Chapter 15. Coastal Oceans

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KEY FINDINGS

- The combustion of fossil fuels has increased CO_2 in the atmosphere, and by diffusion the oceans have absorbed an equivalent of 20-30% of the released CO_2 on an annual basis. The present annual uptake by the oceans of 1.3-2.3 Gt C is well constrained, has slightly acidified the oceans and may ultimately affect ocean ecosystems in unpredictable ways.
- The carbon budgets of ocean margins (coastal regions) are not as 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 anthropogenic carbon stored in the coastal regions of North America or to predict future scenarios.
- New air-sea flux observations reveal that on average, nearshore waters surrounding North America are neither a source nor a sink of CO_2 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 $\pm$ 22 Mt C yr^{-1}. This equates to 1% of the global ocean uptake.
- With the exception of one or two time-series sites, almost nothing is known about historical trends in air-sea 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.
- 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. Ocean carbon sequestration studies should be continued.

- Highly variable air-sea CO_2 fluxes in coastal areas may introduce errors in North American CO_2 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 first introduces the role the oceans play in modulating atmospheric carbon dioxide (CO_2), then quantifies air-sea CO_2 fluxes in coastal waters surrounding North America and considers how the underlying processes affect the air-sea fluxes. 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 carbon compound transformations, and limited data on these processes. The oceans act as a huge reservoir for inorganic carbon, containing about 50 times as much CO_2 as the atmosphere. The ocean's biological pump converts CO_2 to organic particulate carbon by photosynthesis, transports the organic carbon from the surface by sinking, and therefore plays a critical role in removing atmospheric CO_2 in combination with physical and chemical processes (Gruber and Sarmiento, 2002; Sarmiento and Gruber, 2006). Atmospheric concentration of CO_2 would be much higher in the absence of current ocean processes implying that climate-driven changes in ocean circulation, chemical properties or biological rates could result in strong feedbacks to the atmosphere.

The release of CO_2 into the atmosphere by the combustion of fossil fuels has increased pre-industrial concentrations from around 280 ppm to present day levels of 380 ppm. This increase in atmospheric concentrations is driving more CO_2 into the ocean with the present net air-sea CO_2 flux well constrained to about 1,800 ± 500 Mt C [1 Mt = one million (10^6) metric tons] or 1.8 ± 0.5 Gt C yr^{-1} [1 Gt = one billion (10^9) 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 uptake of this anthropogenically-driven CO_2 by the oceans is on average turning them more acidic with negative and potentially catastrophic effects on some biota (Kleypas *et al.*, 2006). The atmosphere is well mixed and nearly homogenous so the large spatial variability in air-sea CO_2 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 air-sea flux of CO_2 in coastal waters surrounding the North American continent.

Table 15-1. Climatological mean distribution of the net air-sea CO_2 flux (in Gt C yr^{-1}) over the global ocean (excluding coastal areas) in reference year 1995. Positive values indicate a source for atmospheric CO_2, and negative values indicate a sink. 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°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 air-sea gas transfer rate are used (Wanninkhof, 1992) for calculating the air-sea flux. The flux, however, depends on the wind speed and air-sea gas transfer rate parameterizations used, and varies by about ± 30% (Takahashi *et al*., 2002). 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 map yields a total annual air-to-sea flux of 1.5 Gt C yr^{-1}. The white line represents zero flux and separates sources (yellow and red) and sinks (blue and purple). Negative values indicate that the ocean is a CO_2 sink for the atmosphere. 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 air-sea 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 towards the California Current and into Monterey Bay. Phytoplankton growth and photosynthesis draw down CO_2 in seawater to low levels in the upwelled water. Phytoplankton carbon eventually sinks or is subducted below the euphotic zone, where it decays, elevating the CO_2 levels of subsurface waters. Where the level of surface seawater CO_2 is higher than the atmosphere, CO_2 is driven into the atmosphere. Conversely, where the level of surface CO_2 is lower than that of atmospheric CO_2, CO_2 is driven from the atmosphere 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: CO_2 dissolved in water, organic carbon dissolved in water, particulate inorganic carbon (e. g. calcium carbonate, $CaCO_3$), 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 CO_2 (or 384 Mt C yr^{-1}), 25% as dissolved organic matter, 21% as organic particles and 17% as $CaCO_3$ particles (Gattuso *et al.*, 1998). Estimates for the riverine dissolved CO_2 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 CO_2 (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 CO_2 and thus complicating the accurate quantification of air-sea CO_2 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 CO_2 removal by primary productivity of 1,200 Mt C yr^{-1} and a large CO_2 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 CO_2 sink of 100 Mt C yr^{-1}, about one-ninth of the estimate by Ducklow and McCallister (2004). Since the estimated air-sea CO_2 flux depends on quantities that are not well constrained, the mass balance provides widely varying results. For this reason, in this chapter the net air-sea flux over coastal waters is estimated on the basis of direct measurements of the air-sea difference of partial pressure of CO_2 (pCO_2).

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) (Cai *et al*., 2003) 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-CO_2 waters to the surface. In both environments, the biological uptake of CO_2 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 CO_2 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 CO_2 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 CO_2 for the surface water (as high as 1,000 μatm), and hence the surface water becomes a strong CO_2 source. This is followed by rapid biological uptake of CO_2, which causes the water to become a strong CO_2 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 air-sea fluxes for the first time.

Table 15-2. Variability of CO_2 distributions and fluxes in U.S. coastal waters from regional surveys and moored measurements (from Doney *et al.* 2004). Negative values indicate that the ocean is a CO_2 sink for the atmosphere.

Synthesis of Available North American Air-Sea Coastal CO_2 Fluxes

A large data set consisting of 550,000 measurements of the partial pressure of CO_2 (pCO_2) in surface waters has been assembled and analyzed (Figure 15-3; see Appendix 15A for details). pCO_2 is measured in a carrier gas equilibrated with seawater and, as such, it is a measure of the outflux/influx tendency of CO_2 from the atmosphere. CO_2 reacts with seawater and 99.5% of the total amount of CO_2 dissolved in seawater is in the form of bicarbonate (HCO_3^-) and carbonate ions ($CO_3^{=}$), which do not exchange with the overlying atmosphere. Only CO_2 molecules, which constitute about 0.5% of the total dissolved CO_2, exchange with the atmosphere. This is expressed as pCO_2, which 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 air-sea pCO_2 difference (ΔpCO_2) 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_2 partial pressure measurements made between 1979 and 2004. (B). The distribution of the net air-sea 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 air-sea CO_2 fluxes (grams of carbon per square meter per year) from 550,000 seawater CO_2 partial pressure (pCO_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 air-sea pCO_2 difference (ΔpCO_2) values were calculated from the weekly mean atmospheric CO_2

concentrations in the GLOBALVIEW-CO2 database (2004) over the same pixel area in the same week and year as the seawater pCO_2 was measured. The monthly net air-sea CO_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 $(\text{wind speed})^2$ formulation for the air-sea gas transfer rate by Wanninkhof (1992). Negative values indicate that the ocean is a CO_2 sink for the atmosphere. The ± uncertainties represent one standard deviation.

Table 15-3. Climatological mean annual air-sea CO_2 flux (grams of carbon per square meter per year) over the oceans surrounding North America. Negative values indicate that the ocean is a CO_2 sink for the atmosphere. N is the number of seawater pCO_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 open ocean data set shown in Figure 15-1. On an annual basis the lower latitudes tend to be a source of CO_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_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 pCO_2 in surface waters based on measurements made in 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 pCO_2), as are coastal upwelling effects off Cape Mendocino (~40°N) (colder, high salinity, and very high pCO_2). These coastal features are confined to within 300 km from the coast. The 1997–2005 time-series data for surface water pCO_2 observed off Monterey Bay (Figure 15-5B) show the large, rapidly fluctuating air-sea CO_2 fluxes during the summer upwelling season in each year as well as the low-pCO_2 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 air-sea pCO_2 difference and the net CO_2 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 air-sea CO_2 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 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 air-sea CO_2 flux from a mooring off Monterey Bay, California (the fluxes are reported in grams of carbon per square meter per year so they can be compared to values throughout the chapter). Seawater is a CO_2 source for the atmosphere during the summer upwelling events, but biological uptake reduces levels very rapidly. The rapid fluctuations seen in (B) 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 air-sea 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. Air-sea CO_2 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 CO_2 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 CO_2 sink, associated with nutrient input and stratification by fresh water from the Columbia River (Hales *et al.*, 2005). On the other hand, coastal pCO_2 values in the 15°N through 40°N zones have pCO_2 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 air-sea CO_2 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 CO_2 with stronger sinks at high latitudes, especially north of 35°N (Figure 15-3B). In contrast the nearshore waters are a CO_2 source between 15°N and 45°N. Accordingly, in contrast to the Pacific coast, the latitude where Atlantic coastal waters become a CO_2 sink is located further north. In the areas north of 45°N, the open ocean waters are a strong CO_2 sink due primarily to the cold Labrador Sea waters.

In the coastal zone very high pCO_2 values (up to 2,600 μatm) are observed occasionally in areas within 10 km offshore of the barrier islands (see small red dots off the coasts of Georgia and Carolinas in Figures 15-3B). These waters which have salinities around 20 and high total CO_2 concentrations 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 this small 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; CO_2 observations are not available during winter seasons. Although data scatter widely, the coastal and open ocean waters are a strong CO_2 sink during the summer months due to photosynthetic drawdown of CO_2. The data in the 70°–75°N zone are from the shallow shelf areas in the Chukchi Sea. These waters are a very strong CO_2 sink (air-sea pCO_2 differences ranging from −80 to −180 μatm) with little changes between the coastal and open ocean areas. The air-sea CO_2 flux during winter months is not known but the summer fluxes are shown in Figure 15-4 for comparison.

Gulf of Mexico and Caribbean Sea

Although observations are limited, available data suggest that these waters are a strong CO_2 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 CO_2 sink due to high biological production.

SYNTHESIS

An analysis of half a million measurements of air-sea flux of CO_2 shows that the nearshore (< 100 km) coastal waters surrounding North America are a net CO_2 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 CO_2 sink on an annual average (Table 15-4; Takahashi *et al.*, 2004). The reported uncertainties reflect the time-space variability but do not reflect uncertainties due to lack of observations in some portions of the Arctic Sea, Bering Sea, Gulf of Alaska, Gulf of Mexico, or Caribbean Sea. 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 CO_2 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 (km^2) and mean annual air-sea CO_2 flux (Mt C yr^{-1}) over four ocean regions surrounding North America. Negative values indicate that the ocean is a CO_2 sink for the atmosphere. 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 CO_2 flux from the coastal zone is small (about 1%) compared with the global ocean uptake flux, which is about 2,000 Mt C y^{-1} (or 2 Gt C yr^{-1}), and hence does not influence the global air-sea CO_2 budget. However, coastal waters undergo large variations in air-sea CO_2 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 CO_2 concentrations over the adjacent continent and need to be considered when using the distribution of CO_2 in calculations of continental fluxes.

Freshwater bodies have not been treated in this analysis except to note the large surface pCO_2 resulting from estuaries along the east coast. The Great Lakes and rivers also represent net sources of CO_2 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 CO_2 (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 air-sea fluxes of CO_2.

The air-sea 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.*, 2006) 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 CO_2 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 CO_2 waters is dramatically reduced along central California (Figure 15-5) so that

flux out of the ocean is reduced. At the same time photosynthetic uptake of CO_2 is also reduced (Chavez *et al*. 2002) reducing ocean uptake. The net effect of climate variability on air-sea fluxes therefore remains uncertain and depends on the time-space integral of the processes.

OPTIONS AND MEASURES

Two options for ocean carbon sequestration have been considered: (1) deep-sea injection of CO_2 (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. However, 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 air-sea CO_2 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 air-sea CO_2 flux events may introduce errors in continental CO_2 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, sustained and inter-disciplinary 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 (OC^3). Given the importance of aquatic systems to atmospheric CO_2 concentrations, these developing efforts must be strongly encouraged. Ocean carbon sequestration studies should also be continued.

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Table 15-1. Climatological mean distribution of the net air-sea 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°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 air-sea 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}

Latitude bands	Pacific	Atlantic	Indian	Southern Ocean	Global
N of 50°N	+0.01	–0.31			–0.30
14°N-50°N	–0.49	–0.25	+0.05		–0.69
14°N-14°S	+0.65	+0.13	+0.13		+0.91
14°S-50°S	–0.39	–0.21	–0.52		–1.12
S of 50°S				–0.30	–0.30
Total flux	–0.23	–0.64	–0.34	–0.30	–-1.50
% of flux	15	42	23	20	100
Area (10^6 km^2)	152.0	74.6	53.0	41.1	320.7
% of area	47	23	17	13	100

Table 15-2. Variability of CO_2 distributions and fluxes in U.S. coastal waters from regional surveys and moored measurements (from Doney *et al.*, 2004)

Location	Surface seawater pCO_2 (µatm)	Instantaneous CO_2 flux (mol/m^{-2} yr^{-1})	Annual average (mol m^{-2} yr^{-1})	Sampling method	Reference
New Jersey Coast	211–658	–17 to +12	–0.65	Regional survey	Boehme *et al.* (1998)
Cape Hatteras, North Carolina	ND*	–1.0 to +1.2	ND	Moored meas.	DeGrandpre *et al.* (1997)
Middle Atlantic Bight, inner shelf	150–620	ND	–0.9	Regional survey	DeGrandpre *et al.* (2002)
Middle Atlantic Bight, middle shelf	220–480	ND	–1.6	Regional survey	DeGrandpre *et al.* (2002)
Middle Atlantic Bight, outer shelf	300–430	ND	–0.7	Regional survey	DeGrandpre *et al.* (2002)
Florida Bay, Florida	325–725	ND	ND	Regional survey	Millero *et al.* (2001)
Southern California Coastal Fronts	130–580	ND	ND	Regional survey	Simpson (1985)
Coastal Calif. (M-1; Monterey Bay)	245–550	–8 to +50	1997–98: –1.0 1998–99: +1.1	Moored meas.	Friederich *et al.* (2002)
Oregon Coast	250–640	ND	ND	Regional survey	van Geen *et al.* (2000)
Bering Sea Shelf in spring (April–June)	130–400	–8 to –12	–8	Regional survey	Codispoti *et al.* (1986)
South Atlantic Bight	300–1200	ND	2.5	Regional survey	Cai *et al.* (2003)
Miss. River Plume (summer)	80–800	ND	ND	Regional survey	Cai *et al.* (2003)
Bering Sea (Aug–Sep.)	192–400	ND	ND	Regional survey	Park *et al.* (1974)

* ND = no data available

Table 15-3. Climatological mean annual air-sea CO_2 flux (g C m^{-2} yr^{-1}) over the oceans surrounding North America. Negative values indicate that the ocean is a CO_2 sink for the atmosphere. N is the number of seawater pCO_2 measurements. The ± uncertainty is given by one standard deviation of measurements used for analysis and represents primarily the seasonal variability.

Ocean regions	Coastal boxes		First offshore		Second offshore		Third offshore		Open ocean	
	Flux	N	Flux	N	Flux	N	Flux	N	Flux	N
North Atlantic	3.2± 142	80,417	–1.4± 94	65,148	–7.3± 57	35,499	–10.4± 76.4	15,771	–26± 83	37,667
North Pacific	–0.2± 105	164,838	–6.0± 81	69,856	–4.3± 66	32,045	–5.3± 60	16,174	–1.2± 56	84,376
G. Mexico Caribbean	9.4± 24	75,496	8.4± 23	61,180	11.5± 17.0	8,410	13± 20	1,646		
Bering/ Chukchi	28.0± 110	892	–28± 128	868	–44± 104	3,399	–53± 110	1,465	–63± 130	1,848

Table 15-4. Areas (km^2) and mean annual air-sea CO_2 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.

Ocean areas (km^2)					Mean air-sea CO_2 flux (10^{12} grams or Mt C yr^{-1})				
Coastal boxes	**First offshore**	**Second offshore**	**Third offshore**	**Open ocean**	**Coast box**	**First offshore**	**Second offshore**	***Third offshore***	**Open ocean**
North Atlantic coast (8° N to 45°N)									
625,577	651,906	581,652	572,969	3,388,500	2.7±9.5	-0.5±9.3	-4.0±4.9	-6.5±6.3	-41.5±28.1
North Pacific coast (8°N to 55°N)									
1,211,555	855,626	874,766	646,396	7,007,817	2.1±17.1	-7.0±14.1	-4.8±12.5	-3.7±5.3	-53.8±60.7
Gulf of Mexico and Caribbean Sea (8°N to 30°N)									
1,519,335	1,247,413	935,947	1,008,633		13.6±8.9	10.9±7.5	6.8±5.00	6.6±5.0	
Bering and Chukchi Seas (50°N to 70°N)									
481,872	311,243	261,974	117,704	227,609	0.8±3.1	-6.2±9.5	-5.3±7.5	-3.7±3.0	-9.8±3.7
Total ocean areas surrounding North America									
3,838,339	3,066,188	2,654,339	2,300,702	10,623,926	19.1±21.8	-2.8±20.7	-7.4±16.2	-7.3±10.1	-105.2±67.0

1

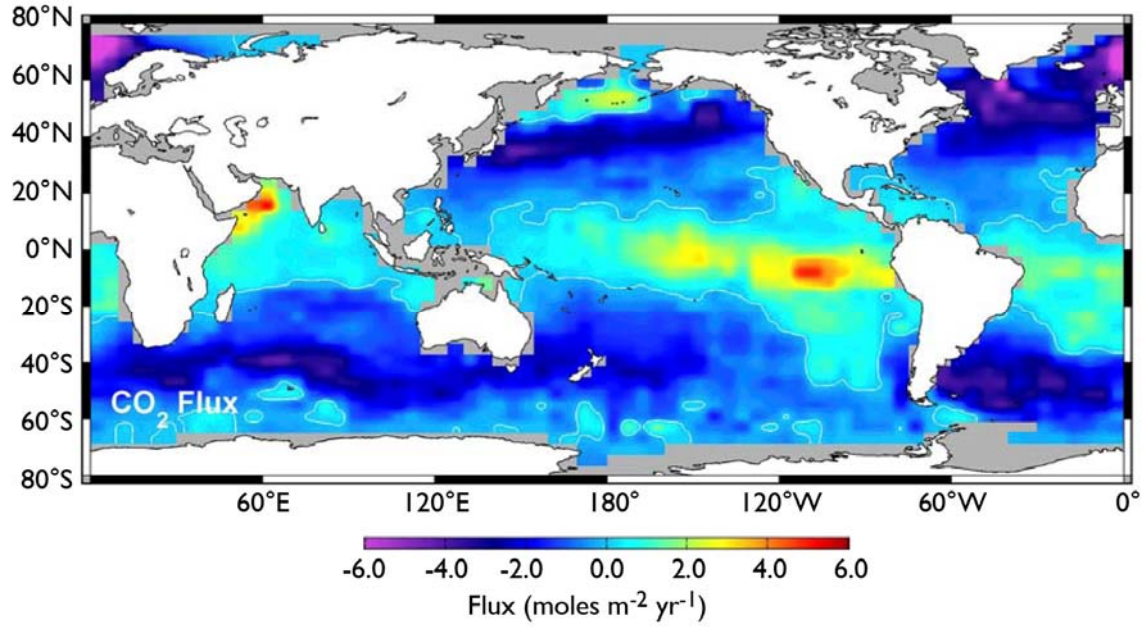


Figure 15-1. Global distribution of air-sea CO_2 flux. The white line represents zero flux and separates sources and sinks. The sources are primarily in the tropics (yellow and red) with a few areas of deep mixing at high latitudes. Updated from Takahashi *et al.* (2002).

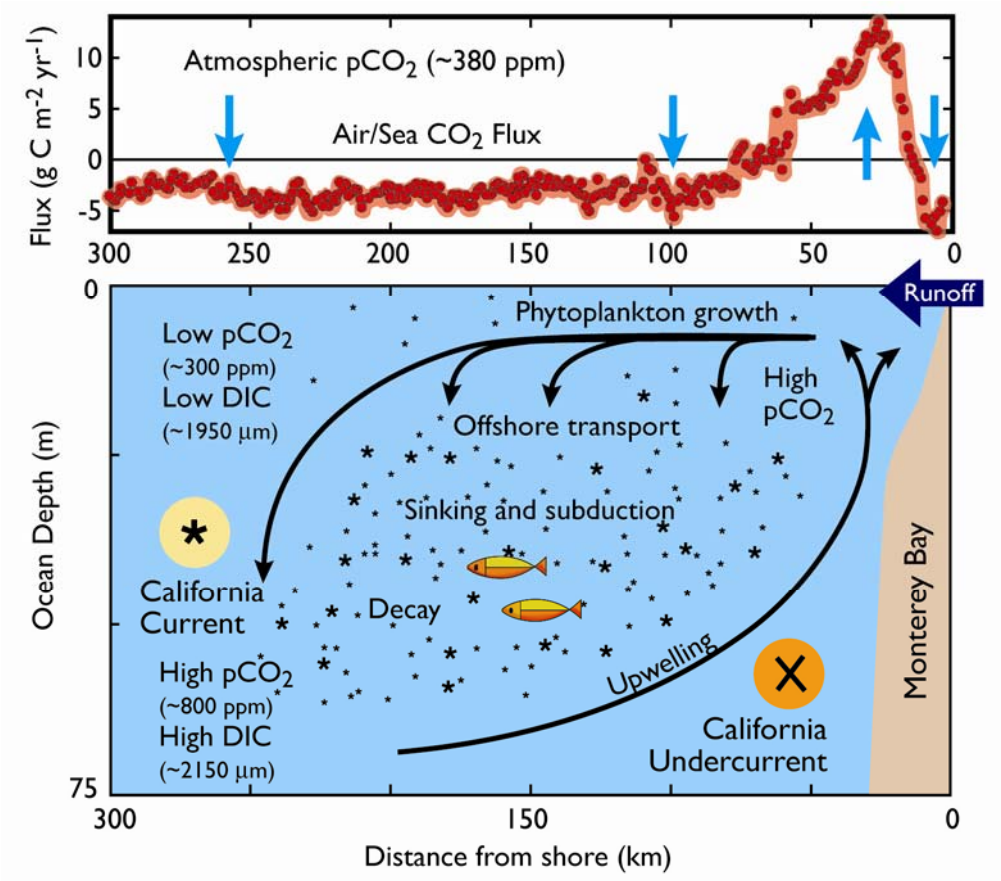
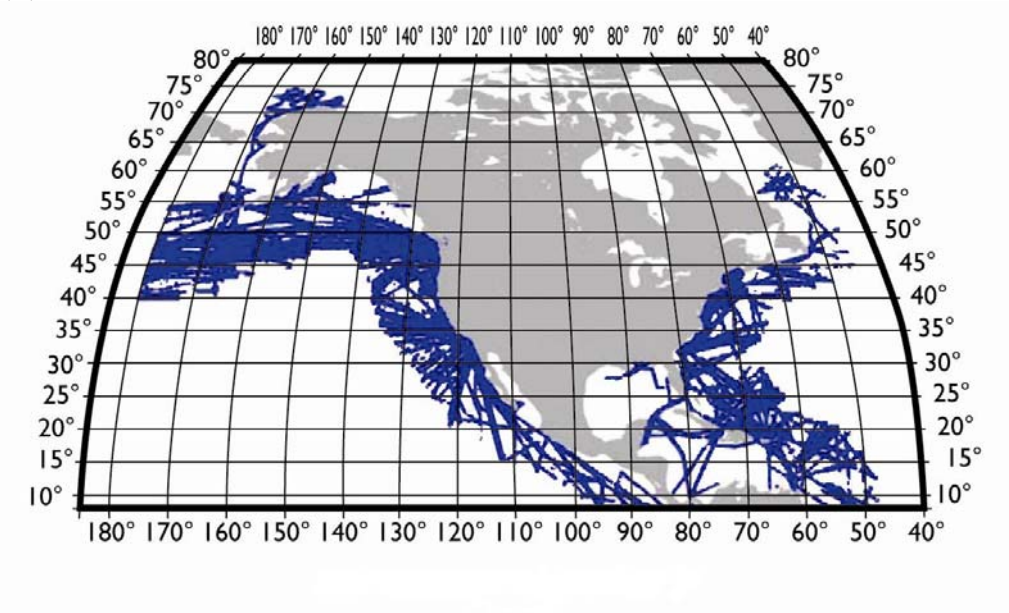


Figure 15-2. In the top panel, mean air-sea CO_2 flux is calculated from shipboard measurements on a line perpendicular to the central California coast. Flux within Monterey Bay (~0–20 km offshore) is into the ocean, flux across the active upwelling region (~20–75 km offshore) is from the ocean, and 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 CO_2 levels of subsurface waters. Where the level of surface CO_2 is higher than the level of atmospheric CO_2, diffusion drives CO_2 into the atmosphere. Conversely, where the level of surface CO_2 is lower than that of atmosphericCO_2, diffusion drives CO_2 into the ocean. The net air-sea flux on this spatial scale is near zero. DIC = dissolved inorganic carbon; POC = particulate organic carbon. Updated from Pennington et al. (in press).

1
2

(A)



(B)

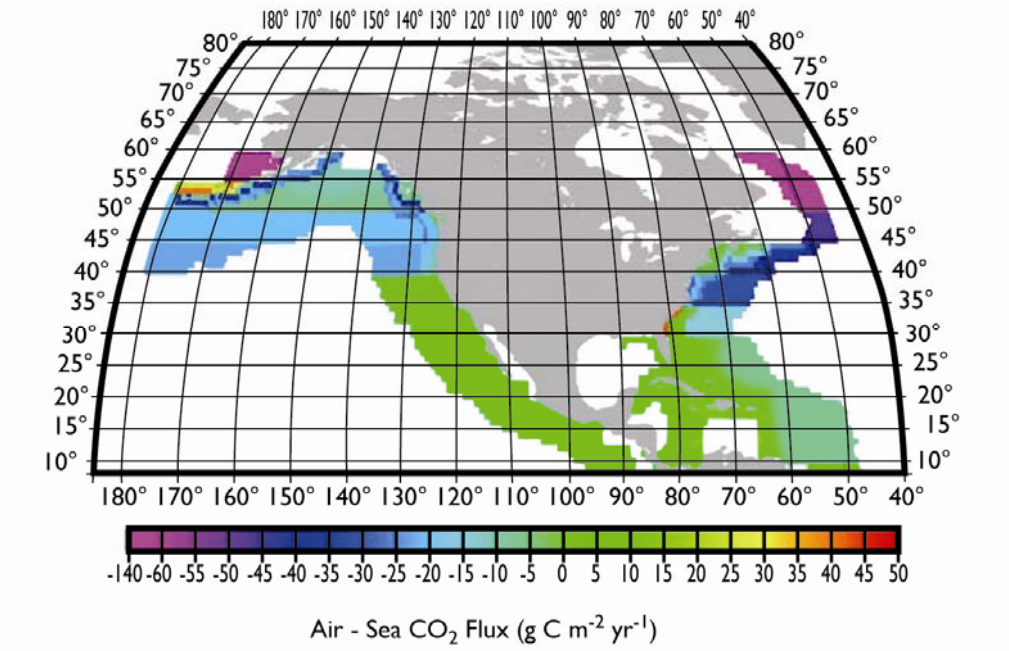
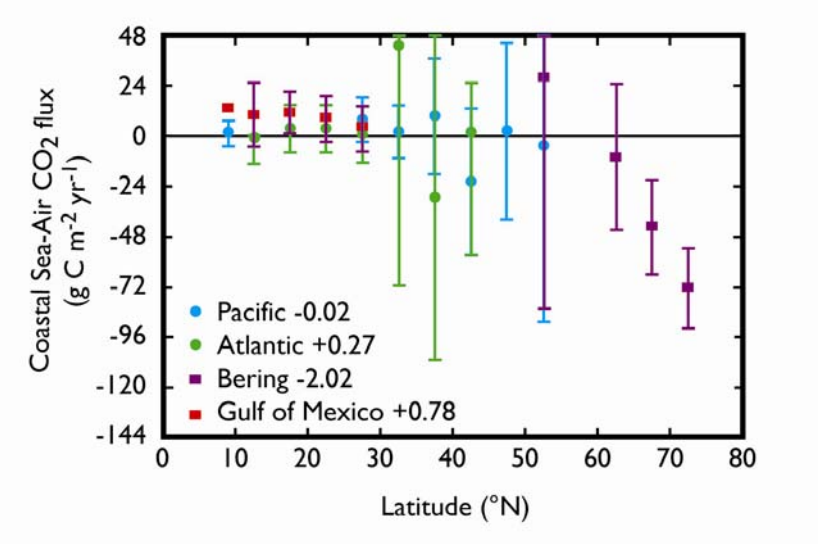


Figure 15-3. (A). Distribution of coastal CO_2 partial pressure measurements made between 1979 and 2004. (B). The distribution of the net air-sea CO_2 flux over 1° × 1° pixel areas (N-S 100 km, E-W 80 km) around North America. The flux (grams of carbon per square meter per year) represents the climatological 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).

1

(A)



(B)

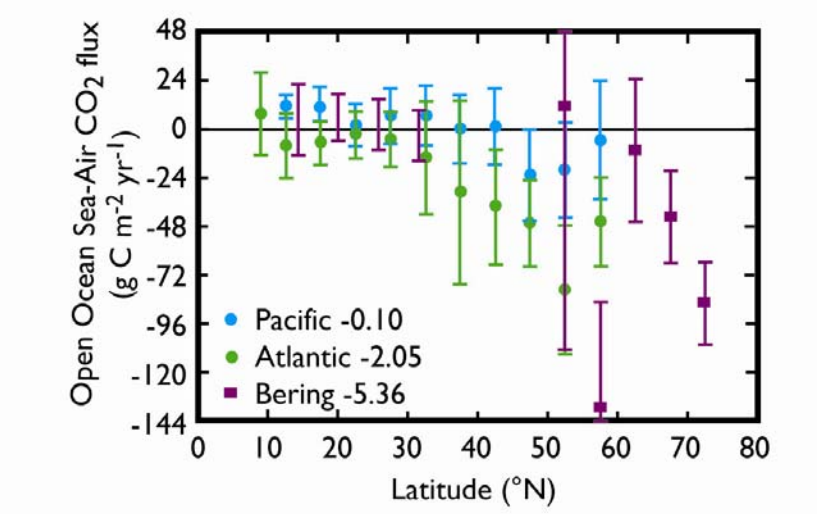
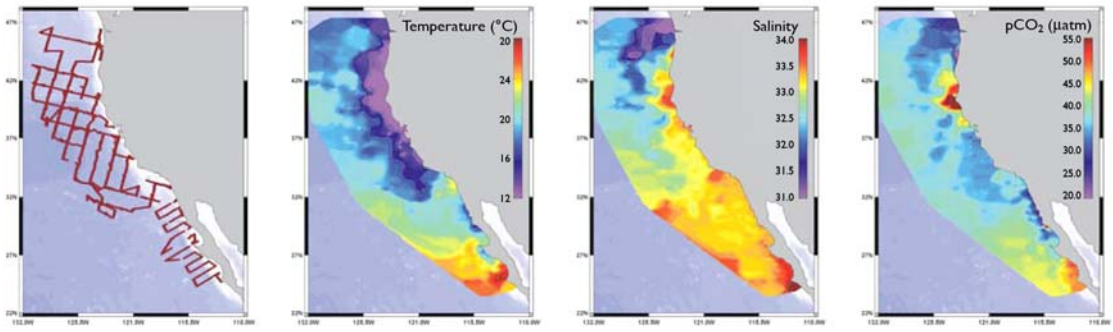


Figure 15-4. Estimated air-sea CO_2 fluxes (grams of carbon per square meter per year) from 550,000 seawater CO_2 partial pressure (pCO_2) observations made from 1979 to 2004 in ocean waters surrounding the North American continent. (A) Waters within one degree (about 80 km) of the coast and (B) open ocean waters between 300 and 900 km from the shore (see Figure 15-3B). The annual mean air-sea pCO_2 difference (delta pCO_2) values were calculated from the weekly mean atmospheric CO_2 concentrations in the GLOBALVIEW-CO2 database (2004) over the same pixel area in the same week and year as the seawater pCO_2 was measured. The monthly net air-sea CO_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)^2 formulation for the air-sea gas transfer rate by Wanninkhof (1992). The ± uncertainties represent one standard deviation.

1

(A)



(B)

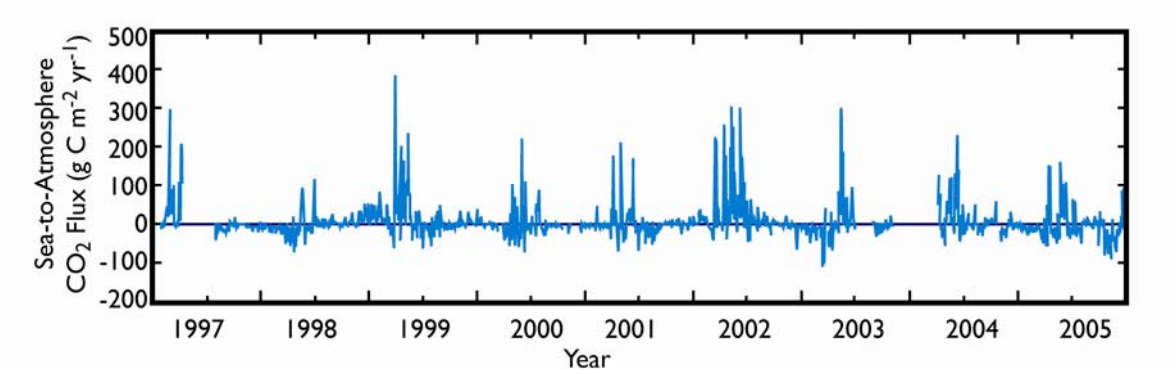


Figure 15-5. Time-space variability of coastal waters off the west coast of North America. (A) Quasi-synoptic distribution of the temperature, salinity, and pCO_2 in surface waters during July–September 2005. The Columbia River plume (~46°N) and the upwelling of deep waters off the Cape Mendocino (~40°N) are clearly seen. (B) 1997–2005 time-series data for air-sea 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 air-sea 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. Air-sea CO_2 flux was low during the 1997–1998 and 2002–2003 El Niño periods.

2

Appendix 15A
Database and Methods

A database for pCO_2, 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 pCO_2 observations were made from 1979 to 2004 by the authors and collaborators of Chapter 15. The pCO_2 data have been obtained by a method using an infrared gas analyzer or gas-chromatograph for the determination of CO_2 concentrations in a carrier gas equilibrated with seawater at a known temperature and total pressure. The precision of pCO_2 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 pCO_2, 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 pCO_2 in each zone where computed first. Then the air-sea pCO_2 difference, which represents the thermodynamic driving potential for air-sea CO_2 gas transfer, was estimated using the atmospheric CO_2 concentration data. Finally, the net air-sea CO_2 flux was computed using transfer coefficients estimated on the basis of climatological mean monthly wind speeds using the $(\text{wind speed})^2$ formulation of Wanninkhof (1992). The transfer coefficient depends on the state of turbulence above and below the air-sea 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 pCO_2 changes at much slower rates in space and time than the wind speed and that the seawater pCO_2 does not correlate with the wind speed.

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