

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 CO₂ 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 CO₂ 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 CO₂ in the future or become a sink.
- Options and measures for sequestration of carbon in the ocean include deep-sea injection of CO₂ and iron fertilization, although it is unresolved how important, feasible or acceptable any of these options might be for the North American region.

- 1 • Highly variable sea-air CO₂ fluxes in coastal areas may introduce errors in North American CO₂ fluxes
2 calculated by atmospheric inversion methods. Reducing these errors will require ocean observatories
3 utilizing fixed and mobile platforms with instrumentation to measure critical stocks and fluxes as part
4 of coordinated national and international research programs. Ocean carbon sequestration studies
5 should also be continued.
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9 **INVENTORIES (STOCKS AND FLUXES, QUANTIFICATION)**

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

19 The ocean's biological pump converts inorganic carbon in the upper ocean to organic particulate
20 carbon by photosynthesis, transports the organic carbon from the surface by sinking, and therefore plays a
21 critical role in removing atmospheric CO₂ (Gruber and Sarmiento, 2002) in combination with physical
22 and chemical processes. The net sea-air CO₂ flux over the global ocean appears to be well constrained to
23 be about $1,800 \pm 500$ Mt C [1 Mt = one million (10^6) metric tons] or 1.8 ± 0.5 Gt C yr⁻¹ [1 Gt = one
24 billion (10^9) metric tons] from the atmosphere into the ocean (Figure 15-1 and Table 15-1). (See Chapter
25 2 for a description of how ocean carbon fluxes relate to the global carbon cycle.) The atmosphere is well
26 mixed and nearly homogenous. The large spatial variability in sea-air CO₂ fluxes shown in Figure 15-1 is
27 driven by a combination of physical, chemical, and biological processes in the ocean. The flux over the
28 coastal margins has neither been well characterized (Liu *et al.*, 2000) nor integrated into global
29 calculations because there are large variations over small spatial and temporal scales, and observations
30 have been limited. The need for higher spatial resolution to resolve the coastal variability has hampered
31 modeling efforts. In the following sections we review existing information on the coastal ocean carbon
32 cycle and its relationship to the global ocean, and we present the results of a new analysis of about a half
33 million observations of sea-air flux of CO₂ in coastal waters surrounding the North American continent.

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

13
14 **Figure 15-1. Global distribution of air-sea CO₂ flux.** The white line represents zero flux and separates
15 sources and sinks. The sources are primarily in the tropics (yellow and red) with a few areas of deep mixing
16 at high latitudes. Updated from Takahashi *et al.* (2002).

17 18 **Global Coastal Ocean Carbon Fluxes**

19 The carbon cycle in coastal oceans involves a series of processes, including runoff from terrestrial
20 environments, upwelling and mixing of high CO₂ water from below, photosynthesis at the sea surface,
21 sinking of organic particles, respiration, production and consumption of dissolved organic carbon, and
22 sea-air CO₂ fluxes (Figure 15-2). Although fluxes in the coastal oceans are large relative to surface area,
23 there is disagreement as to whether these regions are a net sink or a net source of CO₂ to the atmosphere
24 (Tsunogai *et al.*, 1999; Cai and Dai, 2004; Thomas *et al.*, 2004). Great uncertainties remain in coastal
25 carbon fluxes, which are complex and dynamic, varying rapidly over short distances and at high
26 frequencies. Only recently have new technologies allowed for the measurement of these rapidly changing
27 fluxes (Friederich *et al.*, 1995 and 2002; Hales and Takahashi, 2004).

28
29 **Figure 15-2. In the top panel, mean air/sea CO₂ flux is calculated from shipboard measurements on a**
30 **line perpendicular to the central California coast.** Flux within Monterey Bay (~0–20 km offshore) is
31 into the ocean, flux across the active upwelling region (~20–75 km offshore) is from the ocean, and flux in
32 the California Current (75–300 km) is on average into the ocean. These fluxes result from the processes
33 shown in the bottom panel. California Undercurrent water, which has a high CO₂ partial pressure, upwells
34 near shore, and is advected offshore into the California Current and into Monterey Bay. Phytoplankton
35 growing in the upwelled water use CO₂ as a carbon source, and CO₂ is drawn to low levels in those areas.
36 Phytoplankton carbon eventually sinks or is subducted below the euphotic zone, where it decays, elevating

1 the CO₂ levels of subsurface waters. Where the level of surface CO₂ is higher than the level of atmospheric
2 CO₂, diffusion drives CO₂ into the atmosphere. Conversely, where the level of surface CO₂ is lower than
3 that of atmospheric CO₂, diffusion drives CO₂ into the ocean. The net sea/air flux on this spatial scale is
4 near zero. DIC = dissolved inorganic carbon; POC = particulate organic carbon. Updated from Pennington
5 *et al.* (in press).

6
7 Carbon is transported from land to sea mostly by rivers in four components: CO₂ dissolved in water,
8 organic carbon dissolved in water, particulate inorganic carbon (e. g. calcium carbonate, CaCO₃), and
9 particulate organic carbon. The global rate of river input has been estimated to be 1,000 Mt C yr⁻¹, about
10 38% of it as dissolved CO₂ (or 384 Mt C yr⁻¹), 25% as dissolved organic matter, 21% as organic particles
11 and 17% as CaCO₃ particles (Gattuso *et al.*, 1998). Estimates for the riverine dissolved CO₂ flux vary
12 from 385 to 429 Mt C yr⁻¹ (Sarmiento and Sundquist, 1992). The Mississippi River, the seventh-largest in
13 freshwater discharge in the world, delivers about 13 Mt C yr⁻¹ as dissolved CO₂ (Cai, 2003). Organic
14 matter in continental shelf sediments exhibits only weak isotope and chemical signatures of terrestrial
15 origin, suggesting that riverine organic matter is reprocessed in coastal environments on a time scale of 20
16 to 130 years (Hedges *et al.*, 1997; Benner and Opsahl, 2001). Of the organic carbon, about 30% is
17 accumulating in estuaries, marshes, and deltas, and a large portion (20% to 60%) of the remaining 70% is
18 readily and rapidly oxidized in coastal waters (Smith and Hollibaugh, 1997). Only about 10% is estimated
19 to be contributed by human activities, such as agriculture and forest clearing (Gattuso *et al.*, 1998), and
20 the rest is a part of the natural carbon cycle.

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

31 32 **North American Coastal Carbon**

33 Two important types of North American coastal ocean environments can be identified: (1) river-
34 dominated coastal margins with large inputs of fresh water, organic matter, and nutrients from land (e.g.,

1 Mid- and South-Atlantic Bights) and (2) coastal upwelling zones (e.g., the California-Oregon-Washington
2 coasts, along the eastern boundary of the Pacific) where physical processes bring cool, high-nutrient and
3 high-CO₂ waters to the surface (Cai *et al.*, 2003). In both environments, the biological uptake of CO₂
4 plays an important role in determining whether an area becomes a sink or a source for the atmosphere.

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

13 A review of North American coastal carbon fluxes has been carried out by Doney *et al.* (2004) (Table
14 15-2). The information reviewed was very limited in space (only 13 locations) and time, leading Doney *et*
15 *al.* to conclude that it was unrealistic to reliably estimate an annual flux for North American coastal
16 waters. Measurement programs have increased recently, and we have used the newly available data to
17 calculate annual North American coastal fluxes for the first time.

18
19 **Table 15-2. Variability of CO₂ distributions and fluxes in U.S. coastal waters from regional surveys**
20 **and moored measurements (from Doney *et al.* 2004).**
21

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

23 A large data set consisting of 550,000 measurements of the partial pressure of CO₂ (pCO₂) in surface
24 waters has been assembled and analyzed (Figure 15-3; see Appendix 15A for details). pCO₂ is measured
25 in a carrier gas equilibrated with seawater and, as such, it is a measure of the outflux/influx tendency of
26 CO₂ from the atmosphere. pCO₂ is affected by physical and biological processes increasing with
27 temperature and decreasing with photosynthesis. The data were obtained by the authors and collaborators,
28 quality-controlled, and assembled in a uniform electronic format for analysis (available at
29 www.ldeo.columbia.edu/res/pi/CO2). Observations in each 1° × 1° pixel area were compiled into a single
30 year and were analyzed for time-space variability. Seasonal and interannual variations were not well
31 characterized except in a few locations (Friederich *et al.*, 2002). The annual mean sea-air pCO₂ difference
32 (delta pCO₂) was computed for 5°-wide zones along the North American continent and was plotted as a
33 function of latitude for four regions (Figure 15-4): North Atlantic, Gulf of Mexico/Caribbean, North
34 Pacific, and Bering/Chukchi Seas. Figure 15-4A shows the fluxes in the first nearshore band, and Figure

1 15-4B shows the fluxes for a band that is several hundred kilometers from shore. The average fluxes for
2 them and for the intermediate bands are given in Table 15-3. The flux and area data are listed in Table 15-
3 4. A full complement of seasonal observations are lacking in the Arctic Sea, including Hudson Bay, the
4 northern Labrador Sea, and the Gulf of St. Lawrence; the northern Bering Sea; the Gulf of Alaska; the
5 Gulf of California; and the Gulf of Mexico and the Caribbean Sea.

6
7 **Figure 15-3. (A). Distribution of coastal CO₂ partial pressure measurements made between 1979 and**
8 **2004. (B). The distribution of the net sea-air CO₂ flux over 1° × 1° pixel areas (N-S 100 km, E-W 80**
9 **km) around North America.** The flux (grams of carbon per square meter per year) represents the
10 climatological mean over the 25-year period. The magenta-blue colors indicate that the ocean water is a
11 sink for atmospheric CO₂, and the green-yellow-orange colors indicate that the sea is a CO₂ sink. The data
12 were obtained by the authors and collaborators of this chapter and are archived at the Lamont-Doherty
13 Earth Observatory (www.ldeo.columbia.edu/res/pi/CO2).

14
15 **Figure 15-4. Estimated sea-air CO₂ fluxes (grams of carbon per square meter per year) from 550,000**
16 **seawater CO₂ partial pressure (pCO₂) observations made from 1979 to 2004 in ocean waters**
17 **surrounding the North American continent.** (A) Waters within one degree (about 80 km) of the coast
18 and (B) open ocean waters between 300 and 900 km from the shore (see Figure 15-3B). The annual mean
19 sea-air pCO₂ difference (delta pCO₂) values were calculated from the weekly mean atmospheric CO₂
20 concentrations in the GLOBALVIEW-CO₂ database (2004) over the same pixel area in the same week and
21 year as the seawater pCO₂ was measured. The monthly net sea-air CO₂ flux was computed from the mean
22 monthly wind speeds in the National Centers for Environmental Prediction/National Center for
23 Atmospheric Research (NCEP/NCAR) database in the (wind speed)² formulation for the sea-air gas
24 transfer rate by Wanninkhof (1992). The ± uncertainties represent one standard deviation.

25
26 **Table 15-3. Climatological mean annual sea-air CO₂ flux (g C m⁻² yr⁻¹) over the oceans surrounding**
27 **North America.** Negative values indicate that the ocean is a CO₂ sink for the atmosphere. N is the number
28 of seawater pCO₂ measurements. The ± uncertainty is given by one standard deviation of measurements
29 used for analysis and represents primarily the seasonal variability.

30
31 The offshore patterns follow the same general trend found in the global data set shown in Figure 15-1.
32 On an annual basis the lower latitudes tend to be a source of CO₂ to the atmosphere, whereas the higher
33 latitudes tend to be sinks (Figures 15-3B and 15-4B). The major difference in the coastal waters is that the
34 latitude where CO₂ starts to enter the ocean is further north than it is in the open ocean, particularly in the
35 Atlantic. A more detailed region-by-region description follows.

1 Pacific Ocean

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

17
18 **Figure 15-5. Time-space variability of coastal waters off the west coast of North America.** (A) Quasi-
19 synoptic distribution of the temperature, salinity, and pCO₂ in surface waters during July–September 2005.
20 The Columbia River plume (~46°N) and the upwelling of deep waters off the Cape Mendocino (~40°N) are
21 clearly seen. (B) 1997–2005 time-series data for sea-air CO₂ flux from a mooring off Monterey Bay,
22 California. Seawater is a CO₂ source for the atmosphere during the summer upwelling events, but
23 biological uptake reduces levels very rapidly. These rapid fluctuations can affect atmospheric CO₂ levels.
24 For example, if CO₂ from the sea is mixed into a static column, a 500-m-thick planetary boundary layer
25 over the course of one day, atmospheric CO₂ concentration would change by 2.5 µatm. If the column of air
26 is mixed vertically through the troposphere to 500 mbar, a change of about 0.5 µatm would occur. The
27 effects would be diluted as the column of air mixes laterally. However, this demonstrates that the large
28 fluctuations of sea-air CO₂ flux observed over coastal waters could affect the concentration of CO₂
29 significantly enough to affect estimates of air-land flux based on the inversion of atmospheric CO₂ data.
30 Sea-air CO₂ flux was low during the 1997–1998 and 2002–2003 El Niño periods.

31
32 The open ocean Pacific waters south of 30°N are on the annual average a CO₂ source to the
33 atmosphere, whereas the area north of 40°N is a sink, and the zone between 30° and 40°N is neutral
34 (Takahashi *et al.*, 2002). Coastal waters in the 40°N through 45°N zone (northern California-Oregon
35 coasts) are even a stronger CO₂ sink, associated with nutrient input and stratification by the Columbia

1 River (Hales *et al.*, 2005). On the other hand, coastal pCO₂ values in the 15°N through 40°N zones have
2 pCO₂ values similar to open ocean values and to the atmosphere. In the zones 15°N through 40°N, the
3 annual mean values for the net sea-air CO₂ flux are nearly zero, consistent with the finding by Pennington
4 *et al.* (in press).

6 **Atlantic Ocean**

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

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

21 **Bering and Chukchi Seas**

22 Although measurements in these high-latitude waters are limited, the relevant data for the Bering Sea
23 (south of 65°N) and Chukchi Sea (north of 65°N) are plotted as a function of the latitude in Figure 15-4.
24 The values for the areas north of 55°N are for the summer months only; CO₂ observations are not
25 available during winter seasons. Although data scatter widely, the coastal and open ocean waters are a
26 strong CO₂ sink during the summer months due to photosynthetic draw-down of CO₂. The data in the
27 70°–75°N zone are from the shallow shelf areas in the Chukchi Sea. These waters are a very strong CO₂
28 sink (sea-air pCO₂ differences ranging from –80 to –180 µatm) with little changes between the coastal
29 and open ocean areas. The sea-air CO₂ flux during winter months is not known.

31 **Gulf of Mexico and Caribbean Sea**

32 Although observations are limited, available data suggest that these waters are a strong CO₂ source
33 (Figure 15-4 and Table 15-3). A subsurface anoxic zone has been formed in the Texas-Louisiana coast as
34 a result of the increased addition of anthropogenic nutrients and organic carbon by the Mississippi River

1 (e.g., Lohrenz *et al.*, 1999). The carbon-nutrient cycle in the northern Gulf of Mexico is also being
2 investigated (e.g., Cai, 2003), and the studies suggest that at times those waters are locally a strong CO₂
3 sink due to high biological production.

4 5 **SYNTHESIS**

6 An analysis of half a million measurements of sea-air flux of CO₂ shows that the nearshore
7 (< 100 km) coastal waters surrounding North America are a net CO₂ source for the atmosphere on an
8 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
9 Gulf of Mexico and Caribbean Sea. The open oceans are a net CO₂ sink on an annual average (Table 15-
10 4; Takahashi *et al.*, 2004). The results do not include some portions of the Arctic Sea, Bering Sea, Gulf of
11 Alaska, Gulf of Mexico, or Caribbean Sea because of insufficient data. Observations in these areas will be
12 needed to improve estimates. These results are consistent with recent global estimates that suggest that
13 nearshore areas receiving terrestrial organic carbon input are sources of CO₂ to the atmosphere and that
14 marginal seas are sinks (Borges, 2005; Borges *et al.*, in press). Hence, the net contribution from North
15 American ocean margins is small and difficult to distinguish from zero. It is not clear how much of the
16 open ocean sink results from photosynthesis driven by nutrients of coastal origin.

17
18 **Table 15-4. Areas (km²) and mean annual sea-air CO₂ flux (Mt C yr⁻¹) over four ocean regions**
19 **surrounding North America.** Since the observations in the areas north of 60°N in the Chukchi Sea were
20 made only during the summer months, the fluxes from that area are not included. The ± uncertainty is given
21 by one standard deviation of measurements used for analysis and represents primarily the seasonal
22 variability.

23 24 **TRENDS AND DRIVERS**

25 The sea-to-air CO₂ flux from the coastal zone is small (about 1%) compared with the global ocean
26 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-
27 sea CO₂ budget. However, coastal waters undergo large variations in sea-air CO₂ flux on daily to seasonal
28 time scales and on small spatial scales (Figure 15-5). Fluxes can change on the order of 250 g C m⁻² yr⁻¹
29 or 0.7 g C m⁻² day⁻¹ on a day to day basis (Figure 15-5). These large fluctuations can significantly
30 modulate atmospheric CO₂ concentrations over the adjacent continent and need to be considered when
31 using the distribution of CO₂ in calculations of continental fluxes.

32 Freshwater bodies have not been treated in this analysis except to note the large surface pCO₂
33 resulting from estuaries along the east coast. The Great Lakes and rivers also represent net sources of CO₂
34 as, in the same manner as the estuaries, organic material from the terrestrial environment is oxidized so

1 that respiration exceeds photosynthesis. Interestingly, the effect of fresh water is opposite along the coast
2 of the Pacific northwest, where increased stratification and iron inputs enhance photosynthetic activity
3 (Ware and Thomson, 2005), resulting in a large sink for atmospheric CO₂ (Figure 15-3). A similar
4 process may be at work at the mouth of the Amazon (Körtzinger, 2003). This emphasizes once again the
5 important role of biological processes in controlling the sea-air fluxes of CO₂.

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

19 20 **OPTIONS AND MEASURES**

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

29 30 **R&D NEEDS VIS A VIS OPTIONS**

31 Waters with highly variable sea-air CO₂ fluxes are located primarily within 100 km of the coast
32 (Figure 15-5). With the exception of a few areas, the available observations are grossly inadequate to
33 resolve the high-frequency, small-spatial-scale variations. These high intensity sea-air CO₂ flux events
34 may introduce errors in continental CO₂ fluxes calculated by atmospheric inversion methods. Achieving a

1 comprehensive understanding of the carbon cycle in waters surrounding the North American continent
2 will require development of advanced technologies and sustained research efforts. Both of these seem to
3 be on the horizon with (1) the advent of ocean observatories that include novel fixed and mobile
4 platforms together with developing instrumentation to measure critical stocks and fluxes and (2) national
5 and international research programs that include the Integrated Ocean Observing System (IOOS) and
6 Ocean Carbon and Climate Change (OC³). Given the importance of aquatic systems to atmospheric CO₂
7 concentrations, these developing efforts must be strongly encouraged. Ocean carbon sequestration studies
8 should also be continued.

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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

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 (10⁶ km²)	152.0	74.6	53.0	41.1	320.7
% of area	47	23	17	13	100

17
18

1 **Table 15-2. Variability of CO₂ distributions and fluxes in U.S. coastal waters from regional surveys and**
 2 **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 <i>et al.</i> (1998)
Cape Hatteras, North Carolina	ND*	-1.0 to +1.2	ND	Moored meas.	DeGrandpre <i>et al.</i> (1997)
Middle Atlantic Bight, inner shelf	150–620	ND	-0.9	Regional survey	DeGrandpre <i>et al.</i> (2002)
Middle Atlantic Bight, middle shelf	220–480	ND	-1.6	Regional survey	DeGrandpre <i>et al.</i> (2002)
Middle Atlantic Bight, outer shelf	300–430	ND	-0.7	Regional survey	DeGrandpre <i>et al.</i> (2002)
Florida Bay, Florida	325–725	ND	ND	Regional survey	Millero <i>et al.</i> (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 <i>et al.</i> (2002)
Oregon Coast	250–640	ND	ND	Regional survey	van Geen <i>et al.</i> (2000)
Bering Sea Shelf in spring (April–June)	130–400	-8 to -12	-8	Regional survey	Codispoti <i>et al.</i> (1986)
South Atlantic Bight	300–1200	ND	2.5	Regional survey	Cai <i>et al.</i> (2003)
Miss. River Plume (summer)	80–800	ND	ND	Regional survey	Cai <i>et al.</i> (2003)
Bering Sea (Aug–Sep.)	192–400	ND	ND	Regional survey	Park <i>et al.</i> (1974)

3 * ND = no data available

1
 2 **Table 15-3. Climatological mean annual sea-air CO₂ flux (g C m⁻² yr⁻¹) over the oceans surrounding North**
 3 **America.** Negative values indicate that the ocean is a CO₂ sink for the atmosphere. N is the number of seawater
 4 pCO₂ measurements. The ± uncertainty is given by one standard deviation of measurements used for analysis and
 5 represents primarily the seasonal variability.

6

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

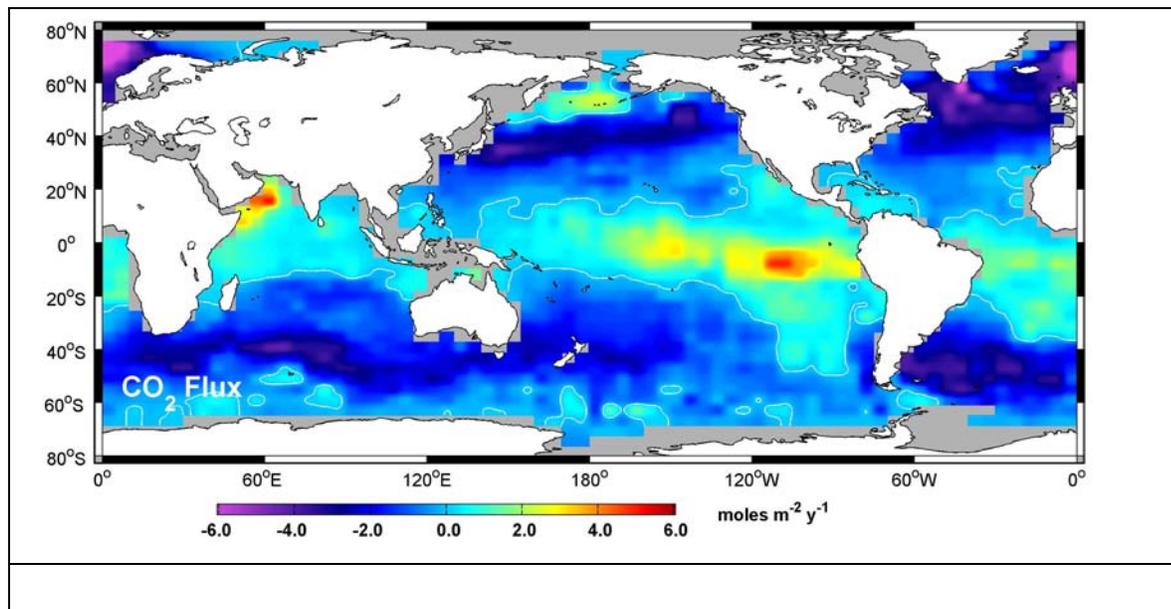
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1
 2 **Table 15-4. Areas (km²) and mean annual sea-air CO₂ flux (Mt C yr⁻¹) over four ocean regions surrounding**
 3 **North America.** Since the observations in the areas north of 60°N in the Chukchi Sea were made only during the
 4 summer months,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

Ocean areas (km ²)					Mean sea-air 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

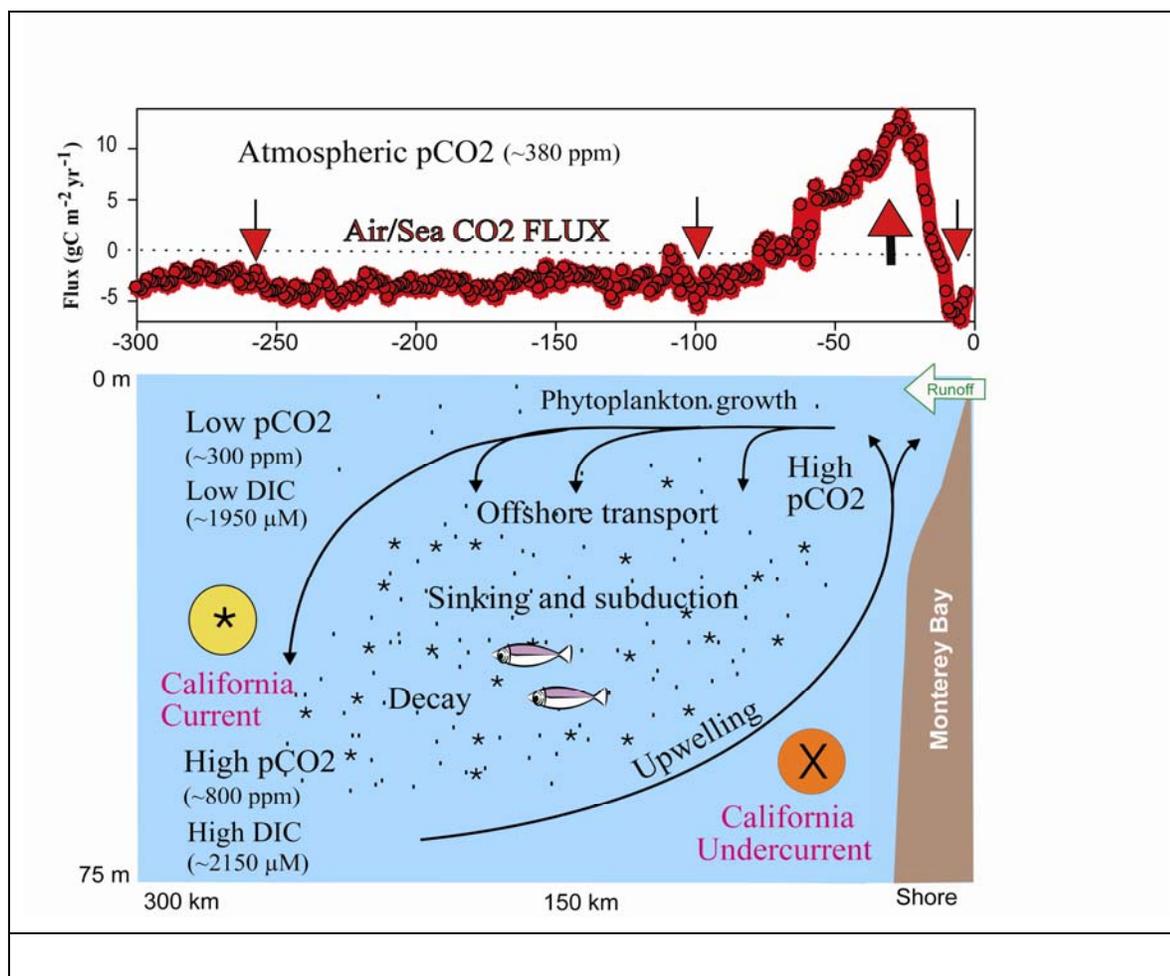
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- 1 **Figure 15-1. Global distribution of air-sea CO₂ flux. The white line represents zero flux and separates sources**
- 2 **and sinks.** The sources are primarily in the tropics (yellow and red) with a few areas of deep mixing at high
- 3 latitudes. Updated from Takahashi *et al.* (2002).

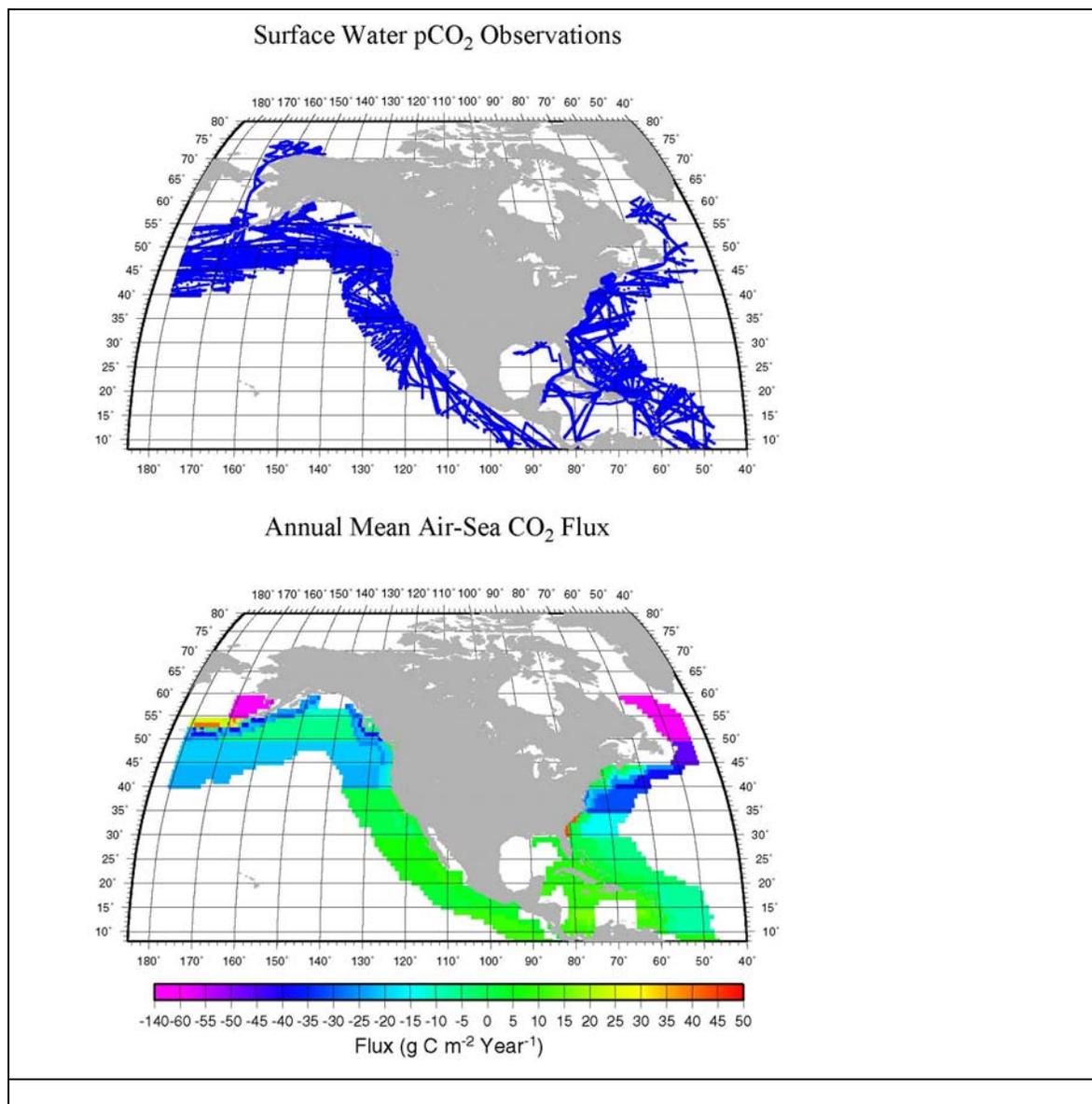


1 **Figure 15-2. In the top panel, mean air/sea CO₂ flux is calculated from shipboard measurements on a line**
 2 **perpendicular to the central California coast.** Flux within Monterey Bay (~0–20 km offshore) is into the ocean,
 3 flux across the active upwelling region (~20–75 km offshore) is from the ocean, and flux in the California Current
 4 (75–300 km) is on average into the ocean. These fluxes result from the processes shown in the bottom panel.
 5 California Undercurrent water, which has a high CO₂ partial pressure, upwells near shore, and is advected offshore
 6 into the California Current and into Monterey Bay. Phytoplankton growing in the upwelled water use CO₂ as a
 7 carbon source, and CO₂ is drawn to low levels in those areas. Phytoplankton carbon eventually sinks or is subducted
 8 below the euphotic zone, where it decays, elevating the CO₂ levels of subsurface waters. Where the level of surface
 9 CO₂ is higher than the level of atmospheric CO₂, diffusion drives CO₂ into the atmosphere. Conversely, where the
 10 level of surface CO₂ is lower than that of atmospheric CO₂, diffusion drives CO₂ into the ocean. The net sea/air flux
 11 on this spatial scale is near zero. DIC = dissolved inorganic carbon; POC = particulate organic carbon. Updated from
 12 Pennington *et al.* (in press).

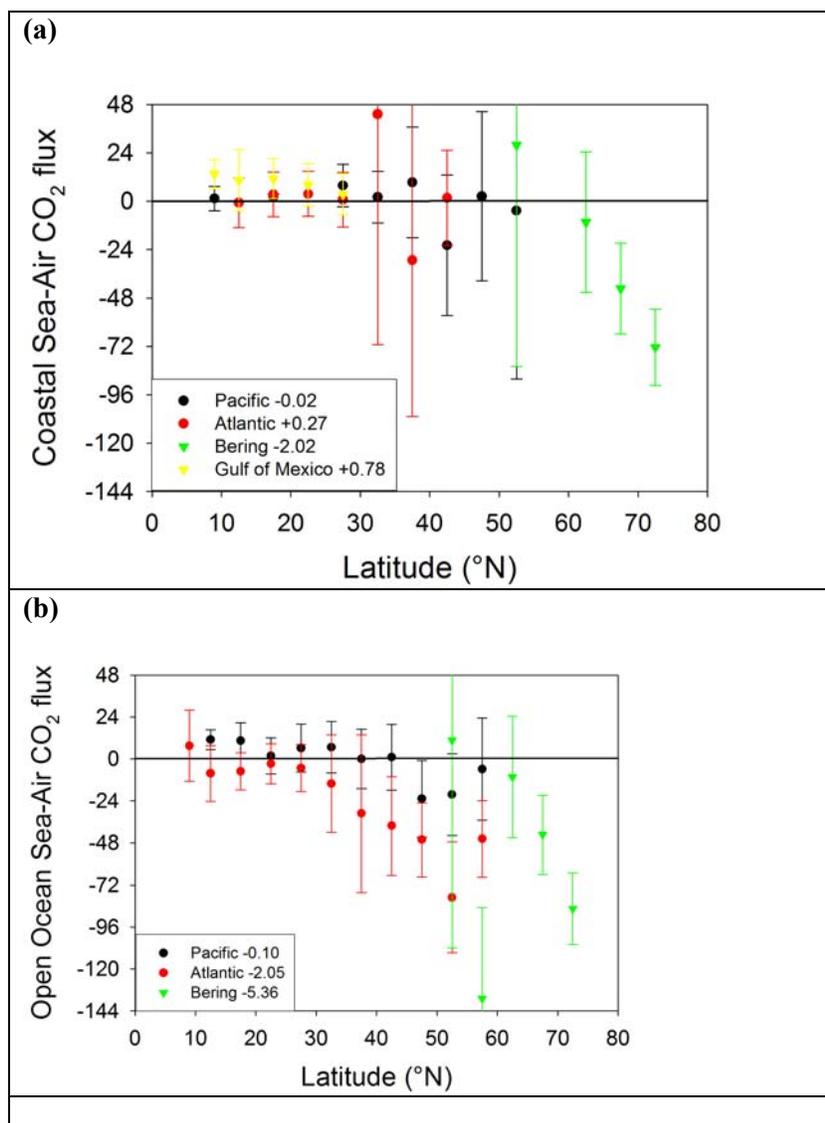
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1 **Figure 15-3. (A). Distribution of coastal CO₂ partial pressure measurements made between 1979 and 2004.**
 2 **(B). The distribution of the net sea-air CO₂ flux over 1° × 1° pixel areas (N-S 100 km, E-W 80 km) around**
 3 **North America.** The flux (grams of carbon per square meter per year) represents the climatological mean over the
 4 25-year period. The magenta-blue colors indicate that the ocean water is a sink for atmospheric CO₂, and the green-
 5 yellow-orange colors indicate that the sea is a CO₂ sink. The data were obtained by the authors and collaborators of
 6 this chapter and are archived at the Lamont-Doherty Earth Observatory (www.ldeo.columbia.edu/res/pi/CO2).
 7

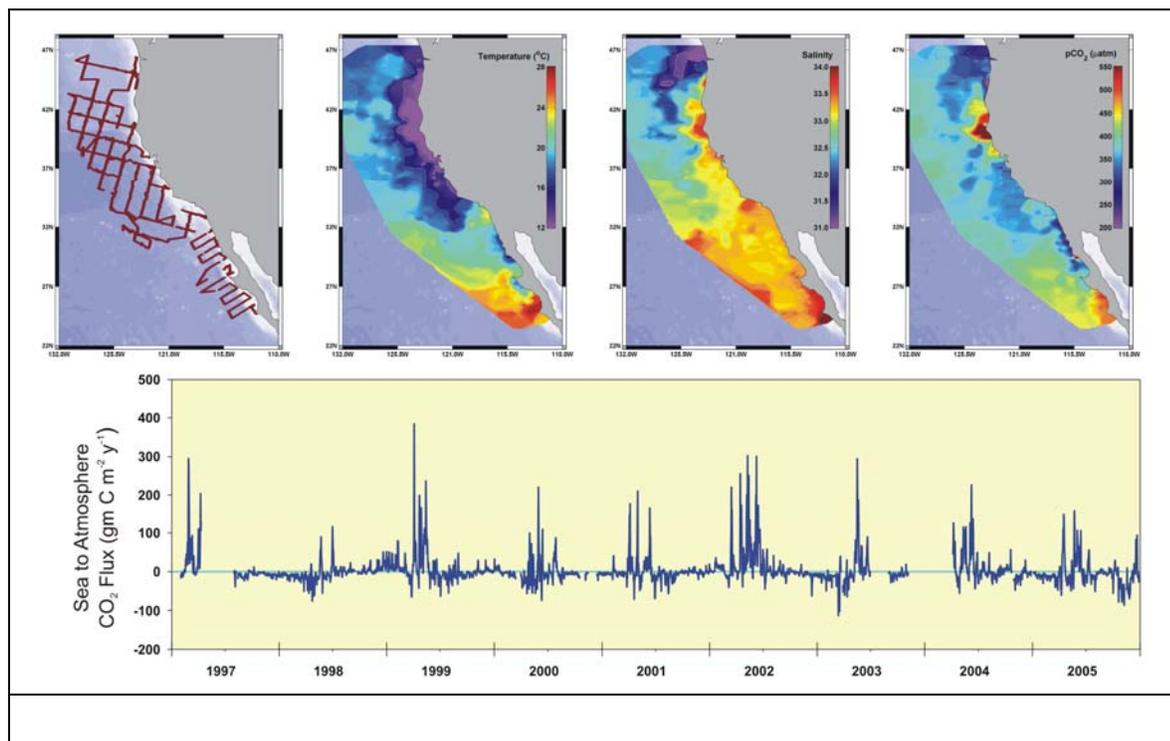


1 **Figure 15-4. Estimated sea-air CO₂ fluxes (grams of carbon per square meter per year) from 550,000**
 2 **seawater CO₂ partial pressure (pCO₂) observations made from 1979 to 2004 in ocean waters surrounding the**
 3 **North American continent. (A) Waters within one degree (about 80 km) of the coast and (B) open ocean waters**
 4 between 300 and 900 km from the shore (see Figure 15-3B). The annual mean sea-air pCO₂ difference (delta pCO₂)
 5 values were calculated from the weekly mean atmospheric CO₂ concentrations in the GLOBALVIEW-CO₂ database
 6 (2004) over the same pixel area in the same week and year as the seawater pCO₂ was measured. The monthly net
 7 sea-air CO₂ flux was computed from the mean monthly wind speeds in the National Centers for Environmental
 8 Prediction/National Center for Atmospheric Research (NCEP/NCAR) database in the (wind speed)² formulation for
 9 the sea-air gas transfer rate by Wanninkhof (1992). The ± uncertainties represent one standard deviation.



1 **Figure 15-5. Time-space variability of coastal waters off the west coast of North America.** (A) Quasi-synoptic
 2 distribution of the temperature, salinity, and pCO₂ in surface waters during July–September 2005. The Columbia
 3 River plume (~46°N) and the upwelling of deep waters off the Cape Mendocino (~40°N) are clearly seen. (B) 1997–
 4 2005 time-series data for sea-air CO₂ flux from a mooring off Monterey Bay, California. Seawater is a CO₂ source
 5 for the atmosphere during the summer upwelling events, but biological uptake reduces levels very rapidly. These
 6 rapid fluctuations can affect atmospheric CO₂ levels. For example, if CO₂ from the sea is mixed into a static column,
 7 a 500-m-thick planetary boundary layer over the course of one day, atmospheric CO₂ concentration would change
 8 by 2.5 μatm. If the column of air is mixed vertically through the troposphere to 500 mbar, a change of about 0.5
 9 μatm would occur. The effects would be diluted as the column of air mixes laterally. However, this demonstrates
 10 that the large fluctuations of sea-air CO₂ flux observed over coastal waters could affect the concentration of CO₂
 11 significantly enough to affect estimates of air-land flux based on the inversion of atmospheric CO₂ data. Sea-air CO₂
 12 flux was low during the 1997–1998 and 2002–2003 El Niño periods.

13



14

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 were 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

1 measured SST and climatological mean salinity (Da Silva *et al.* 1994). The flux values in a given month
2 are then averaged to yield a climatological mean flux (and standard deviation) for each month. This
3 procedure assumes implicitly that the seawater pCO₂ changes at much slower rates in space and time than
4 the wind speed and that the seawater pCO₂ does not correlate with the wind speed.

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