Chapter 15. Coastal Oceans, Lakes and Rivers

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KEY FINDINGS

• The global oceans currently take up between 1.3 and 2.3 Gt C yr$^{-1}$ from the atmosphere.

• The carbon budgets of ocean margins (coastal regions) are not well-characterized due to lack of observations coupled with complexity and highly localized spatial variability. Existing data are insufficient, for example, to estimate the amount of carbon stored in the coastal regions of North America.

• New observations reveal that on average, nearshore waters surrounding North America are neither a source nor a sink to the atmosphere. A small net source of CO$_2$ to the atmosphere of 19 Mt C yr$^{-1}$ is estimated mostly from waters around the Gulf of Mexico and the Caribbean Sea, with a variation (standard deviation) around that number of ±22 Mt C yr$^{-1}$.

• With the exception of one or two time-series sites, almost nothing is known about historical trends in sea-air fluxes and the source-sink behavior of North America’s coastal oceans.

• The Great Lakes and estuarine systems of North America may be net sources of CO$_2$ where terrestrially-derived organic material is decomposing, while reservoir systems may be storing carbon through sediment transport and burial.

• There are no existing projections of whether North America’s coastal oceans will remain a source of CO$_2$ in the future or become a sink.

• Options and measures for sequestration of carbon in the ocean include deep-sea injection of CO$_2$ and iron fertilization, although it is unresolved how important, feasible or acceptable any of these options might be for the North American region.
Highly variable sea-air CO₂ fluxes in coastal areas may introduce errors in North American CO₂ fluxes calculated by atmospheric inversion methods. Reducing these errors will require ocean observatories utilizing fixed and mobile platforms with instrumentation to measure critical stocks and fluxes as part of coordinated national and international research programs. Ocean carbon sequestration studies should also be continued.

INVENTORIES (STOCKS AND FLUXES, QUANTIFICATION)

This chapter focuses on the role that aquatic systems play in modulating atmospheric carbon dioxide (CO₂). The chapter quantifies water-atmosphere CO₂ fluxes and considers how the underlying stocks and rate processes affect them. Aquatic stocks of living carbon are small relative to stocks in the terrestrial environments, but turnover rates are very high. In addition aquatic stocks are not well characterized because of their spatial and temporal variability. The complexity of transformations in aquatic systems, the limited data on the transformations, and space considerations have led to the focus on water-atmosphere CO₂ fluxes. Aquatic systems, primarily the oceans, act as a huge reservoir for inorganic carbon, containing about 50 times as much CO₂ as the atmosphere, and atmospheric concentration of CO₂ would be much higher in the absence of current ocean processes.

The ocean’s biological pump converts inorganic carbon in the upper ocean to organic particulate carbon by photosynthesis, transports the organic carbon from the surface by sinking, and therefore plays a critical role in removing atmospheric CO₂ (Gruber and Sarmiento, 2002) in combination with physical and chemical processes. The net sea-air CO₂ flux over the global ocean appears to be well constrained to be about 1,800 ± 500 Mt C [1 Mt = one million (10⁶) metric tons] or 1.8 ± 0.5 Gt C yr⁻¹ [1 Gt = one billion (10⁹) metric tons] from the atmosphere into the ocean (Figure 15-1 and Table 15-1). (See Chapter 2 for a description of how ocean carbon fluxes relate to the global carbon cycle.) The atmosphere is well mixed and nearly homogenous. The large spatial variability in sea-air CO₂ fluxes shown in Figure 15-1 is driven by a combination of physical, chemical, and biological processes in the ocean. The flux over the coastal margins has neither been well characterized (Liu et al., 2000) nor integrated into global calculations because there are large variations over small spatial and temporal scales, and observations have been limited. The need for higher spatial resolution to resolve the coastal variability has hampered modeling efforts. In the following sections we review existing information on the coastal ocean carbon cycle and its relationship to the global ocean, and we present the results of a new analysis of about a half million observations of sea-air flux of CO₂ in coastal waters surrounding the North American continent.
Table 15-1. Climatological mean distribution of the net sea-air CO$_2$ flux (in Gt C yr$^{-1}$) over the global ocean regions (excluding coastal areas) in reference year 1995. The fluxes are based on about 1.75 million partial pressure measurements for CO$_2$ in surface ocean waters, excluding the measurements made in the equatorial Pacific ($10^\circ$N- $10^\circ$S) during El Niño periods (see Takahashi et al., 2002). The NCAR/NCEP 42-year mean wind speeds and the (wind speed)$^2$ dependence for sea-air gas transfer rate are used (Wanninkhof, 1992). Plus signs indicate that the ocean is a source for atmospheric CO$_2$, and negative signs indicate that ocean is a sink. The ocean uptake has also been estimated on the basis of the following methods: temporal changes in atmospheric oxygen and CO$_2$ concentrations (Keeling and Garcia, 2002; Bender et al., 2005), $^{13}$C/$^{12}$C ratios in sea and air (Battle et al., 2000; Quay et al., 2003), ocean CO$_2$ inventories (Sabine et al., 2004), and coupled carbon cycle and ocean general circulation models (Sarmiento et al., 2000; Gruber and Sarmiento, 2002). The consensus is that the oceans take up 1.3 to 2.3 Gt C yr$^{-1}$

Figure 15-1. Global distribution of air-sea CO$_2$ flux. The white line represents zero flux and separates sources and sinks. The sources are primarily in the tropics (yellow and red) with a few areas of deep mixing at high latitudes. Updated from Takahashi et al. (2002).

Global Coastal Ocean Carbon Fluxes

The carbon cycle in coastal oceans involves a series of processes, including runoff from terrestrial environments, upwelling and mixing of high CO$_2$ water from below, photosynthesis at the sea surface, sinking of organic particles, respiration, production and consumption of dissolved organic carbon, and sea-air CO$_2$ fluxes (Figure 15-2). Although fluxes in the coastal oceans are large relative to surface area, there is disagreement as to whether these regions are a net sink or a net source of CO$_2$ to the atmosphere (Tsunogai et al., 1999; Cai and Dai, 2004; Thomas et al., 2004). Great uncertainties remain in coastal carbon fluxes, which are complex and dynamic, varying rapidly over short distances and at high frequencies. Only recently have new technologies allowed for the measurement of these rapidly changing fluxes (Friederich et al., 1995 and 2002; Hales and Takahashi, 2004).

Figure 15-2. In the top panel, mean air/sea CO$_2$ flux is calculated from shipboard measurements on a line perpendicular to the central California coast. Flux within Monterey Bay (~0–20 km offshore) is into the ocean, flux across the active upwelling region (~20–75 km offshore) is from the ocean, and flux in the California Current (75–300 km) is on average into the ocean. These fluxes result from the processes shown in the bottom panel. California Undercurrent water, which has a high CO$_2$ partial pressure, upwells near shore, and is advected offshore into the California Current and into Monterey Bay. Phytoplankton growing in the upwelled water use CO$_2$ as a carbon source, and CO$_2$ is drawn to low levels in those areas. Phytoplankton carbon eventually sinks or is subducted below the euphotic zone, where it decays, elevating
the CO2 levels of subsurface waters. Where the level of surface CO2 is higher than the level of atmospheric CO2, diffusion drives CO2 into the atmosphere. Conversely, where the level of surface CO2 is lower than that of atmospheric CO2, diffusion drives CO2 into the ocean. The net sea/air flux on this spatial scale is near zero. DIC = dissolved inorganic carbon; POC = particulate organic carbon. Updated from Pennington et al. (in press).

Carbon is transported from land to sea mostly by rivers in four components: CO2 dissolved in water, organic carbon dissolved in water, particulate inorganic carbon (e.g., calcium carbonate, CaCO3), and particulate organic carbon. The global rate of river input has been estimated to be 1,000 Mt C yr⁻¹, about 38% of it as dissolved CO2 (or 384 Mt C yr⁻¹), 25% as dissolved organic matter, 21% as organic particles and 17% as CaCO3 particles (Gattuso et al., 1998). Estimates for the riverine dissolved CO2 flux vary from 385 to 429 Mt C yr⁻¹ (Sarmiento and Sundquist, 1992). The Mississippi River, the seventh-largest in freshwater discharge in the world, delivers about 13 Mt C yr⁻¹ as dissolved CO2 (Cai, 2003). Organic matter in continental shelf sediments exhibits only weak isotope and chemical signatures of terrestrial origin, suggesting that riverine organic matter is reprocessed in coastal environments on a time scale of 20 to 130 years (Hedges et al., 1997; Benner and Opsahl, 2001). Of the organic carbon, about 30% is accumulating in estuaries, marshes, and deltas, and a large portion (20% to 60%) of the remaining 70% is readily and rapidly oxidized in coastal waters (Smith and Hollibaugh, 1997). Only about 10% is estimated to be contributed by human activities, such as agriculture and forest clearing (Gattuso et al., 1998), and the rest is a part of the natural carbon cycle.

One of the major differences between coastal and open ocean systems is the activity of the biological pump. In coastal environments, the pump operates much more efficiently, leading to rapid reduction of surface CO2 and thus complicating the accurate quantification of sea-air CO2 fluxes. For example, Ducklow and McCallister (2004) constructed a carbon balance for the coastal oceans using the framework of the ocean carbon cycle of Gruber and Sarmiento (2002) and estimated a net CO2 removal by primary productivity of 1,200 Mt C yr⁻¹ and a large CO2 sink of 900 Mt C yr⁻¹ for the atmosphere. In contrast, Smith and Hollibaugh (1993) estimated a biological pump of about 200 Mt C yr⁻¹ and concluded that the coastal oceans are a weak CO2 sink of 100 Mt C yr⁻¹, about one-ninth of the estimate by Ducklow and McCallister (2004). Since the estimated sea-air CO2 flux depends on quantities that are not well constrained, the mass balance provides widely varying results.

North American Coastal Carbon

Two important types of North American coastal ocean environments can be identified: (1) river-dominated coastal margins with large inputs of fresh water, organic matter, and nutrients from land (e.g.,
Mid- and South-Atlantic Bights) and (2) coastal upwelling zones (e.g., the California-Oregon-Washington coasts, along the eastern boundary of the Pacific) where physical processes bring cool, high-nutrient and high-CO₂ waters to the surface (Cai et al., 2003). In both environments, the biological uptake of CO₂ plays an important role in determining whether an area becomes a sink or a source for the atmosphere.

High biological productivity fueled by nutrients added to coastal waters can lead to seawater becoming a CO₂ sink during the summer growing season, as observed in the Bering Sea Shelf (Codispoti and Friederich, 1986) and the northwest waters off Oregon and Washington (van Geen et al., 2000; Hales et al., 2005). Similar CO₂ draw-downs may occur in the coastal waters of the Gulf of Alaska and in the Gulf of Mexico near the Mississippi River outflow. Coastal upwelling results in a very high concentration of CO₂ for the surface water (as high as 1,000 μatm), and hence the surface water becomes a strong CO₂ source. This is followed by rapid biological uptake of CO₂, which causes the water to become a strong CO₂ sink (Friederich et al., 2002; Hales et al., 2005).

A review of North American coastal carbon fluxes has been carried out by Doney et al. (2004) (Table 15-2). The information reviewed was very limited in space (only 13 locations) and time, leading Doney et al. to conclude that it was unrealistic to reliably estimate an annual flux for North American coastal waters. Measurement programs have increased recently, and we have used the newly available data to calculate annual North American coastal fluxes for the first time.

### Table 15-2. Variability of CO₂ distributions and fluxes in U.S. coastal waters from regional surveys and moored measurements (from Doney et al. 2004).

**Synthesis of Available North American Sea-Air Coastal CO₂ Fluxes**

A large data set consisting of 550,000 measurements of the partial pressure of CO₂ (pCO₂) in surface waters has been assembled and analyzed (Figure 15-3; see Appendix 15A for details). pCO₂ is measured in a carrier gas equilibrated with seawater and, as such, it is a measure of the outflux/influx tendency of CO₂ from the atmosphere. pCO₂ is affected by physical and biological processes increasing with temperature and decreasing with photosynthesis. The data were obtained by the authors and collaborators, quality-controlled, and assembled in a uniform electronic format for analysis (available at www.ldeo.columbia.edu/res/pi/CO2). Observations in each 1° × 1° pixel area were compiled into a single year and were analyzed for time-space variability. Seasonal and interannual variations were not well characterized except in a few locations (Friederich et al., 2002). The annual mean sea-air pCO₂ difference (delta pCO₂) was computed for 5°-wide zones along the North American continent and was plotted as a function of latitude for four regions (Figure 15-4): North Atlantic, Gulf of Mexico/Caribbean, North Pacific, and Bering/Chukchi Seas. Figure 15-4A shows the fluxes in the first nearshore band, and Figure
15-4B shows the fluxes for a band that is several hundred kilometers from shore. The average fluxes for
them and for the intermediate bands are given in Table 15-3. The flux and area data are listed in Table 15-
4. A full complement of seasonal observations are lacking in the Arctic Sea, including Hudson Bay, the
northern Labrador Sea, and the Gulf of St. Lawrence; the northern Bering Sea; the Gulf of Alaska; the
Gulf of California; and the Gulf of Mexico and the Caribbean Sea.

Figure 15-3. (A). Distribution of coastal CO\textsubscript{2} partial pressure measurements made between 1979 and
2004. (B). The distribution of the net sea-air CO\textsubscript{2} flux over 1° × 1° pixel areas (N-S 100 km, E-W 80
km) around North America. The flux (grams of carbon per square meter per year) represents the
climatological mean over the 25-year period. The magenta-blue colors indicate that the ocean water is a
sink for atmospheric CO\textsubscript{2}, and the green-yellow-orange colors indicate that the sea is a CO\textsubscript{2} sink. The data
were obtained by the authors and collaborators of this chapter and are archived at the Lamont-Doherty
Earth Observatory (www.ldeo.columbia.edu/res/pi/CO2).

Figure 15-4. Estimated sea-air CO\textsubscript{2} fluxes (grams of carbon per square meter per year) from 550,000
seawater CO\textsubscript{2} partial pressure (pCO\textsubscript{2}) observations made from 1979 to 2004 in ocean waters
surrounding the North American continent. (A) Waters within one degree (about 80 km) of the coast
and (B) open ocean waters between 300 and 900 km from the shore (see Figure 15-3B). The annual mean
sea-air pCO\textsubscript{2} difference (delta pCO\textsubscript{2}) values were calculated from the weekly mean atmospheric CO\textsubscript{2}
concentrations in the GLOBALVIEW-CO\textsubscript{2} database (2004) over the same pixel area in the same week and
year as the seawater pCO\textsubscript{2} was measured. The monthly net sea-air CO\textsubscript{2} flux was computed from the mean
monthly wind speeds in the National Centers for Environmental Prediction/National Center for
Atmospheric Research (NCEP/NCAR) database in the (wind speed)\textsuperscript{2} formulation for the sea-air gas
transfer rate by Wanninkhof (1992). The ± uncertainties represent one standard deviation.

Table 15-3. Climatological mean annual sea-air CO\textsubscript{2} flux (g C m\textsuperscript{-2} yr\textsuperscript{-1}) over the oceans surrounding
North America. Negative values indicate that the ocean is a CO\textsubscript{2} sink for the atmosphere. N is the number
of seawater pCO\textsubscript{2} measurements. The ± uncertainty is given by one standard deviation of measurements
used for analysis and represents primarily the seasonal variability.

The offshore patterns follow the same general trend found in the global data set shown in Figure 15-1.
On an annual basis the lower latitudes tend to be a source of CO\textsubscript{2} to the atmosphere, whereas the higher
latitudes tend to be sinks (Figures 15-3B and 15-4B). The major difference in the coastal waters is that the
latitude where CO\textsubscript{2} starts to enter the ocean is further north than it is in the open ocean, particularly in the
Atlantic. A more detailed region-by-region description follows.
Pacific Ocean

Observations made in waters along the Pacific coast of North America illustrate how widely coastal waters vary in space and time, in this case driven by upwelling and relaxation (Friederich et al., 2002). Figure 15-5A shows a summertime quasi-synoptic distributions of temperature, salinity, and pCO2 in surface waters based on measurements made for July through September 2005. The effects of the Columbia River plume emanating from ~46°N are clearly seen (colder temperature, low salinity, and low pCO2), as are coastal upwelling effects off Cape Mendocino (~40°N) (colder, high salinity, and very high pCO2). These coastal features are confined to within 300 km from the coast. The 1997–2005 time-series data for surface water pCO2 observed off Monterey Bay (Figure 15-5B) show the large, rapidly fluctuating sea-air CO2 fluxes during the summer upwelling season in each year as well as the low-pCO2 periods during the 1997–1998 and 2002–2003 El Niño events. In spite of the large seasonal variability, ranging from 200 to 750 µatm, the annual mean sea-air pCO2 difference and the net CO2 flux over the waters off Monterey Bay areas (~37°N) are close to zero (Pennington et al., in press). The seasonal amplitude decreases away from the shore and in the open ocean bands, where the sea-air CO2 flux changes seasonally in response to seawater temperature (out of the ocean in summer and into the ocean in winter).

Figure 15-5. Time-space variability of coastal waters off the west coast of North America. (A) Quasi-synoptic distribution of the temperature, salinity, and pCO2 in surface waters during July–September 2005. The Columbia River plume (~46°N) and the upwelling of deep waters off the Cape Mendocino (~40°N) are clearly seen. (B) 1997–2005 time-series data for sea-air CO2 flux from a mooring off Monterey Bay, California. Seawater is a CO2 source for the atmosphere during the summer upwelling events, but biological uptake reduces levels very rapidly. These rapid fluctuations can affect atmospheric CO2 levels. For example, if CO2 from the sea is mixed into a static column, a 500-m-thick planetary boundary layer over the course of one day, atmospheric CO2 concentration would change by 2.5 µatm. If the column of air is mixed vertically through the troposphere to 500 mbar, a change of about 0.5 µatm would occur. The effects would be diluted as the column of air mixes laterally. However, this demonstrates that the large fluctuations of sea-air CO2 flux observed over coastal waters could affect the concentration of CO2 significantly enough to affect estimates of air-land flux based on the inversion of atmospheric CO2 data. Sea-air CO2 flux was low during the 1997–1998 and 2002–2003 El Niño periods.

The open ocean Pacific waters south of 30°N are on the annual average a CO2 source to the atmosphere, whereas the area north of 40°N is a sink, and the zone between 30° and 40°N is neutral (Takahashi et al., 2002). Coastal waters in the 40°N through 45°N zone (northern California-Oregon coasts) are even a stronger CO2 sink, associated with nutrient input and stratification by the Columbia
River (Hales et al., 2005). On the other hand, coastal pCO₂ values in the 15°N through 40°N zones have pCO₂ values similar to open ocean values and to the atmosphere. In the zones 15°N through 40°N, the annual mean values for the net sea-air CO₂ flux are nearly zero, consistent with the finding by Pennington et al. (in press).

**Atlantic Ocean**

With the exception of the 5°N–10°N zone, the open ocean areas are an annual net sink for atmospheric CO₂. The open oceans become more intense CO₂ sinks toward higher latitudes, especially north of 35°N (Figure 15-3B). Between 15°N and 45°N, the open ocean waters are a CO₂ sink (Takahashi et al., 2002), whereas the nearshore waters are a CO₂ source. Accordingly, in contrast to the Pacific coast, the latitude where Atlantic coastal waters become a CO₂ sink is located further north than that for the open ocean fluxes. In the areas north of 45°N, the open ocean waters are a strong CO₂ sink due primarily to the cold Labrador Sea waters.

In the coastal zone very high pCO₂ values (up to 2,600 μatm) are observed occasionally in areas within 10 km offshore of the barrier islands. These waters have salinities around 20 and appear to represent outflow of estuarine/marsh waters rich in carbon (Cai et al., 2003). The large contribution of fresh water that is rich in organic matter relative to the Pacific contributes to the coastal Atlantic source. Offshore fluxes are in phase with the seasonal cycle of warming and cooling; fluxes are out of the ocean in summer and fall and are the inverse in winter and spring.

**Bering and Chukchi Seas**

Although measurements in these high-latitude waters are limited, the relevant data for the Bering Sea (south of 65°N) and Chukchi Sea (north of 65°N) are plotted as a function of the latitude in Figure 15-4. The values for the areas north of 55°N are for the summer months only; CO₂ observations are not available during winter seasons. Although data scatter widely, the coastal and open ocean waters are a strong CO₂ sink during the summer months due to photosynthetic draw-down of CO₂. The data in the 70°–75°N zone are from the shallow shelf areas in the Chukchi Sea. These waters are a very strong CO₂ sink (sea-air pCO₂ differences ranging from −80 to −180 μatm) with little changes between the coastal and open ocean areas. The sea-air CO₂ flux during winter months is not known.

**Gulf of Mexico and Caribbean Sea**

Although observations are limited, available data suggest that these waters are a strong CO₂ source (Figure 15-4 and Table 15-3). A subsurface anoxic zone has been formed in the Texas-Louisiana coast as a result of the increased addition of anthropogenic nutrients and organic carbon by the Mississippi River
(e.g., Lohrenz et al., 1999). The carbon-nutrient cycle in the northern Gulf of Mexico is also being investigated (e.g., Cai, 2003), and the studies suggest that at times those waters are locally a strong CO2 sink due to high biological production.

SYNTHESIS

An analysis of half a million measurements of sea-air flux of CO2 shows that the nearshore (< 100 km) coastal waters surrounding North America are a net CO2 source for the atmosphere on an annual average of about 19 ± 22 Mt C yr⁻¹ (Table 15-4). Most of the flux (14 ± 9 Mt C yr⁻¹) occurs in the Gulf of Mexico and Caribbean Sea. The open oceans are a net CO2 sink on an annual average (Table 15-4; Takahashi et al., 2004). The results do not include some portions of the Arctic Sea, Bering Sea, Gulf of Alaska, Gulf of Mexico, or Caribbean Sea because of insufficient data. Observations in these areas will be needed to improve estimates. These results are consistent with recent global estimates that suggest that nearshore areas receiving terrestrial organic carbon input are sources of CO2 to the atmosphere and that marginal seas are sinks (Borges, 2005; Borges et al., in press). Hence, the net contribution from North American ocean margins is small and difficult to distinguish from zero. It is not clear how much of the open ocean sink results from photosynthesis driven by nutrients of coastal origin.

Table 15-4. Areas (km²) and mean annual sea-air CO2 flux (Mt C yr⁻¹) over four ocean regions surrounding North America. Since the observations in the areas north of 60°N in the Chukchi Sea were made only during the summer months, the fluxes from that area are not included. The ± uncertainty is given by one standard deviation of measurements used for analysis and represents primarily the seasonal variability.

TRENDS AND DRIVERS

The sea-to-air CO2 flux from the coastal zone is small (about 1%) compared with the global ocean uptake flux, which is about 2,000 Mt C yr⁻¹ (or 2 Gt C yr⁻¹), and hence does not influence the global air-sea CO2 budget. However, coastal waters undergo large variations in sea-air CO2 flux on daily to seasonal time scales and on small spatial scales (Figure 15-5). Fluxes can change on the order of 250 g C m⁻² yr⁻¹ or 0.7 g C m⁻² day⁻¹ on a day to day basis (Figure 15-5). These large fluctuations can significantly modulate atmospheric CO2 concentrations over the adjacent continent and need to be considered when using the distribution of CO2 in calculations of continental fluxes.

Freshwater bodies have not been treated in this analysis except to note the large surface pCO2 resulting from estuaries along the east coast. The Great Lakes and rivers also represent net sources of CO2 as, in the same manner as the estuaries, organic material from the terrestrial environment is oxidized so
that respiration exceeds photosynthesis. Interestingly, the effect of fresh water is opposite along the coast of the Pacific northwest, where increased stratification and iron inputs enhance photosynthetic activity (Ware and Thomson, 2005), resulting in a large sink for atmospheric CO₂ (Figure 15-3). A similar process may be at work at the mouth of the Amazon (Körtzinger, 2003). This emphasizes once again the important role of biological processes in controlling the sea-air fluxes of CO₂.

The sea-air fluxes and the underlying carbon cycle processes that determine them (Figure 15-2) vary seasonally, interannually, and on longer time scales. The eastern Pacific, including the U.S. west coast, is subject to changes associated with large-scale climate oscillations such as El Niño (Chavez et al., 1999; Feely et al., 2002; Feely et al., in press) and the Pacific Decadal Oscillation (PDO) (Chavez et al., 2003; Hare and Mantua, 2000; Takahashi et al., 2003). These climate patterns, and others like the North Atlantic Oscillation (NAO), alter the oceanic CO₂ sink/source conditions directly through seawater temperature changes as well as ecosystem variations that occur via complex physical-biological interactions (Hare and Mantua, 2000; Chavez et al., 2003; Patra et al., 2005). For example, during El Niño, upwelling of high CO₂ waters is dramatically reduced along central California (Figure 15-5) but so is photosynthetic uptake of CO₂ (Chavez et al. 2002) so the net effect of climate variability and change on sea-air fluxes remains uncertain. What is certain is that the biological, chemical and physical processes controlling the sea-air fluxes of CO₂ are strongly affected by natural and anthropogenic change and that efforts to track them need to be considered in global carbon management plans.

OPTIONS AND MEASURES

Two options for ocean carbon sequestration have been considered: (1) deep-sea injection of CO₂ (Brewer, 2003) and (2) ocean iron fertilization (Martin, 1990). The first might be viable in North American coastal waters, although cost and potential biological side effects are unresolved issues. The largest potential for iron fertilization resides in the equatorial Pacific and the Southern Ocean, although it could be considered for the open ocean waters of the Gulf of Alaska and offshore waters of coastal upwelling systems. Iron fertilization would be an economical alternative, but there is still disagreement over how much carbon would be sequestered (Bakker et al., 2001; Boyd et al., 2000; Coale et al., 2004; Gervais et al., 2002) and what the potential side effects would be (Chisholm et al., 2001).

R&D NEEDS VIS A VIS OPTIONS

Waters with highly variable sea-air CO₂ fluxes are located primarily within 100 km of the coast (Figure 15-5). With the exception of a few areas, the available observations are grossly inadequate to resolve the high-frequency, small-spatial-scale variations. These high intensity sea-air CO₂ flux events may introduce errors in continental CO₂ fluxes calculated by atmospheric inversion methods. Achieving a
comprehensive understanding of the carbon cycle in waters surrounding the North American continent will require development of advanced technologies and sustained research efforts. Both of these seem to be on the horizon with (1) the advent of ocean observatories that include novel fixed and mobile platforms together with developing instrumentation to measure critical stocks and fluxes and (2) national and international research programs that include the Integrated Ocean Observing System (IOOS) and Ocean Carbon and Climate Change (OC³). Given the importance of aquatic systems to atmospheric CO₂ concentrations, these developing efforts must be strongly encouraged. Ocean carbon sequestration studies should also be continued.

REFERENCES


Borges, A.V. (2005) Do we have enough pieces of the jigsaw to integrate CO₂ fluxes in the Coastal Ocean?, Estuaries, 28, 3–27.


Table 15-1. Climatological mean distribution of the net sea-air CO₂ flux (in Gt C yr⁻¹) over the global ocean regions (excluding coastal areas) in reference year 1995. The fluxes are based on about 1.75 million partial pressure measurements for CO₂ in surface ocean waters, excluding the measurements made in the equatorial Pacific (10°N- 10°S) during El Niño periods (see Takahashi et al., 2002). The NCAR/NCEP 42-year mean wind speeds and the (wind speed)² dependence for sea-air gas transfer rate are used (Wanninkhof, 1992). Plus signs indicate that the ocean is a source for atmospheric CO₂, and negative signs indicate that ocean is a sink. The ocean uptake has also been estimated on the basis of the following methods: temporal changes in atmospheric oxygen and CO₂ concentrations (Keeling and Garcia, 2002; Bender et al., 2005), ¹³C/¹²C ratios in sea and air (Battle et al., 2000; Quay et al., 2003), ocean CO₂ inventories (Sabine et al., 2004), and coupled carbon cycle and ocean general circulation models (Sarmiento et al., 2000; Gruber and Sarmiento, 2002). The consensus is that the oceans take up 1.3 to 2.3 Gt C yr⁻¹.

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<th>Southern Ocean</th>
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</tr>
</tbody>
</table>
**Table 15-2. Variability of CO₂ distributions and fluxes in U.S. coastal waters from regional surveys and moored measurements (from Doney et al., 2004)**

<table>
<thead>
<tr>
<th>Location</th>
<th>Surface seawater pCO₂ (μatm)</th>
<th>Instantaneous CO₂ flux (mol/m² yr⁻¹)</th>
<th>Annual average (mol m⁻² yr⁻¹)</th>
<th>Sampling method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Jersey Coast</td>
<td>211–658</td>
<td>−17 to +12</td>
<td>−0.65</td>
<td>Regional survey</td>
<td>Boehme et al. (1998)</td>
</tr>
<tr>
<td>Cape Hatteras, North Carolina</td>
<td>ND*</td>
<td>−1.0 to +1.2</td>
<td>ND</td>
<td>Moored meas.</td>
<td>DeGrandpre et al. (1997)</td>
</tr>
<tr>
<td>Middle Atlantic Bight, inner shelf</td>
<td>150–620</td>
<td>ND</td>
<td>−0.9</td>
<td>Regional survey</td>
<td>DeGrandpre et al. (2002)</td>
</tr>
<tr>
<td>Middle Atlantic Bight, middle shelf</td>
<td>220–480</td>
<td>ND</td>
<td>−1.6</td>
<td>Regional survey</td>
<td>DeGrandpre et al. (2002)</td>
</tr>
<tr>
<td>Middle Atlantic Bight, outer shelf</td>
<td>300–430</td>
<td>ND</td>
<td>−0.7</td>
<td>Regional survey</td>
<td>DeGrandpre et al. (2002)</td>
</tr>
<tr>
<td>Florida Bay, Florida</td>
<td>325–725</td>
<td>ND</td>
<td>ND</td>
<td>Regional survey</td>
<td>Millero et al. (2001)</td>
</tr>
<tr>
<td>Southern California Coastal Fronts</td>
<td>130–580</td>
<td>ND</td>
<td>ND</td>
<td>Regional survey</td>
<td>Simpson (1985)</td>
</tr>
<tr>
<td>Oregon Coast</td>
<td>250–640</td>
<td>ND</td>
<td>ND</td>
<td>Regional survey</td>
<td>van Geen et al. (2000)</td>
</tr>
<tr>
<td>Bering Sea Shelf in spring (April–June)</td>
<td>130–400</td>
<td>−8 to −12</td>
<td>−8</td>
<td>Regional survey</td>
<td>Codispoti et al. (1986)</td>
</tr>
<tr>
<td>South Atlantic Bight</td>
<td>300–1200</td>
<td>ND</td>
<td>2.5</td>
<td>Regional survey</td>
<td>Cai et al. (2003)</td>
</tr>
<tr>
<td>Miss. River Plume (summer)</td>
<td>80–800</td>
<td>ND</td>
<td>ND</td>
<td>Regional survey</td>
<td>Cai et al. (2003)</td>
</tr>
<tr>
<td>Bering Sea (Aug–Sep.)</td>
<td>192–400</td>
<td>ND</td>
<td>ND</td>
<td>Regional survey</td>
<td>Park et al. (1974)</td>
</tr>
</tbody>
</table>

* ND = no data available
Table 15-3. Climatological mean annual sea-air CO₂ flux (g C m⁻² yr⁻¹) over the oceans surrounding North America. Negative values indicate that the ocean is a CO₂ sink for the atmosphere. N is the number of seawater pCO₂ measurements. The ± uncertainty is given by one standard deviation of measurements used for analysis and represents primarily the seasonal variability.

<table>
<thead>
<tr>
<th>Ocean regions</th>
<th>Coastal boxes</th>
<th>First offshore</th>
<th>Second offshore</th>
<th>Third offshore</th>
<th>Open ocean</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flux</td>
<td>N</td>
<td>Flux</td>
<td>N</td>
<td>Flux</td>
</tr>
<tr>
<td>North Atlantic</td>
<td>3.2± 142</td>
<td>80,417</td>
<td>−1.4± 94</td>
<td>65,148</td>
<td>−7.3± 57</td>
</tr>
<tr>
<td>North Pacific</td>
<td>−0.2± 105</td>
<td>164,838</td>
<td>−6.0± 81</td>
<td>69,856</td>
<td>−4.3± 66</td>
</tr>
<tr>
<td>G. Mexico Caribbean</td>
<td>9.4± 24</td>
<td>75,496</td>
<td>8.4± 23</td>
<td>61,180</td>
<td>11.5± 17.0</td>
</tr>
<tr>
<td>Bering/Chukchi</td>
<td>28.0± 110</td>
<td>892</td>
<td>−28± 128</td>
<td>868</td>
<td>−44± 104</td>
</tr>
</tbody>
</table>
Table 15-4. Areas (km$^2$) and mean annual sea-air CO$_2$ flux (Mt C yr$^{-1}$) over four ocean regions surrounding North America. Since the observations in the areas north of 60$^\circ$N in the Chukchi Sea were made only during the summer months, the fluxes from that area are not included. The ± uncertainty is given by one standard deviation of measurements used for analysis and represents primarily the seasonal variability.

<table>
<thead>
<tr>
<th>Ocean areas (km$^2$)</th>
<th>Coastal boxes</th>
<th>First offshore</th>
<th>Second offshore</th>
<th>Third offshore</th>
<th>Open ocean</th>
<th>Coast box</th>
<th>First offshore</th>
<th>Second offshore</th>
<th>Third offshore</th>
<th>Open ocean</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>North Atlantic coast (8$^\circ$ N to 45$^\circ$N)</strong></td>
<td>625,577</td>
<td>651,906</td>
<td>581,652</td>
<td>572,969</td>
<td>3,388,500</td>
<td>2.7±9.5</td>
<td>-0.5±9.3</td>
<td>-4.0±4.9</td>
<td>-6.5±6.3</td>
<td>-41.5±28.1</td>
</tr>
<tr>
<td><strong>North Pacific coast (8$^\circ$N to 55$^\circ$N)</strong></td>
<td>1,211,555</td>
<td>855,626</td>
<td>874,766</td>
<td>646,396</td>
<td>7,007,817</td>
<td>2.1±17.1</td>
<td>-7.0±14.1</td>
<td>-4.8±12.5</td>
<td>-3.7±5.3</td>
<td>-53.8±60.7</td>
</tr>
<tr>
<td><strong>Gulf of Mexico and Caribbean Sea (8$^\circ$N to 30$^\circ$N)</strong></td>
<td>1,519,335</td>
<td>1,247,413</td>
<td>935,947</td>
<td>1,008,633</td>
<td>13.6±8.9</td>
<td>10.9±7.5</td>
<td>6.8±5.0</td>
<td>6.6±5.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Bering and Chukchi Seas (50$^\circ$N to 70$^\circ$N)</strong></td>
<td>481,872</td>
<td>311,243</td>
<td>261,974</td>
<td>117,704</td>
<td>227,609</td>
<td>0.8±3.1</td>
<td>-6.2±9.5</td>
<td>-5.3±7.5</td>
<td>-3.7±3.0</td>
<td>-9.8±3.7</td>
</tr>
<tr>
<td><strong>Total ocean areas surrounding North America</strong></td>
<td>3,838,339</td>
<td>3,066,188</td>
<td>2,654,339</td>
<td>2,300,702</td>
<td>10,623,926</td>
<td>19.1±21.8</td>
<td>-2.8±20.7</td>
<td>-7.4±16.2</td>
<td>-7.3±10.1</td>
<td>-105.2±67.0</td>
</tr>
</tbody>
</table>
Figure 15-1. Global distribution of air-sea CO₂ flux. The white line represents zero flux and separates sources and sinks. The sources are primarily in the tropics (yellow and red) with a few areas of deep mixing at high latitudes. Updated from Takahashi et al. (2002).
Figure 15-2. In the top panel, mean air/sea CO₂ flux is calculated from shipboard measurements on a line perpendicular to the central California coast. Flux within Monterey Bay (~0–20 km offshore) is into the ocean, flux across the active upwelling region (~20–75 km offshore) is from the ocean, and flux in the California Current (75–300 km) is on average into the ocean. These fluxes result from the processes shown in the bottom panel. California Undercurrent water, which has a high CO₂ partial pressure, upwells near shore, and is advected offshore into the California Current and into Monterey Bay. Phytoplankton growing in the upwelled water use CO₂ as a carbon source, and CO₂ is drawn to low levels in those areas. Phytoplankton carbon eventually sinks or is subducted below the euphotic zone, where it decays, elevating the CO₂ levels of subsurface waters. Where the level of surface CO₂ is higher than the level of atmospheric CO₂, diffusion drives CO₂ into the atmosphere. Conversely, where the level of surface CO₂ is lower than that of atmospheric CO₂, diffusion drives CO₂ into the ocean. The net sea/air flux on this spatial scale is near zero. DIC = dissolved inorganic carbon; POC = particulate organic carbon. Updated from Pennington et al. (in press).
Figure 15-3. (A). Distribution of coastal CO$_2$ partial pressure measurements made between 1979 and 2004.
(B). The distribution of the net sea-air CO$_2$ flux over 1° × 1° pixel areas (N-S 100 km, E-W 80 km) around North America. The flux (grams of carbon per square meter per year) represents the climatological mean over the 25-year period. The magenta-blue colors indicate that the ocean water is a sink for atmospheric CO$_2$, and the green-yellow-orange colors indicate that the sea is a CO$_2$ sink. The data were obtained by the authors and collaborators of this chapter and are archived at the Lamont-Doherty Earth Observatory (www.ldeo.columbia.edu/res/pi/CO2).
Figure 15-4. Estimated sea-air CO₂ fluxes (grams of carbon per square meter per year) from 550,000 seawater CO₂ partial pressure (pCO₂) observations made from 1979 to 2004 in ocean waters surrounding the North American continent. (A) Waters within one degree (about 80 km) of the coast and (B) open ocean waters between 300 and 900 km from the shore (see Figure 15-3B). The annual mean sea-air pCO₂ difference (delta pCO₂) values were calculated from the weekly mean atmospheric CO₂ concentrations in the GLOBALVIEW-CO₂ database (2004) over the same pixel area in the same week and year as the seawater pCO₂ was measured. The monthly net sea-air CO₂ flux was computed from the mean monthly wind speeds in the National Centers for Environmental Prediction/National Center for Atmospheric Research (NCEP/NCAR) database in the (wind speed)² formulation for the sea-air gas transfer rate by Wanninkhof (1992). The ± uncertainties represent one standard deviation.
Figure 15-5. Time-space variability of coastal waters off the west coast of North America. (A) Quasi-synoptic distribution of the temperature, salinity, and pCO$_2$ in surface waters during July–September 2005. The Columbia River plume (~46°N) and the upwelling of deep waters off the Cape Mendocino (~40°N) are clearly seen. (B) 1997–2005 time-series data for sea-air CO$_2$ flux from a mooring off Monterey Bay, California. Seawater is a CO$_2$ source for the atmosphere during the summer upwelling events, but biological uptake reduces levels very rapidly. These rapid fluctuations can affect atmospheric CO$_2$ levels. For example, if CO$_2$ from the sea is mixed into a static column, a 500-m-thick planetary boundary layer over the course of one day, atmospheric CO$_2$ concentration would change by 2.5 µatm. If the column of air is mixed vertically through the troposphere to 500 mbar, a change of about 0.5 µatm would occur. The effects would be diluted as the column of air mixes laterally. However, this demonstrates that the large fluctuations of sea-air CO$_2$ flux observed over coastal waters could affect the concentration of CO$_2$ significantly enough to affect estimates of air-land flux based on the inversion of atmospheric CO$_2$ data. Sea-air CO$_2$ flux was low during the 1997–1998 and 2002–2003 El Niño periods.
Appendix 15A

Database and Methods

A database for pCO₂, temperature and salinity in surface waters within about 1,000 km from the shore of the North American continent has been assembled. About 550,000 seawater pCO₂ observations were made from 1979 to 2004 by the authors and collaborators of Chapter 15. The pCO₂ data have been obtained by a method using an infrared gas analyzer or gas-chromatograph for the determination of CO₂ concentrations in a carrier gas equilibrated with seawater at a known temperature and total pressure. The precision of pCO₂ measurements has been estimated to be about ± 0.7% on average. The quality-controlled data are archived at www.ldeo.columbia.edu/res/pi/CO2.

The zonal distribution of the surface water pCO₂, sea surface temperature (SST), and salinity data shows that the greatest variability is confined within 300 km from the shores of both the Atlantic and Pacific. Observations made in various years were combined into a single year and were averaged into 1° × 1° pixels (approximately N-S 100 km by E-W 80 km) for the analysis. Accordingly, the results represent a climatological mean condition over the past 25 years. Finer resolutions (10 × 10 km) may be desirable for some areas close to shore because of outflow of estuarine and river waters and upwelling. However, for this study, which is aimed at a broad picture of waters surrounding the continent, the fine scale measurements have been incorporated into the 1° × 1° pixels. In addition, data with salinities of less than 16.0 are considered to be inland waters and have been excluded from the analysis.

Climatological monthly and annual mean values for pCO₂ in each zone where computed first. Then the sea-air pCO₂ difference, which represents the thermodynamic driving potential for sea-air CO₂ gas transfer, was estimated using the atmospheric CO₂ concentration data. Finally, the net sea-air CO₂ flux was computed using transfer coefficients estimated on the basis of climatological mean monthly wind speeds using the (wind speed)² formulation of Wanninkhof (1992). The transfer coefficient depends on the state of turbulence above and below the sea-air interface and is commonly parameterized as a function of wind speeds (corrected to 10 m above the sea surface). However, selection of wind data is problematic because wind speeds vary with the time scale (hourly, diurnal, or seasonal). For example, fluxes calculated for the South Atlantic Bight from 6-h mean wind speeds in the NCEP/NCAR version 2 file (1° × 1° mean) were lower than those estimated using the monthly mean. This discrepancy suggests that ships used commonly for coastal carbon studies tend to be small and hence are rarely at sea under high wind conditions, so observations are biased toward lower winds. Taking into account that the observations have been made infrequently over multiple years, the gas transfer coefficients estimated from climatological mean monthly wind speeds may be more representative. The Schmidt number is computed using
measured SST and climatological mean salinity (Da Silva et al. 1994). The flux values in a given month are then averaged to yield a climatological mean flux (and standard deviation) for each month. This procedure assumes implicitly that the seawater pCO₂ changes at much slower rates in space and time than the wind speed and that the seawater pCO₂ does not correlate with the wind speed.