocean ("continental shelf pump"); and exchange of atmospheric CO_2

across the air/sea interface. The net transfer of organic matter across these interfaces dictates the metabolic balance of the coastal ocean. If organic matter synthesis by primary production is balanced by *in situ* consumption, the system is in metabolic balance. If organic matter is exported from the coastal ocean, the system leans toward net autotrophy. Ultimately, transports of allochthonous (externally-produced) organic matter from land set the bounds for the metabolic balance of the coastal ocean system (Smith and Hollibaugh 1993). These ideas are also discussed in Chapter 8.

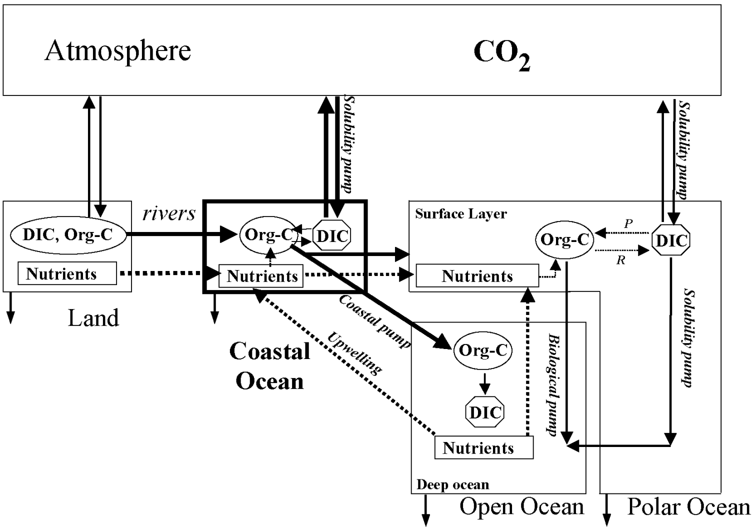

Figure 9.1 Carbon and nutrient exchanges between land, the coastal ocean and the open ocean, showing the three carbon pumps regulating the allocation of CO2 between the surface and deep ocean (solubility, biological and continental shelf pumps). Biologically mediated exchanges (P, photosynthesis; R, respiration) between inorganic and organic carbon pools are indicated by the ovals and hexagons in the ocean boxes. Heavy lines and arrows indicate the primary processes covered in this chapter.

The most important factor regulating the exchange of CO_2 between the coastal ocean and atmosphere is the difference in the partial pressure of CO_2 (ΔpCO_2) between these two reservoirs. ΔpCO_2 varies in space and time and is influenced on the ocean side by both physical and biological processes. The purely physicochemical process of gas exchange across the air-water interface (the solubility pump in Figure 9.1) proceeds independently of the biological processes governing ΔpCO_2. This separation of physical and biological influences, and the variability of ΔpCO_2 in time and space, mean that the ocean as a whole can simultaneously be net heterotrophic (with biological processes serving as a CO_2 source) yet also function as a net sink for atmospheric CO_2 (see also Chapter 8), a point often misunderstood by chemists and biologists alike. In the present-day ocean, ΔpCO_2 and the air-sea flux of CO_2 are influenced more by the concentration of anthropogenic CO_2 in the atmosphere than by heterotrophic CO_2 production in the sea.

The source-sink character of the coastal ocean also depends on the magnitude of organic matter export to the open sea. The coastal ocean will only function as an effective long term sink for atmospheric CO_2 if the net CO_2 taken up is transported into the deep ocean (e.g., by bottom water formation at high latitude) or fixed into organic matter and then exported to the deep ocean by the continental shelf pump (Figure 9.1). Dissolved inorganic carbon (DIC, see below) and carbon fixed into organic matter that are retained in the coastal ocean will likely be returned to the atmosphere due to its shallow depth and relatively short residence time (Tsunogai et al., 1999; Liu et al., 2000b). The key processes affecting CO_2 storage (primary production, $\Delta p\mathrm{CO}_2$, the metabolic balance and the continental shelf CO_2 pump) are addressed in the following sections.

3. Inputs from land.

Table 9.1 summarizes the globally averaged fluxes of carbon, nitrogen and phosphorus into the coastal ocean by riverine inputs, a topic reviewed extensively elsewhere (Meybeck 1993; Ludwig et al. 1996; Frankignoulle et al. 1998; Gattuso et al. 1998; Wollast 1998). The carbon input is 40–45% organic, whereas N inputs are 85–90% organic, emphasizing the potential for organic loading in the immediate coastal zone, and for export offshore. Overall, the terrestrial input of dissolved material is enriched in C and N, relative to P, as shown by the elemental ratios presented in Table 9.1. This C:N:P stoichiometry suggests P-limitation of the primary production derived from the terrestrial input (see next section). The particulate fraction is rich in P, due to a large contribution of P adsorbed onto clay minerals but the magnitude of this flux is uncertain (Meybeck, 1993). The fate of the organic and particulate fractions is also poorly understood. Smith and Hollibaugh (1993) estimated that 11 Tmol of the 34 Tmol of organic matter exported to the coastal ocean was buried, leaving 23 Tmol available for oxidation in the water column. The subsidy provided by anthropogenic additions is also uncertain, and known only to within an order of magnitude (Gattuso et al. 1998).

In terms of C, the annual export from rivers is quantitatively significant. Globally, rivers deliver ~20 Tmol of dissolved organic carbon (DOC) per year to the ocean (Meybeck, 1982; Hedges, 1992; Hedges et al., 1997), an amount large enough to sustain the turnover of the entire pool of marine DOC (685 PgC over 5000 yr). Likewise the magnitude of particulate organic carbon (POC) (~ 13 Tmol) transported by rivers is sufficient to account for the total organic C buried in coastal sediments each year (Hedges and Keil, 1995; Hedges et al., 1997). Despite the magnitude of these inputs and the presumed recalcitrance of riverine organic matter, organic matter dissolved in seawater or buried in sediments bears little isotopic or chemical evidence of a terrigenous origin (Hedges and Keil, 1995; Hedges et al., 1997). Although these findings suggest extensive and efficient remineralization of land-derived OM, the biogeochemical processes responsible for this rapid turnover remain as yet unresolved.

Terrigenous OM is frequently traced through the use of either bulk characteristics (e.g. isotopic values, C:N, etc.) or molecular (lignin phenols, lipids etc.) tracers. Historically, the resolution of molecular level detail in the dissolved phase (DOM) has not been commensurate with analyses of particulate OM (POM), owing in part to the limitations imposed by the required sample size and interference by salt. However the advent of tangential flow ultrafiltration (Benner et al., 1992; Bianchi et al., 1995; Santschi et al., 1995; Bauer et al., 1996) coupled with lowered detection thresholds for many molecular tracers now allow for greater insights into the composition of and relationships between POM and DOM. Although terrestrial OM in the particulate phase (POM) is primarily deposited within the nearshore coastal zone (Prahl et al., 1994; Shi et al., 2001), adsorptive/desorptive exchange between particulate and dissolved reservoirs (Henrichs and Sugai, 1993; Wang and Lee, 1993; Hedges and Keil, 1999; Komada and Reimers, 2001) simultaneously dispels our once simplistic view and complicates our ability to delineate the seaward flow of terrigenous OM.

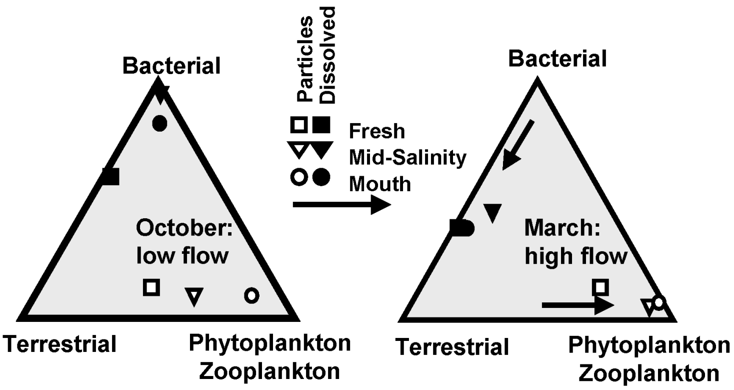

Figure 9.2 Source classification of fatty acid (FA) biomarkers in particulate organic matter (POM) and high molecular weight dissolved organic matter fractions along the York River, Virginia estuary under low and high flow conditions. The vertices of the triangles are the sources of POM and DOM in the estuarine system, characterizing Phytoplankton/ Zooplankton (polyunsaturated FA C18, C20, and C22); Bacteria (iso and anteiso-C13, C15, and C17 FA) and vascular plants (long chain saturated FA: C24-C30). Each particulate and dissolved sample is normalized to the ranges in potential sources (e.g., phytoplankton/zooplankton; bacterial; terrestrial) representative of the dataset as a whole. Figure after McCallister (2002).

Biogeochemical processing in estuaries is the primary control regulating the relocation of terrigenous OM from land to the coastal ocean. The predominately conservative transport of riverine DOC through estuaries (Mantoura and Woodward, 1983; Ittekkot, 1989; Aminot et al., 1990; Alvarez-Salgado and Miller, 1998) is based on bulk DOC concentrations. Molecular level analysis of DOC composition provides greater sensitivity with which to trace the flow and fate of terrigenous DOM (Hedges et al., 1997; Benner and Opsahl, 2001; Aluwihare et al., 2002). A recent study employing fatty acid biomarkers to trace sources of OM suggest a substantial terrigenous signature persists in the dissolved phase along the estuarine salinity gradient (Figure 9.2). In contrast, the seaward-flowing particulate counterpart is dominated by a mixed phytoplankton/zooplankton source with a nominal terrestrial influence. The physical state of OM (i.e., particulate vs dissolved) inherently predisposes it to select pathways of physico-chemical transformations and sinks (e.g., sedimentation and flocculation, adsorption and desorption etc.) within an estuary. However, the ultimate persistence of OM within each physical state is not predetermined, as both biogeochemical and physico-chemical processes may result in OM exchange between phases (Henrichs and Sugai, 1993; Wang and Lee, 1993; Hedges and Keil, 1999; Komada and Reimers, 2001).

Sharp gradients in physical and chemical properties such as the boundary between the landward intrusion of salt and freshwater (i.e. estuarine turbidity maximum) are zones of active partitioning between the particulate and dissolved OM phases. Analogous gradients in pH, redox potential, and solute concentrations between sediments and porewaters may contribute to the adsorption/desorption of OM (Gu et al., 1995; Gu et al., 1996; Thimsen and Keil, 1998) and disperse formerly sediment-bound OM back to the water column (Keil et al., 1997). Physical resuspension of sediments may likewise produce abrupt physico-chemical gradients and thus initiate extensive exchange between particulate and dissolved OM reservoirs (Komada and Reimers, 2001). The terrigenous (Bianchi et al., 1997; Mannino and Harvey, 2000; Mitra et al., 2000) and/or aged (Guo and Santschi, 2000; Komada et al., 2002) signature of solubilized OM suggests that sediment-derived subsidies of terrigenous OM may preserve an allochthonous signature in the dissolved phase throughout estuarine transit.

The handful of studies that measured lignin phenols in high molecular weight (>1 kDa) DOM (HMW DOM), an unequivocal biomarker for vascular plants and a terrigenous origin (Hedges and Mann, 1979), report terrigenous sources may account for ~5–60% of HMW DOM in coastal ocean systems (Opsahl and Benner, 1997; Kattner et al., 1999; Mannino and Harvey, 2000; Benner and Opsahl, 2001; Aluwihare et al., 2002). In comparison land-derived OM comprised a mere 0.7–2.4% of the open ocean HMW DOM (Opsahl and Benner, 1997). These data suggest a rapid (21–132 yr) turnover (Opsahl and Benner, 1997) of the terrigenous pool when compared to bulk DOC ages of 4000–6000 yr ((Williams and Druffel, 1988; Bauer et al., 1992). In contrast to the POM pool, a major sink for terrestrial OM in the dissolved phase may occur in the coastal ocean. The susceptibility of highly colored, strongly light adsorbing (Morris et al., 1995; Reche et al., 1999) terrestrial humics to photochemical losses (Miller, 1999) may be enhanced in coastal waters as a result of increased sunlight penetration into the water column (Amon and Benner, 1996; Bushaw et al., 1996). Furthermore, the photochemical removal of terrestrial OM components may generate a residual signal of photochemical processing in HMW DOM which has been detected in the waters of the Mississippi River plume and the open Pacific and Atlantic oceans (Benner and Opsahl, 2001). Varying degrees of susceptibility of terrigenous particulate and dissolved OM to physico-chemical processes may ultimately regulate the persistence of terrestrial-derived OM in the hydrosphere and determine the re-location of riverine OM to regions of net heterotrophy (Section 6; Smith and Hollibaugh, 1993; del Giorgio et al., 1997; Duarte et al., 2001; del Giorgio and Duarte, 2002). These processes will also influence the relative amounts of terrestrial and marine OM entering the oceanic carbon inventory, after transport and processing in the coastal ocean.

4. Organic matter production within the global coastal ocean.

Primary production in the coastal ocean, as in the open sea, is dominated by unicellular phytoplankton but the composition and physiology of the flora and the relative importance of nutrient, light and grazing as limiting factors on phytoplankton growth differ in important ways from the open sea. The fundamental influence of coastal physical processes on primary production and foodweb structure and dynamics are discussed in detail in Chapter 13 as well as by Cullen et al. (2002), and the effects with regard to coastal ocean systems can be summarized as follows. The relatively shallow depth of most coastal ocean environments and enhanced stratification resulting from terrestrial inputs of freshwater limit the vertical extent of mixing. These processes may ameliorate light limitation, compared to the open sea, although greater turbidity and self-shading due to high plankton biomass and other suspended solids will counteract buoyancy-related effects. Turbulent kinetic energy in the water column is dissipated more rapidly in shallower, more protected inshore areas than in the open sea, so phytoplankton blooms are induced earlier and faster in the coastal ocean, especially in bays and bights (Smetacek and Passow, 1990). Large fluxes of macronutrients transported horizontally across the continental slope and shelf break and into the coastal ocean (Chapter 9) and from terrestrial and anthropogenic sources (Table 9.1) as well as vertical inputs from underlying sediments support high production rates in coastal ocean waters. The flux of nutrients from the oceanic boundary is poorly known and difficult to characterize but certainly dominates as a source of N and P to the coastal ocean (Wollast, 1998). Supply of micronutrients (e.g., iron) is also generally greater due to the proximity of terrestrial dust sources, sediments (Johnson et al., 1999) and anthropogenic inputs. The combined effects of enhanced turbulence and greater nutrient supply interact with the physiological requirements of phytoplankton, leading to predictable dominance (blooms) of larger-celled organisms (Malone, 1971; Margalef, 1978; Cullen and MacIntyre, 1998). Smaller-celled phytoplankton constitute a more uniform background flora (Redalje et al., 2002). In general, coastal ocean systems fall under Cullen et al's (2002) high-turbulence, high-nutrient category and are characterized by high production of large phytoplankton forms (diameter > ~10 μm including diatoms, dinoflagellates and prymnesiophytes – mainly *Phaeocystis*). In spite of this generalization, it is also important to recognize that higher nutrient inputs, though favoring the larger-celled flora, also stimulate growth of the small-celled 'background' plankton, which are dominated by coccoid cyanobacteria and nanoplankton (Malone et al., 1991). Coastal ocean systems have higher stocks and production of both large and small phytoplankton, compared to the open sea, as revealed by ocean color images. Higher biomass and a greater proportion of larger (more rapidly sinking) forms generally means that the vertical transport of surface production to depth will be more efficient. That is, the ratio of sedimentation to primary production will be greater in nearshore and coastal seas than in the ocean. The magnitude of lateral export (i.e., the continental shelf pump in Figure 9.1) will be examined further below, after a synthesis of recent estimates of PP in the global coastal ocean.

Early estimates of net primary production (NPP) over continental shelves were reviewed by Walsh (1988) and Smith and Hollibaugh (1993). These reviews indicated that NPP averaged 160 gC m^{-2} y^{-1} (13 Mol C m^{-2} y^{-1}; range for global shelf regions 60 – 600 mgC m^{-2} y^{-1}). The magnitude of primary production in continental shelf and other marine systems is summarized in Tables 9.2 and 9.3. Gattuso et al. (1998) compiled recent data from those studies which considered both gross primary production (GPP) and community respiration (R)[2]. Areal rates of gross primary production in the coastal ocean are high and comparable to those measured in estuaries (18 vs 22 Mol C m^{-2} yr^{-1}). The coastal ocean, with just 6% of the marine surface area, contributes 10% of the gross primary production but 33% of the global net ecosystem production (NEP = GPP-R), according to Gattuso et al.'s compilation (Table 9.2). The NEP is approximately equivalent to the new production (Dugdale and Goering, 1967) or export production (Ducklow et al., 2001) supported by external inputs of new (allochthonous) nutrients. An independent set of estimates confirms the disproportionate share of net primary production contributed by coastal ocean systems. Longhurst et al. (1995) derived regional estimates of NPP for 57 coastal and oceanic ecological provinces using remotely sensed sea surface color observations, from which global estimates were extrapolated (Table 9.3). In their analysis, the Coastal domain, including Arctic and Antarctic marginal ice zones and covering 11% of the global ocean surface, contributed 29% of the total marine NPP. The discrepancy between the two sets of estimates derives from Longhurst et al.'s large estimate of 32.1 mol C m^{-2} y^{-1} for *net* primary production in the Coastal Domain. This value is about twice as large as Gattuso et al.'s *gross* primary production estimate of 17.4 mol C m^{-2} y^{-1}. Longhurst's estimate includes the upwelling provinces with the coastal ocean domain, whereas those areas are in the open ocean category in Table 9.2. NPP and NEP cannot be easily compared, further complicating the comparison, but it seems clear that coastal ocean systems contribute a disproportionate share of the global marine planktonic production. This raises the question of their importance as potential sinks for atmospheric carbon dioxide.

The nutrient demand from external sources supporting NPP in the coastal ocean can be estimated by considering the amount of NPP that sinks or is advected out of the photic zone. This quantity is the export flux and it is equivalent to the new production over sufficiently large time and space scales, i.e. near steady state (Eppley and Peterson, 1979). Leaving aside the question as to whether the global coastal ocean can be so considered, the export or E-ratio (export divided by NPP) gives a rough estimate of the proportion of the net primary production supported by externally supplied nutrients. In Wollast's (1998) summary, the export flux over the continental shelves was given as 13.3 Mol C m^{-2} y^{-1} (70% of his NPP estimate of 19.2 Mol C m^{-2} y^{-1}), in contrast to 1.3 Mol C m^{-2} y^{-1} (15% of the NPP) in the open sea. The magnitude of NPP and export quoted by Wollast (1993) are both high, relative to other sources discussed here (see also following section), and an export ratio of 50% is more consistent with most recent analyses (e.g. Walsh 1991). Thus the input of land and oceanic nutrients to coastal ocean could support ~50% of the total NPP, with the remaining 50% sustained by *in situ* nutrient regeneration. The total P input from land (Table 9.1) can be used to estimate an upper limit to the amount of new production supported by terrestrial nutrient sources. Assuming that all the riverine dissolved phosphorus input is regenerated and becomes available

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[2] Gross primary production (GPP) is the total carbon fixed in photosynthesis, including that portion subsequently respired during algal cellular metabolism. GPP minus the phytoplankton respiration is the net primary production available to consumers. Community respiration, R, is the sum total of respiratory activity carried out by phytoplankton plus all consumers and microbes. The amount of organic matter remaining after GPP-R is the net ecosystem production.

for phytoplankton uptake over the shelf, then multiplying by the Redfield C:P ratio (106) gives an upper bound of ~7 Tmol C y^{-1} for terrestrially-derived, P-limited NPP. The NPP supported by phosphorus input from land is a small fraction of the total NPP (7/1195, cf. Table 9.3), but is about 22% of the terrestrial input of organic matter (7/31 from Table 9.1). Accordingly, most of the new production in the coastal ocean must be sustained by onshore transport of nutrients from the open sea. The latter input must be large. Possibly 21 Tmol N y^{-1} is denitrified in shelf and slope regions (Codispoti et al., 2001). Just to balance the nitrogen budget for the coastal ocean, and assuming no losses (certainly not true), the N input from the ocean must exceed the river input by a factor of 5.

Regeneration and utilization of the terrestrial C and N (particulate and dissolved) associated with phosphorus uptake during photosynthesis leaves behind ~90% of the C and ~40% of the N supplied in excess of the Redfield ratios. These unutilized nutrients are available for export into the open sea (Hydes et al., 2001). Although it may be relatively small, the terrestrial input plays a large role in setting the sign of the metabolic balance because the P:R of these ecosystems is so finely poised (Table 9.2).

TABLE 9.2.
Areal extent and primary production rates in marine systems
(after Gattuso et al., 1998).

System	**Surface area 10^6 km^2**	**GPP Mol C m^{-2} yr^{-1}**	**GPP Tmol C yr^{-1}**	**NEP Tmol C yr^{-1}**	**GPP:R**[1]
Estuaries	1.4	22	31	-8	0.8±0.05
Saltmarshes	0.4	206	83	82	1.0
Other margins[3]	3.2	119	381	68	1.2±0.06
Shelves	21.4	18	377	171	1.3±0.3
Inner Shelvesand bays	10	23	230	-36	0.9±0.9
Total Margin[4]	26	31	789	231	1.2±0.05
Open ocean[5]	334	10	3396	340[6]	1.11

[1] recalculated from data available at www.annualreviews.org/supmat/ using a reduced major axis (Model II) regression. The slope of the GPP vs R regression is the GPP:R ratio. GPP, gross primary production; NEP, net ecosystem production (net community production, analogous to export production).

[2] as summarized in Smith and Hollibaugh (1993) and included for comparison (area taken to be -0.3 of total for shelves).

[3] mangroves, macroalgae, seagrasses, coral reefs.

[4] Total margin = estuaries + other margins + shelves as reported in Gattuso et al. 1998.

[5] In this compilation high productivity zones over the continental slope and rise, including major upwelling regimes are included in the open ocean category.

[6] derived from Williams' (2000) GPP:R estimates for the eastern North Atlantic and Southern Oceans, Mediterranean and Arabian Seas and North Pacific Subtropical Gyre and Gattuso et al.'s GPP value.

TABLE 9.3.

Recent estimates of primary production over continental shelves and the open sea.

	Gattuso GPP and NEP[1]					Longhurst NPP[2]				
Region	**Area**	**GPP**	**GPP**	**NEP**	**GPP**	**Area**	**NPP**			
	10^6 km^2	**mol $C/m^2 y^{-1}$**	**Tmol C yr^{-1}**	**Tmol C yr^{-1}**	**%[3]**	**10^6 km^2**	**GtC yr^{-1}**	**mol C/m^2 y^{-1}**	**Tmol C y^{-1}**	**%[3]**
Cont Shelf	21.4	17.6	377	171	10	37.4	14.4	32.1	1195	29
Total Margin	26	30.3	789	231	21	--	--	--	--	--
Open Ocean	334	10.2	3396	340	90	291	35.7	10.2	2963	71
Total Shelf + Open	355	10.6	3773	511	100	328	50.1	12.7	4158	100

[1] after Gattuso et al (1998). "Total margin" includes estuaries, continental shelves, coral reefs, mangrove, saltmarshes and macrophyte-dominated coastal systems. GPP, gross primary production; NEP, net ecosystem production (net community production, analogous to export production). See also Table 1. Gattuso's shelf domain excludes upwelling zones over slope and rise.

[2] after Longhurst et al. (1995). Cont. shelf is Longhurst's Coastal Domain and includes upwelling zones over slope and rise. Open ocean includes his Polar, Westerlies and Trade Winds domains. NPP, Net primary production.

[3] % of global total GPP in region.

5. Export production: what is the fate of organic carbon in the global coastal ocean?

Atmospheric CO_2 absorbed by coastal ocean processes will only enter long-term storage if it is transported laterally offshore to the ocean interior. Vertical export from the euphotic zone consists of large, rapidly sinking particles (Alldredge and Silver, 1988) or exportable DOC mixed or advected away by physical processes (Hansell and Carlson, 2001). Greater stocks of larger phytoplankton in the coastal oceans lead in turn to larger consumers and faster particle sedimentation rates, and thus more efficient vertical export by sinking from the surface layer. In the open sea, the export flux is usually considered in a one-dimensional (vertical) context, since lateral transfers between regions have not been addressed. But the issue of lateral export pathways is critical for understanding fluxes between the coastal and open ocean (continental shelf pump in Figure 9.1). Some of the primary production over the continental shelf, slope and rise settles directly to the bottom, where it is oxidized or buried, and some is transported laterally across the coastal ocean boundary into the open sea where it may sink into deep water. Walsh (1991) calculated that the coastal ocean contributed 50% of the total oceanic particle flux at a depth of 2650 m as a consequence of this transport process. Wollast (1998) estimated that about half the total production exported vertically from the surface layer was subsequently transported laterally off the shelf, with the rest being respired or buried in the shelf sediments. Liu (2000a) estimated that just 5% of the export production was buried in shelf sediments, with the remainder (2.7 PgC yr^{-1}) entering the ocean interior. Here, we use the term *shelf export* to indicate the lateral export from the global coastal ocean into the ocean interior.

Shelf export is controlled by a complex combination of circulation and transport processes that have seldom been resolved at the appropriate time and space scales to allow precise estimates or budgets. These processes were first studied in the Shelf-Edge Exchange Processes (SEEP) studies, during which sediment traps and moored observing systems were deployed over the NE US continental shelf (Biscaye et al., 1988; Biscaye et al., 1994). The export process is apparently highly episodic (Churchill et al., 1994). Adequate resolution requires arrays of high frequency current meters and transmissometers to monitor particle transport during wind events and the resulting upwelling circulation (Walsh et al., 1988) as well as cruise-based studies of isotopic tracers (Bacon et al., 1988) and biomarkers of specific organic source materials (Venkatesan et al., 1988). Cross-shelf sediment trap arrays deployed normal to the alongshore axis of the shelf revealed that near-bottom particle transport in the Ekman layer resulted in enhancement of settling rates at intermediate depths along the shelf-slope region (Biscaye et al., 1988). In the Middle Atlantic Bight off the NE USA, export is driven by Ekman transport and the repeated settling and resuspension of particles derived from the spring phytoplankton bloom. Particles deposited on the seafloor over the shelf are resuspended and transported seaward, eventually reaching depocenters on the continental slope or rise (Biscaye and Anderson, 1994).

Coastal jets and filaments (Chapter 9) may transport both particulate and dissolved organic matter organic matter from shelves into the surface layer of the open ocean. A filament associated with the Gulf Stream transported 0.3 – 2.6 Tmol of riverine DOC and 'new' DOC produced *in situ* from the northeast US continental shelf/slope into the Gulf Stream (Bates and Hansell, 1999; Vlahos et al., 2002). An upwelling filament from the NW Iberian peninsula exports a total of 0.03 Tmol C yr^{-1} into the NE Atlantic Ocean, equally divided between POC and DOC (Alvarez-Salgado, 2001ab). There is great variability in these estimates, and few filaments have been studied, but their importance as mechanisms of coastal export into the surface layer of the open sea demands further attention. The upper end of this range of export estimates suggests a potentially large role for this mode of carbon export (see below).

The magnitude of offshelf transport and storage was unknown until the past decade. The initial debate on this question (Rowe et al., 1986; Walsh, 1989) directly inspired the SEEP Program off the US east coast, and subsequently influenced the Kuroshio Edge Exchange Processes (KEEP; Wong et al. 2000), Ocean Margin Exchange (OMEX, Wollast and Chou 2001) and Gulf of St. Lawrence, Canada (Roy et al., 2000) programs and other studies. A primary aim of all these studies was to quantify the magnitude of export to the ocean interior of organic matter produced over continental shelves. SEEP set out explicitly to test the hypothesis that export from the shelf to the ocean interior was large in relation to *in situ* NPP. Although the complexities of shelf circulation processes, resuspension and near-bottom transport, seasonal variability and sediment trapping make it very challenging to get a definitive answer, it does not appear that the majority of the coastal ocean regions studied to date are intensive export regions, relative to *in situ* NPP, or in an absolute sense (Biscaye and Anderson, 1994; Antia et al., 2001). In particular, lateral export of phytoplankton was just 5% of PP in the area north of Cape Hatteras in the Middle Atlantic Bight (Falkowski et al., 1994). As Boehme et al. (1998) observed for the Middle Atlantic Bight, USA, the 1 Mt of annual net uptake of atmospheric CO_2 represented only a few percent of the annual NPP, suggesting little net export of organic matter from this system.

However not all shelf systems behave similarly. De Haas et al. (2002) reviewed sedimentation and burial budgets for shelf systems worldwide, but only a few have estimates of export to the ocean. More than 90% of the primary production (150 Mt) on the Amazon Shelf (strongly light limited by turbidity in the outflow of the Amazon River) is oxidized in the water column (Aller et al., 1996), but only 50% of the organic matter in the annual river discharge (50 Mt) is buried locally (de Haas et al., 2002). Thus the offshelf flux might be about 40 Mt, equivalent to about 25% of the local PP. 16% of the terrigenous organic carbon entering the Beaufort Shelf in the Canadian Arctic is exported offshelf (Macdonald et al., 1998). 48% of the primary production on the outer shelf in the Bering Sea is exported (Walsh and McRoy, 1986). Organic particle export from the East China Sea off Taiwan may be more important than the other regions studied (Chung and Hung, 2000). There, a cyclonic eddy served as an efficient transport mechanism, moving material offshore into canyons, then to the ocean interior via the Okinawa Trough (Wong et al., 2000). But elsewhere, in areas lacking special circulation and bottom topography, most material produced over the shelves appears to be oxidized and recycled *in situ* (Falkowski et al., 1988; Vezina et al., 2000; Soetaert et al., 2001).

Most of the shelf systems noted above are broad shelves where much of the export production might be expected to be respired; thus the lateral export might be a lower fraction of the total exportable production. Coastal ocean systems at the continental boundary of narrow shelves such as the Peru/Chile upwelling system might be expected to export more material. Walsh's (1981) budget for the Peru system implied that only 8% of the total production was buried or exported before overfishing but almost 60% met that fate after the collapse of the anchovy fishery. As a result of such regional, temporal and anthropogenic effects, estimates of the global shelf export vary by an order of magnitude. Walsh's (1991) estimate of 1 GtC yr^{-1} (83 Tmol C yr^{-1}) was derived from a variety of sediment trap, current meter array and geochemical tracer studies. Smith and Hollibaugh (1993) considered only organic matter of terrestrial origin that drives net heterotrophy in the coastal ocean in their budget. They estimated that about half the riverine input, or 18 Tmol C yr^{-1} was exported to the open sea. This estimate neglects organic matter derived from *in situ* new production supported by offshore nutrient inputs (Chapter 9). Wollast (1998), considering the SEEP and OMEX programs in the North Atlantic, derived an estimate of 183 Tmol (2.2 GtC) yr^{-1}. Liu et al's. (2000a) recent reanalysis included a pass-through of 29 Tmol C of riverine input in their estimate of 225 Tmol C yr^{-1}, so is not much different from the Wollast figure. Thus roughly 100–200 Tmol C yr^{-1} of a total annual NPP of 1200 Tmol (8–16%) is exported into the ocean interior by the continental shelf CO_2 pump. This export flux is equivalent to the 158 Tmol of carbon entering the coastal ocean from the net air-sea exchange (75 Tmol; see Table 9.5 below) and the riverine input (83 Tmol). In essence the coastal ocean ecosystem exports its exogenous inputs to the open sea.

6. The metabolic status of coastal and open ocean systems: autotrophic or heterotrophic?

In the rather small data set considered by Gattuso et al. (1998; for continental shelves, n = only 10 from 7 sources), the continental shelves have a positive metabolic balance, producing slightly more carbon than they respire (net ecosystem production, NEP = GPP-R = +68 Tmol C yr^{-1} globally). In contrast estuaries receive large external inputs of organic matter (Hopkinson and Vallino, 1995) and respire more carbon than they produce internally (Kemp et al., 1997; Raymond et al., 2000). Estuarine NEP was -8 Tmol C yr^{-1} globally in Gattuso et al's. dataset. Earlier data compiled by Smith and Hollibaugh (1993) showed that inner continental shelves, bays and marginal seas also had a negative metabolic balance (Table 9.2). In Chapter 8, Ver and Mackenzie estimate that the coastal ocean is net heterotrophic, with NEP = -20 Tmol C yr^{-1}. In Section 8 below, we conclude that the coastal ocean, including offshore zones of coastal upwelling on the slope and rise, is net autotrophic by 175 Tmol C yr^{-1}.

The impact of organic matter additions appears to vary with distance from land, as one would expect. Wollast (1998) characterized inner shelves as slightly net heterotrophic (i.e., P<R), but concluded that outer shelves tended toward autotrophy (P>R). Gattuso et al.'s (1998) synthesis is consistent with that scheme, with only estuaries having P<R (Table 9.1). Earlier, Garside et al's (1976) analysis suggested that primary production supported by sewage-derived nutrients dominated over respiration of sewage organic matter and extended well offshore in the New York Bight. A catastrophic anoxic event in the same area was the result of sinking

and decay of a phytoplankton bloom, not oxidation of sewage organic matter (Falkowski et al., 1980). Boehme et al.'s (1998) recent model analysis showed that the effect of organic matter decomposition on $p\mathrm{CO}_2$ decreased offshore on the New Jersey shelf, with the largest effect and greatest variability of organic matter influence near the 10-meter isobath.

That nearshore ecosystems would have negative metabolic balance is not at all surprising. Since P:R in most plankton systems is so close to 1 (Table 9.2), organic matter inputs likely render these systems net heterotrophic. Kemp et al. (1997) and Hopkinson and Vallino (1995) concluded that the metabolic balance in estuaries and the nearby coastal zone was dependent on the ratio of inputs of dissolved inorganic nitrogen to labile organic matter, a point also demonstrated by Garside et al. (1976). With increased eutrophication, net ecosystem metabolism could shift toward positive or more negative values, depending on the composition of the input (see Chapters 8, 10, 23). Shifts in either direction would have consequences for the efficiency of the coastal oceans as CO_2 sinks.

But what is surprising is that some offshore regions, including the oligotrophic ocean surface layer have also been characterized as net heterotrophic. del Giorgio et al. (1997) compiled data on bacterial respiration (BR) and NPP from oceanic, coastal, estuarine and lake systems and showed that bacterial respiration exceeded the NPP when NPP was below about 100 μgC l^{-1} d^{-1}. This is a typical value for surface waters in coastal regions and oceanic phytoplankton blooms, comprising about 30% of the global ocean. Subsequently Hoppe et al. (2002), using similar measurements, suggested that bacterial metabolism exceeded NPP over large areas of the tropical Atlantic. Since bacterial metabolism is supported by preformed organic matter, bacterial respiration can only exceed NPP if there are external subsidies or organic matter. The startling conclusion from this analysis is that most oceanic systems, remote from obvious sources of organic matter input, have negative net ecosystem metabolism (P:R < 1). Indeed, Duarte and Agusti (1998) concluded on the basis of a direct comparison of NPP and R in many data sets, that about 80% of the global ocean surface area was heterotrophic. del Giorgio et al's (1997) finding was based on an indirect comparison of independent estimates of NPP and BR, and BR estimates themselves are usually derived from other measurements (del Giorgio and Cole, 1998). Thus this conclusion was criticized and remains controversial (Geider, 1997). NPP and R however, are both based on measurements of oxygen in the same bottles, so the conclusions of Duarte and Agusti (1998) are on firmer technical ground. Even so, their conclusions as well as the del Giorgio et al paper were disputed by Williams and Bowers (1999), referring to (Williams, 1998)'s reanalysis of the NPP:R data, concluding that "…open oceans as a whole are not substantially out of organic carbon balance. There is no evidence of the large regional imbalances observed previously." Williams and Bowers' (1999) statistical analysis was questioned by Duarte et al. (1999) who stated that their conclusions about oligotrophic regions were improperly extrapolated from more productive areas. The debate remains unresolved.

One implication of possible net heterotrophy in open ocean basins is that there must be an import flux of labile organic matter to subsidize the excess respiration. The only two likely possibilities are a vertical flux from deep water or a lateral flux from the coastal ocean. Inputs of labile DOC from atmospheric deposition are poorly known but have been estimated to average less than 58 μmolC m^{-2} d^{-1} (Willey et al. 2002), insufficient to support the necessary level of respiration alone. There is a large reservoir of DOC in the deep ocean that could support heterotrophic metabolism in the surface layer, but it has a mean age of several 1000 years and is generally believed to be highly resistant to biological decomposition (Bauer et al., 1992). However some of this DOC may be rendered more biochemically labile by exposure to ultraviolet radiation when it reenters the surface layer in the thermohaline overturning (Anderson and Williams, 1999). A large supply of labile organic carbon via lateral exchange processes is not a much more likely possibility. The existing data show that the concentration gradients in DOC extending from the ocean margins into the central gyres are not sufficiently steep to support the necessary flux. Williams and Bowers (1999) estimated that the carbon subsidy needed to support the level of net heterotrophy in the open ocean *surface layer* proposed by Duarte and Agusti (1998) amounted to 500 Tmol C y^{-1}. This is over twice the amount supplied by the continental shelf pump (Section 5). Thus shelf export seems insufficient to support large oceanic heterotrophy. Moreover, the shelf export is supplied predominantly at a depth of several 100 meters, not at the surface. In Section 8 we conclude that the open ocean *over the entire water* column is heterotrophic by just 200 Tmol C y^{-1}, less than half what Duarte and Agusti attribute to the surface layer alone. The question of net heterotrophic metabolism in the oceanic euphotic zone remains tantalizing but unresolved, and presents a challenge demanding a better understanding of carbon exchanges between the coastal and open ocean.

7. The carbon balance in the coastal ocean: Is it a sink for atmospheric CO_2?

The chemistry of CO_2 in seawater has now been studied for over 70 years (Buch et al., 1932; Greenberg et al., 1932). Yet in spite of its great biogeochemical reactivity, relatively little is known about the CO_2 balance in the coastal ocean. The state of understanding stands in stark contrast to that of the open ocean, where nearly a million discrete measurements of the partial gas pressure of CO_2 exerted in surface water ($p\mathrm{CO}_2$) have been made since the International Geophysical Year of 1956–59 (Takahashi et al., 2002).

The global ocean is a sink for 1.9–2.2 Pg atmospheric C annually (Houghton et al., 2001; Sarmiento and Gruber, 2002), as estimated from CO_2 (Takahashi et al. 2002) and O_2 measurements (Keeling and Shertz, 1992; Bender et al., 1998), global circulation models (Sarmiento et al., 1992; Murnane et al., 1997) and changes in atmospheric and oceanic $\delta^{13}C$ (Quay et al., 1992). The global (open) ocean is a contemporary sink because of the anthropogenic increase in atmospheric CO_2 since the 18th century, which increased the difference between sea and air $p\mathrm{CO}_2$ ($\Delta p\mathrm{CO}_2$) from near equilibrium ($\Delta p\mathrm{CO}_2$ • 0) to its current global mean value of –4 μatm at a mean atmospheric $p\mathrm{CO}_2$ of 360–370 ppm (Takahashi et al. 2002). This anthropogenically-forced gas pressure opposes the potential biogenic flux of CO_2 out of the ocean (Section 6). The preindustrial ocean as a whole is believed to have been a slight source of CO_2 to the atmosphere (0.2–0.4 PgC y^{-1}), partially balancing carbon inputs of 0.8 PgC from the land (Figure 9.1; Smith and Mackenzie 1987; Sarmiento and Sundquist 1992 and Mackenzie et al., Chapter 7 in this volume).

Surprisingly however, the contemporary source/sink identity of the coastal oceans is unresolved (Kempe, 1995). Yet there has been a large amount of new research on CO_2 exchange and pCO_2 variability in the coastal ocean. Here we provide a comprehensive, critical review of the CO_2 balance of the global coastal ocean, concluding it is likely a strong sink for atmospheric CO_2. This identity may change in the next century (Chapter 8).

7.1 Controls on pCO₂ in the coastal oceans.

Unlike other dissolved gases (especially oxygen), the ocean is the major global reservoir for CO_2 due to the action of the carbonate buffering system in seawater (Figure 9.3). Dissolved CO_2 undergoes reaction with seawater to form carbonic acid, H_2CO_3, which dissociates into the bicarbonate and carbonate ions, HCO_3^- and CO_3^{2-}. At high pH the chemical reactions in Figure 9.3 are forced to the right, so that at the average seawater pH of 8.2, over 95% of the dissolved inorganic carbon (DIC) is in the form of bicarbonate and less than 1% is dissolved CO_2 (Butler, 1982). Of every mole of CO_2 which enters the ocean, most becomes bicarbonate, explaining the huge capacity of the ocean to take up atmospheric CO_2. When the dissolved CO_2 is near equilibrium with the atmosphere (currently ~370 µatm or ~ 15 µM), there is about 2000 µM total DIC in the seawater, and 50 times more DIC in the ocean than CO_2 in the atmosphere (Feely et al., 2001). However if dissolved CO_2 were the only form used by phytoplankton (see below), about 15 µM, rather than 2000 µM of DIC would be directly available for photosynthesis (Riebesell et al., 1993).

pCO_2 in the coastal ocean is controlled by a complex array of climatic, physical and biological factors (Boehme et al., 1998). CO_2 solubility increases inversely with temperature; thus for a fixed concentration of CO_2, the resulting pCO_2 will *increase* as the temperature rises. It would increase by a factor of about 4 over the polar to equator temperature gradient (-1.9 to 30 ﬂC), in the absence of other processes. Proximity to land adds a number of factors important for determining coastal ocean (though not necessarily open ocean) pCO_2, including river outflows, groundwater and rain inputs of dissolved CO_2 gas, and inputs of both dissolved and particulate organic and inorganic carbon from land. Rivers are generally highly supersaturated in dissolved CO_2 (Frankignoulle et al., 1998; Raymond et al., 2000), adding CO_2 to the inner shelf and extending the range of pCO_2 variability compared to the open sea. Several processes transport oceanic properties onto shelves. Coastal upwelling, exchanges mediated by filaments, jets and rings and other frontal exchange processes all directly affect the carbon balance and pCO_2, by bringing onto the shelf higher DIC from greater depths (Huthnance, 1995; Wollast, 1998). Many of these physical processes are still poorly understood (Brink, 2002). Inputs of upwelled DIC have the direct effect of raising shelf pCO_2 (see below). Terrestrial inputs of N and P indirectly affect pCO_2 by providing a source of new nutrients for photosynthesis, which draws down the pCO_2.

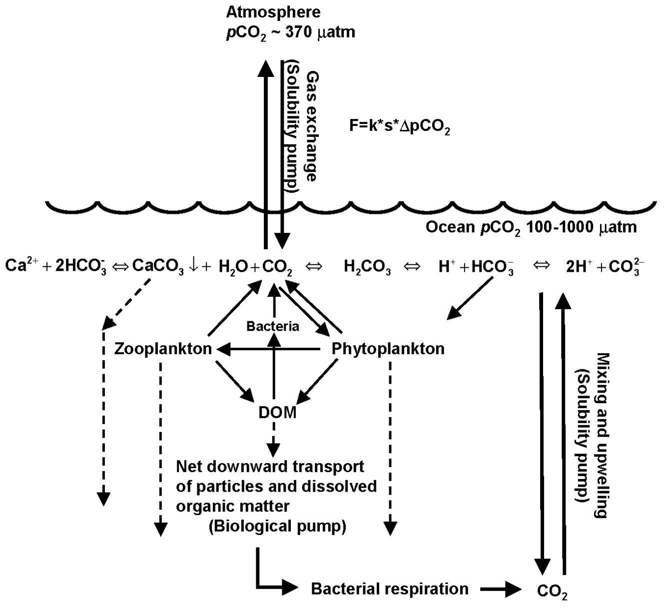

Figure 9.3 Carbon transformations and transport in the ocean water column. See text for details. The biological pump transports organic carbon into the deep sea against the vertical gradient of dissolved inorganic carbon. The solubility pump governs the air-sea exchange and is controlled by physico-chemical processes, principally temperature and wind stress. About 95% of the total DIC is seawater is in the form of bicarbonate, , explaining the enormous capacity of the ocean to store atmospheric CO2. Biogenic formation of calcium carbonate produces one molecule of CO2 for each molecule of carbonate. The carbonate shells sink, contributing the biological pump (hard tissue pump).

Exchange of CO_2 across the atmosphere-ocean interface is a purely physical process. The air-sea flux, *F,* depends on the ΔpCO_2, the solubility of aqueous CO_2 (*s,* a function of temperature and salinity), and the gas transfer coefficient (*k,* a nonlinear function of wind speed):

$$F = k \bullet s \bullet \Delta pCO_2 \qquad (1)$$

(Feely et al., 2001). pCO_2 varies seasonally and geographically by ±20 μatm in the atmosphere (±5%) but by almost a factor of 10, from ~90 to 900 in the coastal ocean (see below). Therefore, ΔpCO_2 is primarily driven by changes in pCO_2 in seawater. The seawater pCO_2 is a function of temperature, DIC concentration and alkalinity. The DIC concentration is a function of the balance between photosynthesis and respiration, and alkalinity is primarily controlled by precipitation and dissolution of calcium carbonate. As ocean currents move from lower toward higher latitudes, or as seawater cools seasonally, CO_2 solubility increases, the pCO_2 declines, and Δ pCO_2 increases, causing atmospheric CO_2 to be driven into the water. Conversely, as cold, deep water rises to the surface and warms, CO_2 degasses to the atmosphere. Since deep waters contain high concentrations of CO_2 as a residue of the action of the **biological pump** (Figure 9.3), coastal upwelling may constitute a powerful source of atmospheric CO_2 (Feely et al., 1999). These temperature-driven processes of CO_2 exchange form the **solubility pump** for atmospheric CO_2 (Figure 9.3). Because most upwelling occurs in low altitudes, these regions tend to be CO_2 source areas, whereas high latitudes are sink regions of CO_2 uptake (Takahashi et al., 2002).

7.2. CO_2 uptake by phytoplankton and the biological pump.

A vertically uniform distribution of DIC in a sterile ocean would yield a vertical profile of pCO_2 (ignoring pressure effects) that was slightly higher at the surface and lower at depth as a result of temperature stratification. However DIC and pCO_2 both *increase* with depth as a result of biological processes. Phytoplankton take up inorganic carbon during photosynthesis in the light by transporting either dissolved CO_2 or bicarbonate ion across the cell membrane prior to fixation with the enzyme ribulose-1,5-biphosphate carboxylase/oxygenase (Rubisco; Falkowski and Raven 1997). There is evidence supporting passage of carbonate ion into cells as well (Raven, 1997), but the primary form taken up is generally believed to be dissolved CO_2 (Steeman Nielsen, 1947; Riebesell and Wolf-Gladrow, 2002) and this is the form usually represented in models of the ocean carbon cycle (Antoine and Morel, 1995). The biological processes can be faster than abiotic dehydration of bicarbonate to form CO_2 as this latter reaction is biologically catalyzed by the enzyme carbonic anhydrase (Falkowski and Raven 1997), making the large pool of bicarbonate (~1800 μM) potentially available for uptake. The relative importance of CO_2 and HCO_3^- in uptake processes varies among phytoplankton taxa and is still not well understood or quantified in nature (Tortell et al., 2000; Riebesell and Wolf-Gladrow, 2002). The competitive advantage of bicarbonate acquisition is obvious, as it affords access to a carbon pool 2 orders of magnitude larger than the dissolved CO_2 pool. It is also possible that in coastal regions where pCO_2 declines to below 100 ppm (8 μM), cells using only CO_2 could become carbon limited. However the net result in either case is lowering of the ambient pCO_2 during photosynthesis. pCO_2 drawdown occurs because the timescale for equilibration of CO_2 in the mixed layer with the atmosphere is about one year, much slower than the biological processes.

Photosynthetic removal of DIC and drawdown of pCO_2 forms part of the mechanism of the biological pump for atmospheric CO_2 (Ducklow et al., 2001). The other components include biological consumption and respiration processes, and downward transport of organic matter via gravitational sedimentation and advection (Longhurst and Harrison, 1989). Phytoplankton respire organic carbon back into CO_2, and so do zooplankton and bacteria following consumption (Figure 9.3). The net balance of production (CO_2 uptake) and respiration (CO_2 release) processes influence the sign of pCO_2 change in the water column. In the lower part of the water column below the euphotic zone, respiration is the dominant biological process affecting pCO_2. Biotransformations of calcium carbonate and chemolithotrophic bacterial processes (e.g., nitrification) also affect pCO_2. Direct uptake of DIC by chemosynthetic bacteria is minor in significance compared to the large amount of heterotrophic respiration (del Giorgio and Duarte, 2002). Thus the net effect of the biological pump is to remove CO_2 from the surface in the form of organic matter, transport it to depth, and respire it back into DIC. The resulting vertical profiles of DIC and pCO_2 increase from the surface to the bottom. A third CO_2 pump unique to the coastal ocean, the *continental shelf pump,* is discussed below.

7.3. Influence of terrestrial inputs.

pCO_2 is also inextricably linked to the inputs and cycling of N, P, S and organic matter through both land and ocean metabolism as described previously (Smith and Hollibaugh, 1993; Ver et al., 1999), and therefore depends on the regional as well as local carbon balance. Primary production is supported by inputs N, P and micronutrients like iron in river runoff. Intense primary production during spring and summer blooms or associated with wind-driven coastal upwelling can counteract the effect of warming, and produce large seasonal decreases in pCO_2 (Codispoti et al., 1982; DeGrandpre et al., 2002). N and P inputs from land and sea are accompanied by DIC, and so there will only be a net input of DIC if it is supplied in excess of the Redfield ratio (Table 9.1). The excess DIC may be released into the atmosphere (source) or exported via offshore transport. Conversely, if inorganic inputs are N- or P-rich, the subsequent primary production will draw CO_2 from the atmosphere and serve as a sink for atmospheric CO_2. This reasoning led Walsh et al. (1981) to postulate that coastal eutrophication could be part of the missing sink in the global carbon budget.

Organic matter loadings from the land also influence the carbon balance in the coastal ocean and thus affects its source/sink characteristics. Dissolved (Raymond and Bauer, 2001) and particulate organic matter exported from rivers (Wollast 1998) result in net additions of CO_2 to the coastal ocean if they are decomposed there, raising pCO_2 levels and increasing the potential for release to the atmosphere. The extent of organic matter contributions to local carbon balance depends on the biochemical lability of imported compounds (Section 3) and their residence times in coastal ocean waters. Residence times in rivers are relatively short, indicating that they may export fresh (labile) organic constituents into the coastal ocean, but estuaries have extended residence times and serve as filters and traps for organic matter exported from land or produced *in situ* (Hedges et al., 1997). Smith and Hollibaugh (1997) estimated that 34 ± 10 teramoles (0.4 Gt) C yr^{-1} are transported from land by rivers, of which 11 ± 6 is buried in estuaries, marshes and deltas, leaving 23 ± 12 Tmol in the water column of the coastal ocean. They further estimated that 5–15 Tmol of that is labile on short time scales (< 1 yr). It is this fraction that is apparently oxidized and respired in the coastal ocean, compensating to a varying extent for the pCO_2 drawdown during photosynthesis and cooling. Boehme et al. (1998) provided a detailed analysis of the factors influencing pCO_2 variations in the coastal ocean off New Jersey, USA, using data taken during monthly cross-shelf transects collected over two years. In their analysis, the separate contributions of heating, organic matter production and decomposition, precipitation inputs, carbonate production and dissolution, air-sea exchange and mixing to temporal changes in pCO_2 were assessed by calculating pCO_2 from DIC and alkalinity using the thermodynamic equations for the carbonate system and varying each parameter value in turn (Sabine and Key, 1998). They found that temperature and organic matter production/decomposition had the largest effects on $p\mathrm{CO}_2$, with air-sea exchange and mixing making somewhat smaller contributions. In general effects were larger at inshore stations and smaller offshore, reflecting the decreased variability offshore. The effects of some factors were not symmetrical: changes in photosynthesis and respiration tended to raise $p\mathrm{CO}_2$ rather than lower it, pointing out the importance of upwelled remineralized carbon to surface waters (Figures 9.4, 9.5). Further, the effects of some factors were counterbalanced: in some seasons, some factors had the effect of raising $p\mathrm{CO}_2$ while others lowered it, leaving no net change (Figure 9.4). Differences between observations and model predictions were ascribed to mixing of water masses with unspecified characteristics. This analysis is the most comprehensive attempt to date at dissecting the interplay of physical and biological factors on coastal $p\mathrm{CO}_2$ variability. Boehme et al.'s results show that time series of coastal $p\mathrm{CO}_2$ can be accurately reproduced with just a few parameters, indicating an improved fundamental understanding of how this variability is regulated at local to regional scales.

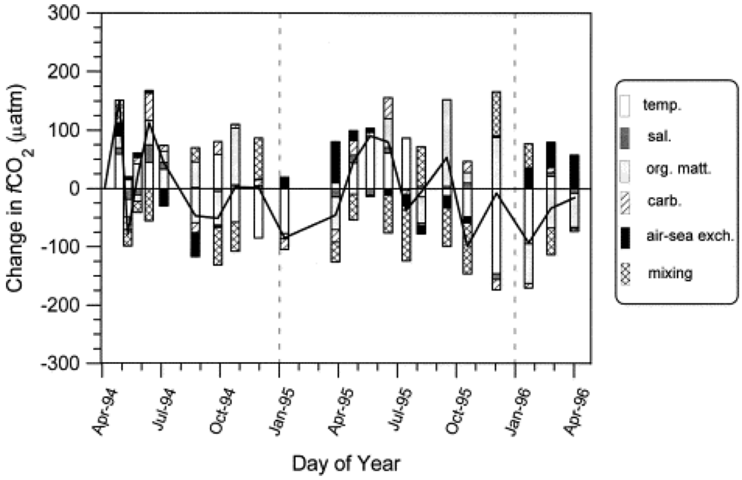

Figure 9.4 Effects of various factors on temporal variations in coastal ocean pCO2 (Figure courtesy Boehme et al. (1998).

7.4 *Survey of $p\mathrm{CO}_2$ in the coastal oceans.*

The relative importance of these factors varies in different regions producing cycles in $p\mathrm{CO}_2$ that are just beginning to be characterized. Here we provide a first attempt at such a characterization, following Longhurst's (1995) province-based scheme for defining variations in biological cycles of production and grazing across ocean provinces (Longhurst 1998; Ducklow 2003 and see Chapter 11). Table 9.4 summarizes studies of $p\mathrm{CO}_2$ in coastal oceans, including systems influenced by continental margin processes that can extend well beyond the shelf (e.g., upwelling off Peru, Oman, etc.). Several aspects are notable. One is that only a few regions of the global coastal ocean have been surveyed extensively, with good areal and seasonal (annual) coverage: the west European shelves, the East China Sea (ECS), the USA Middle Atlantic Bight (MAB) and the coastal upwelling province of the Arabian Sea off the coast of Oman (Figures 9.5, 9.6). Save for a single study off Peru in the 1970's, and recent work in the Arabian Sea, there are no studies from the tropics other than on coral reefs. The other conspicuous and important feature of these studies of coastal ocean $p\mathrm{CO}_2$ is its great variability. The combination of factors influencing $p\mathrm{CO}_2$ variability in coastal seas produces both large under- and supersaturation in dissolved CO_2, with values ranging from 90–980 ppm (Table 9.4), yielding air-sea $\Delta p\mathrm{CO}_2$ values from –270 to +646 μatm. Thus coastal oceans may be from 75% undersaturated to nearly 200% oversaturated, potentially producing large air-sea fluxes in both directions. Closer inspection of the data shows however that only temperate seas have this wide dynamic range of $p\mathrm{CO}_2$ variability. Low values in spring and summer are driven by phytoplankton blooms, whereas high values in autumn and winter are forced by net respiration and riverine runoff (Borges and Frankignoulle, 1999). Note that this cycle (high in winter/low in summer) runs counter to that expected by physical effects alone. An annual temperature cycle ranging from 4 to 25°C, imposed on a closed water body with constant DIC and alkalinity would drive a cycle in $p\mathrm{CO}_2$ ranging from a wintertime low of ~220 μatm to a summer maximum of ~560 μatm (DeGrandpre et al., 2002). The high degree of variability on temperate shelves is in some contrast to the open sea where the peak seasonal amplitude in $p\mathrm{CO}_2$ is generally less than 200 μatm (Takahashi et al. 2002).

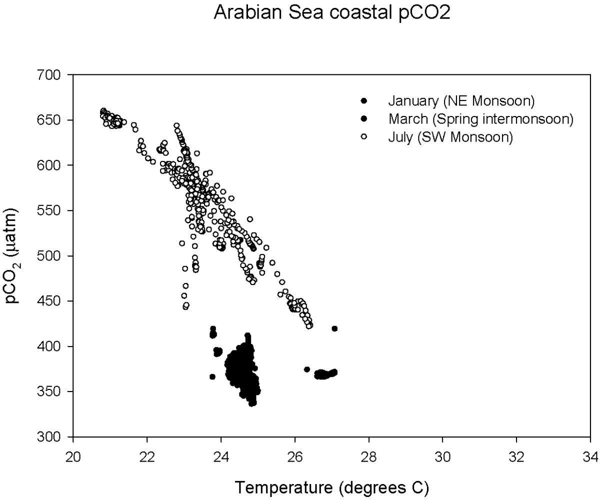

Figure 9.5 pCO2 in the surface coastal ocean of the northwest Arabian Sea, 1995. Data obtained from the US JGOFS database. See also Goyet et al. (1998).

TABLE 9.4
Partial pressure of Carbon dioxide (pCO2) in coastal seas.

Location	Temp Range (°C)[1]	pC0$_2$ Range (µtm)	Mean pCO2 (µatm)[2]	Air-Sea ΔρCO_2 Range (µatm)[3]	Month Season	Reference
			European Shelves			
Portugal Shelf	14–17	360–460		0 to +100	Summer Upwelling	(Perezetal. 1999)
Galicia, Spain	16–21	263–415	342	-46 to +1	Summer Upwelling	(Borges and Frankignoulle 2002)
North Sea	5–17	100–450		-250 to +100	May–June 1986	(Kempe and Pegler 1991)
North Sea (Helgoland)[4]		200–900	480	+155	1962–1978	(Kempe 1995)
North Sea	9–13	220–340		-139 to -19	June, 1991	(Schneider et al. 1992)
English Channel	10–12	100–300		-260 to -10	April–June, 1994	(Frankignoulle et al. 1996)
English Channel	13–15	230–700		-130 to +340	Sept.-Oct, 1994	" "
Bay of Biscay	7–22	306–367	332	-60 to +2	Annual, 1993–99	(Frankignoulle and Borges 2001)
Belgian coast	1–16	90–778		-270 to +410	Annual, 1995–96	(Borges and Frankignoulle 1999)
Dutch coast	2–6	150–200		-148 to -198	Mar.–April, 1986	(Hoppema 1991)
Dutch coast	15–17	300–800		-25 to -40	September, 1993 September, 1995	(Bakkeretal. 1996)
Celtic Shelf	12–17	320–335				(Keiretal. 2001)
			American Shelves			
Bering Sea	-1–8	125–440		-216 to +100	March -June, 1980	(Codispoti et al. 1982)
Mid Atlantic Bight (USA)	2–25	211–658		-149 to +298	1994–1996	(Boehmeetal. 1998)
Mid Atlantic Bight (USA)	4–8	190–400		-35 to -66[5]	Spring	(DeGrandpre et al. 2002)
Mid Atlantic Bight (USA)	8–22	210–630		+49to+61[5]	Summer	" "
Mid Atlantic Bight (USA)	17–26	660–140		+15-+63[5]	Fall	" "
Mid Atlantic Bight (USA)	17–4	510–180		0 to -65[5]	Winter	" "
Mid Atlantic Bight (USA)	19–26	345–655		-13 to +297	Sept.–Oct. 1996	(Bates and Hansell 1999)
West Florida Shelf (USA)	22–25	301–322		-64 to -43	April, 1996	(Wanninkhofetal. 1997)
Oregon coast (USA, 1995)	9–18	150–690		-210 to +330	Summer upwelling	(van Geen et al. 2000)
Monterey Bay CA (USA)	12–14	298–438		-80 to +20	Feb.–Mar. 1993	(Friederich et al. 1995)
Peru upwelling (Cabo Nazca)	19–21	120–980		-214 to +646	May, 1976	(Simpson and Zirino 1980)

Asian Shelves						
Arabian Sea (Oman coast)	20–24	520–720	250	+160 to +360	SW Monsoon (7/95)	(Kortzinger et al. 1997)
Arabian Sea (Oman coast)	24–25	336–411	372	-24 to +51	NE Monsoon (1/95)	(Goyetetal. 1998)[6]
Arabian Sea (Oman coast)	23–27	365–419	374	-4 to +58	Intermonsoon (3/95)	" "
Arabian Sea (Oman coast)	20–27	392–660	565	+30 to +298	SW Monsoon (7/95)	" "
Bay of Bengal (India coast)	26–30	275–400		-75 to +50	Intermonsoon (3/91)	(Kumaretal. 1996)
Bay of Bengal (India coast)	25–26	240–380		-110 to +30	NE Monsoon (11/91)	" "
Funka Bay, Japan	3–20	195–345	292	-165 to -20	Annual, 1995–96	(Nakayama et al. 2000)
East China Sea	15–24	289–392		-72 to +21	Feb.-March, 1993	(Tsunogai et al. 1997)
East China Sea	23–28	320–390		-37 to +33	August, 1994	(Tsunogai et al. 1999)
East China Sea	22–27	307–368		-56 to +4	October, 1993	(Tsunogai et al. 1997)
East China Sea	27	220–370		-37	July, 1992	(Wang et al. 2000)
Coral Reefs						
Bermuda	18–27			-10 to + 33	1994–1996	(Bates 2002)
Enewetak Atoll		190–320		-138 to -8	May- June, 1971	(Smith 1973)
Moorea, Tahiti	27	240–400		-116 to +44	July -Aug. 1992	(Frankignoulle et al. 1996)
Great Barrier Reef	27	250–700		-107 to +343	December, 1993	" "
Palau, Caroline Islands	29		414	+55	April 1992	(Kawahata et al. 1997)
Majuro Atoll, Marshall Is.	30		360	+5	September 1994	" "
Ryukyu Islands, Japan		200–550		-157 to +193	Oct. 93 -July 94	(Kraines et al. 1997)
Arctic and Antarctic shelves						
East Baffin Bay, Canada	-1.8		410	+30	April 1998	(Miller et al. 2002)
East Baffin Bay, Canada	-1-+1	130–150	140	-230	June 1998	" "
NW Greenland Sea	-1.8–3	167–279	218	-189 to -77	July–August, 1992	(Yager et al. 1995)
Ross Sea, Antarctica	0–1	166–314		-19710–49	January, 1997	(Sweeney et al. 2000)[7]
Ross Sea, Antarctica	-1.5–1	150–410		-2 12 to +48	Oct.–April 96–97	(Takahashi et al. 2002)
Gerlache Strait, Antarctica	-1–0	246–363		-150	December, 1995	(Carillo and Karl 1999)

[1] obtained from World Ocean Database 2001 (http://www.nodc.noaa.gov/OC5/WOD01/pr_wod01.html) using Ocean Data View (Schlitzer, 2002) if not given in publication.

[2] Calculated from tabulated data where available if not given in publication.

[3] Positive numbers indicate fluxes from sea to air; values as reported or calculated using Mauna Loa monthly atmospheric values (CD Keeling & TP Whorf, http://cdiac.ornl.gov/ftp/ndp001/maunaloa.co2)

[4] Calculated from continuous moored measurements of pH (W. Hidal, Hamburg).

[5] Seasonal means from continuous mooring data at Buzzards Bay, MA and LEO-15, USA.

[6] Data originated by Catherine Goyet and available from http://usjgofs.whoi.edu/jg/dir/jgofs/arabian/

[7] Data from T. Takahashi measured at 4°C and available from http://usjgofs.whoi.edu/jg/dir/jgofs/southern/nbp97_1/

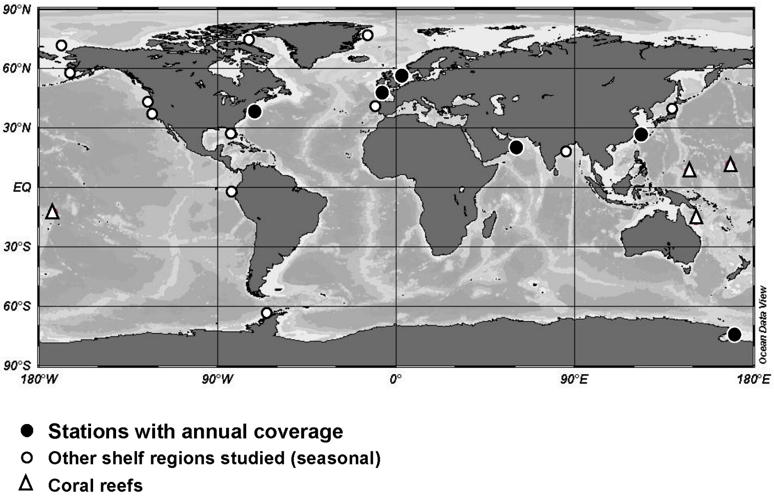

Figure 9.6 Regions in the global coastal ocean where pCO2 has been measured. Figure generated using Ocean Data View (Schlitzer, 2002).

The dramatic effects of biological processes (primary production) in drawing down high $p\text{CO}_2$ are exemplified by observations made in upwelling regimes off Peru, the Iberian Peninsula and Oregon (Simpson and Zirino, 1980; Perez et al., 1999; van Geen et al., 2000; Borges and Frankignoulle, 2002). Cold water from depth, supersaturated in CO_2 ($p\text{CO}_2$ ~400 – 900 μatm) and high in N and P as well, upwells to the surface and then supports intense primary production, which in turn reduces $p\text{CO}_2$ to <200 μatm. The upwelling signature can also be seen in the Arabian Sea (Table 9.4, Figure 9.5), but there the upwelling is seldom fully compensated by biology, in spite of high primary production, even during the Southwest Monsoon (Savidge and Gilpin, 1999; Barber et al., 2001; Dickson et al., 2001; Kinkade et al., 2001). Instead, $p\text{CO}_2$ remained above the atmospheric equilibrium level or just slightly below ($\Delta p\text{CO}_2$ ~ -4 μatm). Goyet et al. (1998) found that the areal average of high-resolution underway $p\text{CO}_2$ measurements remained above the atmospheric equilibrium throughout the year. That is, the coastal Arabian Sea was always a net source for CO_2 flux to the atmosphere. Goyet et al. (1998) estimated that the coastal ocean off Oman released about 1–2 MtC per year (~10 mmol C m^{-2} d^{-1}; Table 9.5), while Kortzinger et al. (1997) suggested that the region outgassed 11–26 MtC (52–119 mmol C m^{-2} d^{-1}) in the SW monsoon period (July-September) alone. The latter flux densities seem very high relative to most other estimates (Table 9.5). The discrepancy in flux estimates illustrates our still-poor understanding of the processes governing the CO_2 balance, even in a comparatively well-studied area.

TABLE 9.5
Annual mean air-sea CCh flux in the global coastal ocean.

Location	Flux density^1 mMol C m· ^{2} d'^{1}	Area of shelf 10^6 km^2	Flux Tmol C yr'^{1}	Reference
European Shelves	7.9	5	14	(Frankignoulle and Borges 2001)
East China Sea	7.9	0.9	2.6	(Tsunogai et al. 1999)
East China Sea	5.5	0.9	1.8	(Wangetal.2000)
Baffin Bay, Canada	20^2	0.08	0.3	(Miller etal. 2002)
Barents Sea	3.2^2	1.4	0.8	(Fransson et al. 2001)
North Sea	3.8	0.51	0.7	(Thomas et al. 2004)
Mid Atlantic Bight (USA)	3.6	0.06	0.1	(DeGrandpre et al. 2002)
Arabian Sea (Oman coast)	-2.5	0.15	-0.13	(Goyetetal. 1998)
Coral reefs	-5	0.6	-1.1	(Frankignoulle et al. 1996)
Global Shelves (model)	7.9	36	49	(Yool and Fasham 2001)
Global coastal ocean	5.6 (4.9)	36^3	73 (65)	Area-weighted mean (Arithmetic mean)

[1] positive fluxes are from air to sea
[2] Assuming 170 day ice-free exchange period (Miller et al., 2002)
[3] the ocean area <200 deep, excluding estuaries, Liu et al., (2000).

Coral reefs are apparently net CO$_2$ source regions, but this generalization is complicated by the diversity of coral reef types and growing anthropogenic influence (Bates, 2002). A large amount of data indicates that although many reef systems have very high rates of gross primary production, their net community production (NEP) is near zero, that is, P:R ratios are not significantly different from 1, and organic metabolism does not contribute to pCO$_2$ disequilibrium (Crossland et al., 1991). However these ecosystems are also areas of intense calcification (Kinsey, 1985). Calcification releases about 0.6 mole of CO$_2$ per mole of CaCO$_3$ precipitated at the current temperature/salinity/alkalinity properties of modern coral reefs (Frankignoulle et al., 1994). When the calcification to net production ratio is 1.67, there is no net CO$_2$ production because the yield from CaCO$_3$ production is balanced by carbon uptake during organic carbon production. But since the NEP is near zero (P:R near 1), the ratio is >1.67 and so reefs are regions of CO$_2$ efflux (Gattuso et al., 1999), with evasion rates of 3 – 7 mmol C m^{-2} d^{-1} (Frankignoulle et al., 1996). The total global surface area of coral reefs is 0.6 x 10^6 km^2, so coral reefs represent a substantial source of CO$_2$ to the atmosphere. But this efflux is dwarfed by CO$_2$ uptake in the larger temperate shelves (see below and Table 9.5). The source/sink balance of coral reefs may change in the future, because anthropogenic CO$_2$ enrichment of the upper ocean is lowering the pH of seawater (Kleypas et al., 1999) and the calcification process is sensitive to pH changes (Langdon et al., 2000).

In contrast to the Arabian Sea and the marked seasonal excursions of the temperate seas, the subtropical East China Sea shows less variability and $p\mathrm{CO}_2$ levels are nearly always below the atmospheric equilibrium or just slightly above (Tsunogai et al., 1999; Table 9.4). In the ECS, wintertime cooling drew $p\mathrm{CO}_2$ below the atmospheric equilibrium, and high primary production, sustained by upwelling of offshore nutrients (Chen, 1996), counteracted the effects of summer warming, maintaining low $p\mathrm{CO}_2$ throughout the year. Based on their observations of an annual mean fugacity deficit ($\approx \Delta p\mathrm{CO}_2$) of 55 µatm in the region, Tsunogai et al. (1999) hypothesized a "continental shelf pump" for absorption of atmospheric CO_2. In their model, surface cooling on the shelf produces denser water and this process in conjunction with primary production enhances absorption of CO_2 from the atmosphere. The absorbed CO_2 is transported below the pycnocline (as organic matter or dissolved gas) and then exported from the shelf region into the open sea. They further suggested that if the global continental shelves all behaved like the ECS, they would account for ~ 1 PgC (1 GtC) of uptake annually. This amount could be in addition to the 2.2 PgC estimated by observations and models to be taken up in the open sea (Liu et al., 2000a and see below). Clearly the ECS is not typical of all the world's shelf seas. But whether or not the ECS is a suitable model for the global coastal ocean, it is an important site of CO_2 uptake on its own, being the third-largest of the world's shelf seas, comprising 3% of the total shelf area shallower than 200 m, and accounting for 20–30 Mt (1.8 – 2.6 Tmol) of CO_2 uptake annually (Table 9.5). One weakness of this study is that site-specific empirical relationships were used to extrapolate from a sparse set of observations to produce regional scale monthly maps of surface $p\mathrm{CO}_2$ and derive the annual fugacity deficit and pumping rate. Comprehensive mass balance studies in the ECS indicate lower fluxes and do not support a high CO_2 sink (Chen and Wang, 1999).

Is there a continental shelf pump? In some areas there clearly is. The west European shelves are huge, 5 million km^2 in area. Although they exhibit large variations in $p\mathrm{CO}_2$, many of the higher values are concentrated near river mouths and coastal plumes (Bakker et al., 1996; Borges and Frankignoulle, 1999), whereas the low values are found throughout the observed shelf area. Even in the Bay of Biscay, where the seasonal amplitude is low, the mean annual $\Delta p\mathrm{CO}_2$ is ~ -30 µatm (Frankignoulle and Borges, 2001). The West European shelves appear to function like the East China Sea, with winter $p\mathrm{CO}_2$ drawdown maintained in summer by inputs of riverine nutrients which support high primary production. Thus these shelves, among the best studied on the planet; also appear to function as CO_2 pumps, taking up a startling 170 MtC (14 Tmol) annually (Table 9.5). However a recent study in the North Sea, including monthlong surveys in consecutive seasons, found a lower areal flux rate more comparable to other temperate regions (Thomas et al., 2004) (Table 9.5).

DeGrandpre et al. (2002) questioned the universality of the shelf-pump hypothesis, basing their argument on analysis of high frequency, cross-shelf measurements of $p\mathrm{CO}_2$ made by moored sensors and underway sampling systems in the

Middle Atlantic Bight, USA (see also Boehme et al. 1998). High-resolution observations in time and space addressed the problem of extrapolation noted in the East China Sea. DeGrandpre et al. (2002) observed large amplitude, short-term changes in $p\text{CO}_2$ >100 μatm (Figure 9.7), forced by local upwelling and mesoscale circulation forcing. In this region, unlike the ECS and European margin, the thermally driven rise in $p\text{CO}_2$ in summer was not compensated by primary production, and waters became supersaturated. Apparently, nutrient inputs are not sufficient to maintain high PP, and the region becomes depleted of N and P following the spring bloom (Malone et al., 1983). The $p\text{CO}_2$ cycle appears to be driven primarily by the annual heating and cooling cycle, and the asymmetry between the thermal cycle and the winds renders it a weak sink region. Because winds are stronger in winter when $p\text{CO}_2$ is low, uptake predominates slightly, and the area takes up about 0.1 Tmol C per year (DeGrandpre et al., 2002; Table 9.5), acting as a weak CO_2 sink. High-resolution measurements of pCO_2, DIC and alkalinity extending from the Georgia salt-marsh estuaries to the Gulf Stream, across the South Atlantic Bight continental shelf revealed a similar pattern with an important addition. Export of DIC from the salt marsh system is sufficiently large that the SAB shelf exports DIC to the open ocean even during the summer when (due to heating) the flux of CO_2 is to the atmosphere (i.e. ΔpCO_2 is positive). Thus, in this type of shelf system, studies of ΔpCO_2 are not sufficient to quantify the sign or magnitude of the flux of DIC from the shelf to the open ocean (Wang 2002 and R. Jahnke, personal communication). Further generalization about whether other continental shelves act more like the ECS or MAB must await exploration and surveying of more shelf systems.

The continental shelf pump (CSP) hypothesis was examined by Yool and Fasham (2001) using a general circulation model. They parameterized the CSP by adding atmospheric CO_2 to model cells intersecting continental shelf areas (depths < 200 m) at the rate estimated by Tsunogai et al. (1999), then used the circulation model to trace the transport and fate of the CO_2 injected into the coastal ocean. Like other GCM's, their model did not explicitly include continental shelf areas, due to relatively coarse spatial resolution. Defining CSP export efficiency as the fraction of CO_2 taken up in a given shelf area which was exported and outgassed elsewhere, they found that the global coastal ocean was 53% efficient at exporting absorbed CO_2 into the open sea. Export efficiencies ranged up to 90% for small, narrow shelves (e.g., Hawaiian shelf), with larger temperate shelves ranging from 28% (North Sea) to 74% (Patagonia). Interestingly, they found that the East China Sea had an export efficiency of 52%, nearly identical to the global mean, and lending support to Tsunogai et al's CSP hypothesis. The results also suggested an global, annual uptake rate of 49 Tmol C, somewhat lower than the amount estimated by Tsunogai et al. (1999). A different modeling approach, emphasizing the coupled cycles of C-N-P-S suggests the coastal ocean is a very weak sink (-5 Tmol C y^{-1}), with strong net heterotrophy lessening the net CO_2 uptake C (Chapter 8).

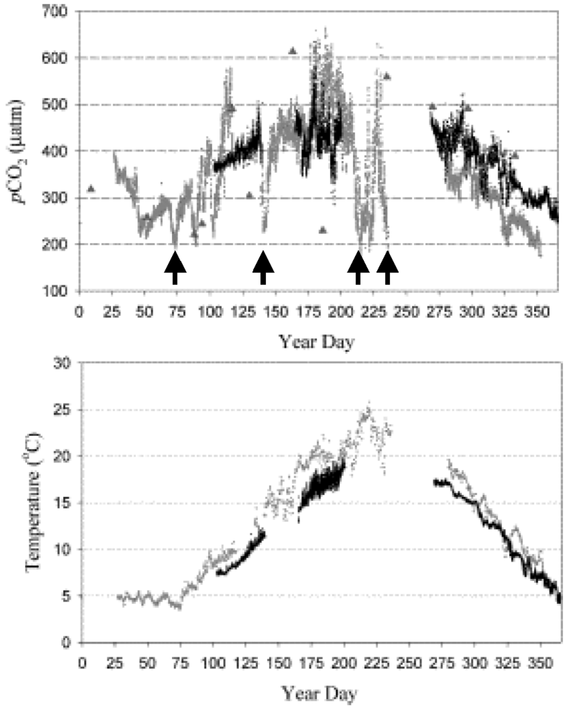

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Figure 9.7 Annual cycles of surface pCO2 and temperature in the Middle Atlantic Bight, USA. Arrows denote large short-term changes due to local upwelling. Figure courtesy deGrandpre et al. (2002).

The modeling approach of Yool and Fasham has the advantage of providing a consistent, defined way of following atmospheric CO_2 from its entry into the coastal ocean to its ultimate fate as outgassing or long-term storage in the ocean interior. But it is a very simplified approach, with no biological transformation of the absorbed CO_2: rather, CO_2 remains in its inorganic form, and acts as a passive tracer of transport in the ocean circulation. Yool and Fasham (2001) addressed this point by performing separate simulation experiments in which the CO_2 was transformed into a DOC-like tracer that did not exchange with the atmosphere and was respired back to CO_2 over seasonal (0.033 d^{-1}) to annual (0.003 d^{-1}) time scales. When the CSP was parameterized with this delay term, it allowed the absorbed CO_2 to survive for a longer period before outgassing; thus the export efficiency of the shelf regions was increased, and 8% more carbon was outgassed in the open sea. It is unclear if a model with more realistic biology, for example including a CSP dominated by sinking particles, would be still more efficient, owing to the uncertainty of representing near-bottom offshelf particle transport (Chapters 4, 19).

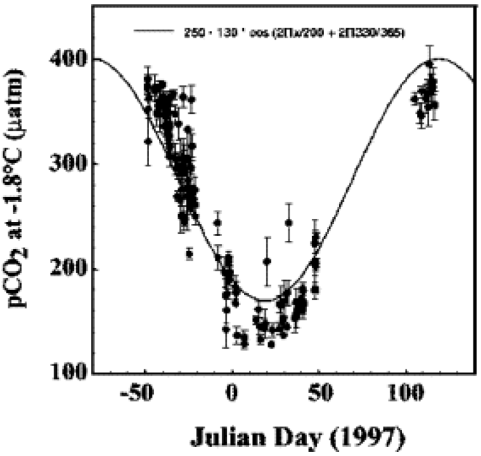

Figure 9.8 Figure 8.Seasonal changes in surface pCO2 along longitude 76.5° in the Ross Sea, Antarctica. The solid trend line is approximated by a simple sine function. Figure courtesy Takahashi et al. 2002).

Shelves covered by seasonal sea ice also act as CO_2 pumps, but for another reason. The Ross Sea is a deep shelf sea with bottom depths ranging from 300–800 m due to isostatic adjustment from the weight of the ice mass on the Antarctic continent. The region was sampled throughout the ice-free season during the US JGOFS AESOPS Program, revealing a seasonal $p\mathrm{CO}_2$ range of 150–410 ppm (Figure 9.8; Takahashi et al. 2002). Sea surface temperature is almost constant near Antarctica and the $p\mathrm{CO}_2$ excursion is almost entirely due to biological drawdown and respiration. Most other ice-margin seas have been sampled only in summer, with similar levels of undersaturation (Table 9.4). Yager et al. (1995) found that the Northeast Water polynya on the Greenland Shelf was strongly undersaturated in the summer, ice-free season. They put forward the "seasonal rectification hypothesis," stating that in marginal ice zones, the ice-free season coincides with the main period of low $p\mathrm{CO}_2$, when the regions act as atmospheric sinks. At other times of the year, when $p\mathrm{CO}_2$ could be well above saturation, the water is covered by sea ice and gas exchange is prevented. In spring, primary production appears to consume excess dissolved inorganic carbon before the ice cover recedes. The extent to which high CO_2 escapes through leads, cracks and persistent polynyas is not known, but cannot be great, since only small areas are exposed. There is also uncertainty in estimates of gas transfer through the sea ice itself (Miller et al., 2002). Yager et al (1995) and Miller et al (2002) assumed complete capping of the air-sea interface by sea ice. Thus in effect they use estimates of CO_2 exchange in the ice-free season as an annual average, leading to very high estimates of the air to sea flux (Table 9.5). Miller et al. (2002) pointed out that if net respiration in autumn (September-October) resulted in increases in $p\mathrm{CO}_2$ prior to restoration of ice cover, the strength of these polynyas as CO_2 sinks would be reduced. They also noted that horizontal advection can move low $p\mathrm{CO}_2$ waters under surrounding ice. Complexity in circulation, timing of biological cycles and interannual variability combine to regulate the efficiency of seasonal polynyas as CO_2 sinks. Fransson et al. (2001) used a budget approach to derive a flux of 9.2 MtC y^{-1} for the Barents Sea (Table 9.5). Yool and Fasham (2001) noted in their model that large concentrations of CO_2 absorbed by the continental shelves in the coastal Arctic were trapped under the permanent sea ice in the central Arctic Ocean, further enhancing the role of these ice-covered seas as regions of atmospheric CO_2 storage. Both the Arctic and Antarctic polar regions are a complex mosaic of sea ice cover in time and space, and few areas have been sampled well even in summer. The potentially large fluxes driven by intense ice-edge blooms bear further study of these remote regimes.

7.5. Synthesis: air-sea CO_2 exchange in the coastal oceans.

It appears from the observations of air-sea pCO_2 made to date, that some shelves do act as CO_2 pumps for a variety of reasons; while others are only weak sinks, or else sources of atmospheric CO_2. Observations of pCO_2 seasonality and its causes are still comparatively scarce, and in many areas insufficient to resolve the sign of the annual flux balance. Some of the largest shelf seas on the planet have been only poorly surveyed (Bering Sea, Arctic Ocean) or not studied at all (Patagonian Shelf, Indonesia/northern Australian marginal seas). Based on the available data (Table 9.4) we present in Table 9.6 a preliminary typology of regional pCO_2 variability in the global coastal ocean, another step toward segmentation of the ocean into true biogeochemical provinces (Platt and Sathyendranath, 1988; Longhurst, 1998; Ducklow, 2003). Seven distinct province types can be recognized. Takahashi et al. (2002) differentiated the open ocean into areas where the seasonal amplitude of pCO_2 excursions was influenced primarily by biological processes or temperature. Their analysis showed that pCO_2 variability in most high latitude regions (> 40fl N or S lat.) and the equatorial zone was controlled primarily by biological processes, whereas temperature effects predominated in the subtropical gyres. Coastal ocean pCO_2 variability is roughly consistent with this general scheme. Biology dominates the air-sea exchange in high latitudes (marginal ice zones) and in the tropics (coral reefs, Peru). In the Arabian Sea, biology modulates the CO_2 efflux, which would be greater but for intense primary production. The balance between physical and biological processes is more complicated in the subtropics and temperate zones. The two sets of effects enhance each other in the East China Sea and European shelves, producing strong sink regions, but are compensating in the US Mid-Atlantic Bight, rendering this region a 50% weaker sink than other temperate areas. If we could classify the rest of the global coastal ocean according to this scheme, it would be possible to extrapolate its contribution to the total CO_2 exchange. But a lack of seasonal and areal coverage still prevents a true objective mapping.

TABLE 9.6

Characteristic patterns *ofpCO*$_2$ variability in the global coastal ocean.

Pattern	Characteristics	Sink / Source	Examples
Subtropical continental shelf CC>2 pump	Temperature and biology effects both favor persistent low/7CO2; strong sink regions.	Sink	East China Sea
Temperate shelf: biology dominant	LowjpCO2 in spring-summer, high in winter and near river mouths, strong net sink regions.	Sink	West European shelves
Temperate shelf: physics dominant	Low/?CC>2 in winter-spring, high in summer and near river mouths, weak net sink regions due to wind- temperature asymmetry (net annual flux unresolved).	???	USA Middle Atlantic Bight
Upwelling: biology dominant	Intense primary production in upwelled water consumes upwelled CO_2.	77?	Iberia, Peru, Oregon, USA
Upwelling: physics dominant	Upwelled high/?CC>2 not fully compensated by biology; weak source regions.	Source ?	Arabian Sea
Coral reefs	Strong diurnal pCU2 cycle; calcification compensates organic production, source regions.	Source	Great Barrier Reef
Polar, ice- rectified CU2 pump	Sea ice cover in winter prevents air- sea exchange, low pCU2 in summer in open water; weak sink regions	Sink	Greenland, Antarctic

A rough global extrapolation that is very much influenced by the European and ECS shelf fluxes, suggests that CO_2 exchange is 1–10 mmol C m^{-2} d^{-1}, into or out of the sea (Table 9.5). Air-sea exchange in Table 9.5 is reported as calculated in the original references. The original authors used a variety of assumptions about the relationship between exchange and wind velocity and the resulting estimates are not consistent. The global coastal ocean is potentially a net sink of 0.5 – 1 PgC annually. The fluxes in better-studied systems suggest an area-weighted mean annual carbon sink of 73 Tmol (0.9 Pg) in the coastal ocean (Table 9.5). This analysis notwithstanding, a common misunderstanding must be kept in mind. A net influx by itself does not render the global coastal ocean a sink for atmospheric CO_2. The subsequent fate of the absorbed CO_2 determines whether, or to what extent these coastal ocean systems are truly atmospheric CO_2 sinks. The absorbed CO_2 must be buried in coastal ocean sediments or else transported to the subsurface waters of the open ocean if it is to be stored over longer time scales (Sarmiento and Siegenthaler, 1992; Liu et al., 2000a). Otherwise the CO_2 stored in organic matter will be respired and released to the atmosphere during organic matter decomposition and denitrification, while any excess dissolved CO_2 could be lost through gas exchange. In the final section we present a new carbon budget for the coastal and open sea, showing how the continental shelf pump exports atmospheric CO_2 (as organic matter) into the open sea where it supports a moderate level of oceanic net heterotrophy. Both the coastal and open oceans are sinks for atmospheric CO_2 in our synthesis.

TABLE 9.7
Carbon budgets[a] for the coastal and open oceans.

Region	Budget components		Tmol y^{-1}	Reference[b]
Coastal Ocean	External Sources	Rivers	83	This
			34	S&H
			67	Liu
		Open ocean	167	This
			--	S&H
			167	Liu
		Atmosphere (net)	73	This
			8	S&H
			8	Liu
	Internal Cycling	Photosynthesis	1200	This
			400	S&H
			833	Liu
		Respiration	-1025	This
			-507	S&H
			-667	Liu
	Internal Sink	Coastal sediments	-13	This
			-9	S&H
			-13	Liu
		Accumulation	-61	This
			-15[c]	S&H
			-4	Liu
	External Sinks	Open oceans	-249	This
			-18	S&H
			-225	Liu
Open Ocean	External Sources	Coastal ocean	249	This
			18	S&H
			225	Liu
		Atmosphere (net)	83	This
			169	S&H
			108	Liu
	Internal Cycling	Photosynthesis	3000	This
			3600	S&H
			3333	Liu
		Respiration	-3196	This
			-3616	S&H
			-2667	Liu
	Internal Sink	Oceanic sediments	-4	This
			-2	S&H
			-4	Liu
		Accumulation	-161	This
			-185[b]	S&H
			-163	Liu
	External sink	Coastal ocean	-167	This
			--	S&H
			-167	Liu

[a] Budgets are balanced by subtracting sinks (including accumulation) from sources, neglecting the internal cycling terms (photosynthesis and respiration).

[b] This study; S&H: Smith and Hollibaugh 1993 (budget for river input of organic matter only); Liu et al. 2000.

[c] Not stated explicitly; calculated as input minus output

8. Synthesis: coastal and open ocean carbon budgets.

Smith and Hollibaugh (1993) presented a thorough analysis of organic metabolism in the coastal ocean, concluding that 18 Tmol of terrigenous organic matter was exported to the open sea. As a result of terrestrial inputs, both systems had negative metabolic balance in their scheme. The 18 Tmol of river-derived organic carbon constituted the entire shelf pump in their analysis. Subsequently Liu et al. (2000a) constructed a new budget, based on a diagnosis of the global carbon cycle by Siegenthaler and Sarmiento (1993). The principal differences in these budgets are given in Table 9.7. In some respects the budgets are not directly comparable because Smith and Hollibaugh focus exclusively on organic carbon, whereas Liu et al present a full carbon budget (organic plus inorganic). In Liu et al's analysis, the coastal ocean was autotrophic, and the continental shelf pump amounted to about 200 Tmol C annually. Both Smith and Hollibaugh (1993) and Liu et al. (2000a) postulated that the coastal ocean was a weak net sink for atmospheric CO_2, taking up 8 Tmol C annually. However the levels they assigned for NPP in the coastal ocean differed significantly: 400 vs 833 Tmol C yr^{-1}, with Smith and Hollibaugh providing the more conservative figure.

Our new analysis (Figure 9.9**,** Table 9.7), based on this review, differs in several ways from the earlier budgets presented by Smith and Hollibaugh (1993) and Liu et al (2000a). The annual river input is increased to 83 Tmol C (45% organic), reflecting data on the anthropogenic subsidy reviewed above. Most of the increase appears to be DIC; thus Smith and Hollibaugh's estimate of 38 Tmol of riverine organic carbon entering the coastal ocean is retained in our budget. Although the global total NPP is similar in all three budgets, we adopt Longhurst et al's (1995) estimate of 1200 Tmol C for the coastal ocean NPP. We further assume an annual mean f- (or export) ratio of 0.5 for the coastal ocean (recall this is for vertical export from the surface layer; Section 4) and 0.2 for the open sea (Eppley and Peterson 1979). From these assumptions about the total NPP and export ratios it follows that the vertical exports from the euphotic zone of the coastal ocean and the open sea are equivalent at 600 Tmol C yr^{-1}. The global net CO_2 uptake is increased to 1.9 GtC (158 Tmol) annually (Sarmiento and Gruber 2002), of which 0.9 GtC (73 Tmol) is absorbed in coastal ocean waters (Table 9.5). The remaining 83 Tmol is absorbed in the open sea.

Our estimate for global oceanic CO_2 uptake, including coastal ocean uptake of 73 Tmol C yr^{-1} is a conservative assumption; the alternative would be that the full 158 Tmol of C uptake is allocated to the open sea, with an *additional* 73 Tmol C taken up by the coastal oceans. The justification for such an allocation would be that previous global estimates tended to ignore the coastal ocean, usually because it is not resolved in global GCM's (Yool and Fasham 2001). The resulting total (233 Tmol or 2.8 PgC) is slightly greater than the high estimate provided by Takahashi et al (2002) of 2.6 PgC. Broecker (2001) noted that if a new cubic relationship between wind velocity and air-sea exchange (Wanninkhof and McGillis, 1999) were valid, the total ocean uptake might be as high as 3.7 PgC yr^{-1}. This global total would easily accommodate an open ocean uptake of 1.9–2.2 PgC yr^{-1} and an additional coastal ocean uptake of 0.9 GtC, although the latter estimate would need to be revised upward as well. As Broecker cautioned, these higher values for the global uptake need to be reconciled with existing tracer (^{13}C, ^{14}C) budgets. So we adopt the most conservative assumption here. Although conservative, it represents a significant increase in coastal ocean CO_2 uptake over previous estimates (Table 9.7).

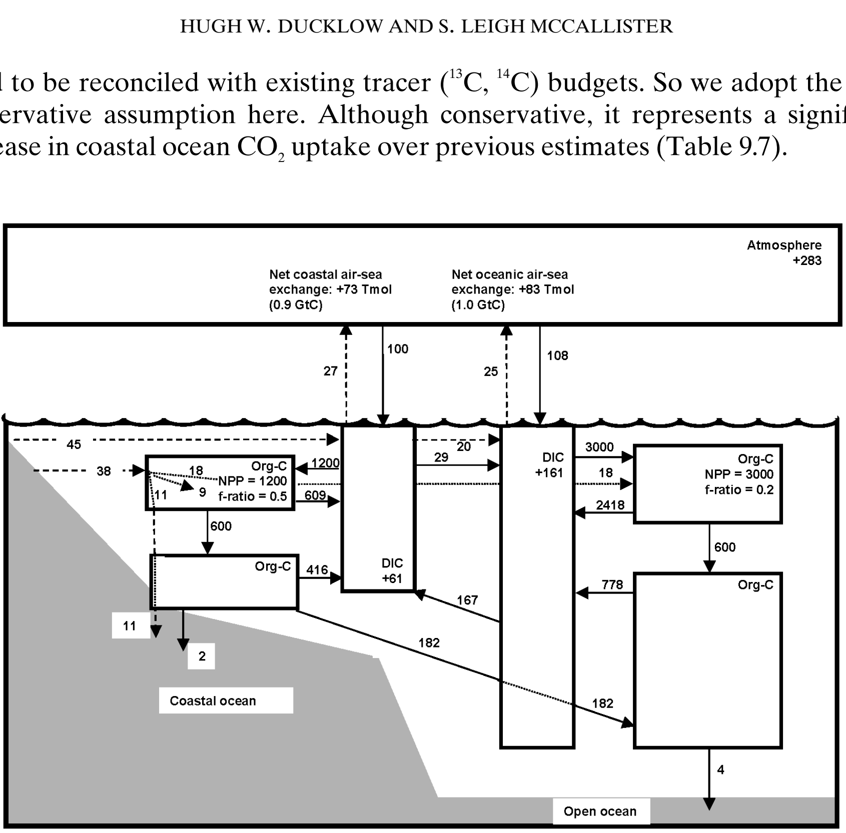

Figure 9.9 A new carbon budget for the global coastal ocean, incorporating fluxes and transports discussed in this chapter. The total (coastal + open ocean) CO2 air-sea exchange is referenced to Sarmiento and Gruber (2002). The principal differences from previous budgets are annual net primary production (NPP) of 1200 Tmol and net air-sea exchange of 73 Tmol in the coastal ocean. As a consequence of the continental shelf pump (182 + 18 Tmol), the open ocean is net heterotrophic by about 200 Tmol per year, although this imbalance is expressed in the midwater column where the continental shelf pump is believed to enter the open sea. Dashed lines trace terrestrial inputs of DIC and organic carbon through the ocean system. Fluxes only terminate at arrowheads. Dotted lines signify pass-throughs of transport from a remote source (e.g., the 18 Tmol of riverine input to the open sea).

Finally, we assumed the continental shelf pump delivers 18 Tmol of riverine organic C to the open ocean surface layer and 182 Tmol C to the oceanic interior via downslope transport processes (Section 5). The small coastal and oceanic burial terms are left unchanged, as there is little evidence they have altered in response to the anthropogenic CO_2 transient (but see Chapter 8 for another view; and Chapters 6,11,12 on burial processes generally). The 167 Tmol C of net DIC flux back into the coastal ocean was derived from Walsh's (1991) estimate of a net ocean to shelf onwelling of ~0.6 Pg NO_3-N yr^{-1} (40 Tmol N x 6.7 = 268 Tmol C, adjusted to 167 to balance budget).

Respiration is derived by mass balance. In the lower layer, respiration is not divided between water column and benthos but benthic respiration is implicit. The resulting budget shows that the coastal ocean is autotrophic by 175 Tmol C y^{-1} (Table 9.7, NPP = 1200, R=1025 and cf. Table 9.2). This excess production is a consequence of exporting 200 Tmol C, which would otherwise be respired *in situ,* increasing R to 1225 and rendering the system very slightly heterotrophic. The excess NEP of 175 Tmol is about 3 times the estimate of 68 derived earlier by Gattuso et al. (1998). The export by the continental shelf pump is 15% of the coastal ocean NPP (not including 18 Tmol of riverine DOM), consistent with the observations (Section 5). This export renders the open sea heterotrophic if respiration in the whole water column is considered (Figure 9.9, NPP=3000, R=3214). The oceanic surface layer is autotrophic (Figure 9.9; P:R=1.24), consistent with some observations (Table 9.2 and Karl et al., 2003), but in contrast to the hypothesis that it is heterotrophic (Duarte and Agusti, 1998) by up to 500 Tmol C yr^{-1}, as calculated by Williams and Bowers (1999). As noted in section 6, this latter estimate of net heterotrophic metabolism in the oceanic surface layer would require a labile C input of 1082 Tmol C yr^{-1}, over five times the amount estimated here, via unknown transport processes. The observed net CO_2 uptake in the open sea is a strong constraint on the CO_2 produced by oceanic respiration; here it contributes to an annual storage rate of 161 Tmol C yr^{-1}, as in Liu et al. (2000a). The storage would be greater except for 167 Tmol C of net return flow into the coastal ocean (see above). Carbon is also being stored in central gyres as DOC (Church et al., 2002), but it remains to be determined if this is a long-term or transient, decade-scale phenomenon. Finally, the global ocean as a whole (coastal ocean plus open sea) is slightly heterotrophic by 38 Tmol, as a result of respiration of the terrestrial input (Smith and Hollibaugh, 1993), yet it remains a net sink for atmospheric CO_2. The identity of both the coastal and open oceans as CO_2 sinks is a consequence of anthropogenic CO_2 addition to the atmosphere, which has had the effect of decoupling ocean metabolism and CO_2 exchange. It is necessary to acknowledge this decoupling to understand the carbon balance in the present-day ocean system.

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