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Air-sea exchange of carbon dioxide in ocean margins: A province-based synthesis

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[1] In determining global sea-to-air CO_2 flux from measurements or models, the ocean margin has not been resolved from the land or the open ocean. Recent studies have indicated that shelves can be either a large sink or a source for atmospheric CO_2. This CO_2 sink/source term may substantially alter our current view of the global carbon budget for land and oceans. However, past fieldwork and synthesis have focused on a few shelves in the northern temperate zone while the vast majority of other shelves are ignored. By dividing the highly heterogeneous shelves into seven provinces, we suggest that the continental shelves are a sink for atmospheric CO_2 at mid-high latitudes (-0.33 Pg C a^{-1}) and a source of CO_2 at low latitudes (0.11 Pg C a^{-1}). Warm temperature and high terrestrial organic carbon input are most likely responsible for the CO_2 release in low latitude shelves. **Citation:** Cai, W.-J., M. Dai, and Y. Wang (2006), Air-sea exchange of carbon dioxide in ocean margins: A province-based synthesis, *Geophys. Res. Lett.*, *33*, L12603, doi:10.1029/2006GL026219.

1. Introduction

[2] Although it is well known that the ocean is a key component of the global climate system that regulates atmospheric CO_2 concentrations on annual to millennial time-scales, important knowledge gaps exist on the transfer of CO_2 between various components of the Earth system [*Prentice*, 2001; *Sabine et al.*, 2004]. For example, of the total amount of anthropogenic CO_2 (7 Pg C) released annually to the atmosphere, the currently known oceanic removal is about 2 Pg and the fate of another 2 Pg C (the so-called residual biosphere sink or "missing sink", which is presumably the CO_2 uptake by terrestrial ecosystems) is the subject of much debate [*Prentice*, 2001; *Sabine et al.*, 2004; *Sarmiento and Gruber*, 2002; *Takahashi et al.*, 2002]. A major uncertainty in balancing the global CO_2 budget is inadequate knowledge of CO_2 uptake or release by the ocean margins including estuaries, continental shelves and slopes [*Chen et al.*, 2003]. Recent estimates suggest that continental shelves may absorb atmospheric CO_2 by up to 1 Pg C a^{-1} or 50% of known open ocean uptake [*Thomas et al.*, 2004; *Tsunogai et al.*, 1999]. However, such estimates have been based largely on data from a single type of shelf located in the northern temperate zone near populated areas. The vast majority of other shelves were ignored. Contrasting observations in subtropical areas have challenged this view of shelves as a large CO_2 sink for the atmosphere [*Cai and Dai*, 2004; *Cai et al.*, 2003]. To further evaluate the pattern of air-sea CO_2 exchange pointed out by *Cai and Dai* [2004] and *Borges et al.* [2005] and to provide a better synthesis scheme, a database is compiled here with all available continental shelf sea-to-air (hereafter sea-air) CO_2 flux data that have a reasonable spatial and temporal coverage such that an annual flux can be estimated (Figure 1 and Table S1).[1] This is the most comprehensive database available so far and more than half of the data were published in the recent few years. It is clear from this compilation that continental shelves are greatly under-sampled and need more extensive observational network. This is particularly true for some parts of the world's ocean margins, especially the low latitude area, and thus extrapolations of studies from a single shelf or a simple area-weighted average of existing data will be biased greatly toward those areas that are relatively data-rich (i.e., part of the mid-latitude shelves of the northern temperate zone).

2. Methods

[3] Continental shelves are tremendously heterogeneous. To provide a reliable estimate of global sea-air CO_2 flux on continental shelves, one must use a suitable classification that accounts for differences in ocean circulation, morphology, latitude, etc and such a classification should be compatible with the availability of data on shelf CO_2 fluxes. Continental shelves can be divided into three major types: non-upwelling shelves associated mostly with western boundary currents (occupying ~77% of the total area); upwelling-dominated shelves associated mostly with eastern boundary currents (~6% of the total shelf area); and polar ocean margins (17%) [*Walsh*, 1988]. Within each type, further differentiation can be made based on latitude. Thus, continental shelves may be divided into seven provinces with distinct physical and biological characteristics [*Ducklow and McCallister*, 2004; *Walsh*, 1988; *Wollast*, 1998]. In this paper, an average sea-air CO_2 flux for each shelf province based on the database compiled in Table S1 is first determined and then a total or net global shelf flux weighted to province areas is calculated (Table 1). A latitudinal pattern of sea-air CO_2 flux is identified from this analysis and then possible mechanisms are discussed. Further methodological details and error analysis are discussed in Supplemental Note 1 in Text S1.

3. Results and Discussion

3.1. Mid-Latitude Non-Upwelling Shelves

[4] Mid-latitude non-upwelling shelves are associated mostly with a western boundary current (including a mar-

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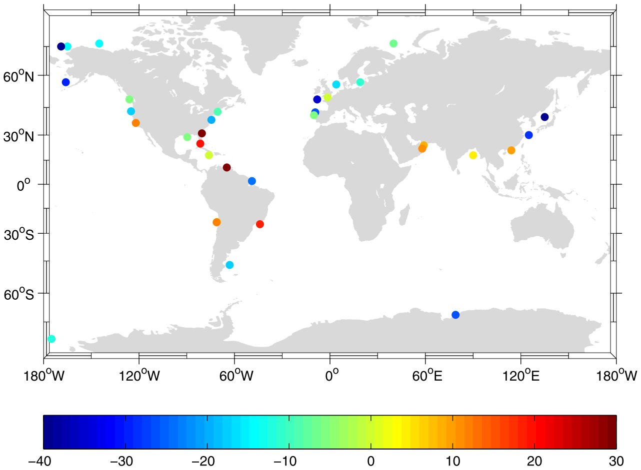

Figure 1. A global distribution of existing data of annual sea-air CO_2 flux measurements. The flux unit is in g C $m^{-2}a^{-1}$. Blue color indicates that the sea absorbs CO_2 from the atmosphere and red color indicates that the sea releases CO_2 to the atmosphere. Some of the flux data are not annually averaged. A complete list of individual shelves, references and method explanations are provided in Table S1 and its footnote. Flux data from estuaries and embayments are excluded from this compilation.

ginal sea-loop current). While shelves located in the northern Europe are not associated with a major western boundary current, it is appropriate to group them together with western boundary current shelves due to their similarities. Western boundary current shelves are generally wide, seasonally stratified, nutrient poor, and do not experience intense upwelling. Their nutrient supply comes largely from subsurface open ocean through shelf-edge exchange processes such as eddy intrusions and from rivers [*Pomeroy et al.*, 2000; *Walsh*, 1988; *Wollast*, 1998]. These shelves can be further divided into low- and mid-latitude shelves. Among the mid-latitude shelves, those receiving substantial anthropogenic nutrients from rivers (located between 30–60°N) are designated eutrophic shelves. Those receiving smaller inputs of anthropogenic nutrients are classified as mesotrophic shelves [*Walsh*, 1988].

[5] Sea-air CO_2 fluxes measured for eutrophic shelves range from as high as about 32 g C $m^{-2}a^{-1}$ in the East China Sea [*Tsunogai et al.*, 1999] and the Gulf of Biscay [*Frankignoulle and Borges*, 2001], to intermediate values of 20 g C $m^{-2}a^{-1}$ in the Mid Atlantic Bight [*DeGrandpre et al.*, 2002] and 17 g C $m^{-2}a^{-1}$ in the North Sea [*Thomas et al.*, 2004], and finally to a low value of 11 g C $m^{-2}a^{-1}$ in the Baltic Sea (Table S1). An area-weighted mean sea-air CO_2 flux of -24 ± 6 g C $m^{-2}a^{-1}$ (or -2.0 mol C $m^{-2}a^{-1}$) is calculated for eutrophic shelves (Table 1, Table S1, and Supplemental Note 1 in Text S1). This is the shelf province where most CO_2 exchange studies have taken place, and thus the estimated sea-air CO_2 flux is the most accurate. Due to the very limited data available for mesotrophic shelves, currently their CO_2 flux cannot be distinguished from that of eutrophic shelves. The question whether excessive anthropogenic nutrients input to the eutrophic shelves enhances shelf uptake of atmospheric CO_2 as postulated by J. Walsh 25 year ago [*Walsh et al.*, 1981] cannot be answered from this compilation alone. Thus an average annual sea-air CO_2 flux of -24 ± 8 g C $m^{-2}a^{-1}$ is assigned tentatively to mesotrophic shelves because of their oceanographic similarity to the eutrophic systems (Table 1 and Table S1). A combined total annual CO_2 uptake by the eutrophic and mesotrophic shelves is 274×10^{12} g C (or 274 Tg C). If these shelves are representative of all continental shelves, the globally extrapolated shelf CO_2 sink would be 0.63 Pg C a^{-1}, similar to other estimates [*Ducklow and McCallister*, 2004; *Thomas et al.*, 2004; *Tsunogai et al.*, 1999; *Yool and Fasham*, 2001].

3.2. Low-Latitude Western Boundary Current Shelves

[6] Low-latitude western boundary current shelves (located between 30°S–30°N) occupy about 30% of the total global shelf area and behave differently from the mid-latitude non-upwelling shelves in their air-sea CO_2 exchange pattern. The high flux of CO_2 release in the subtropical South Atlantic Bight was speculated to be driven by large quantities of organic carbon (OC) and inorganic carbon exported from salt marshes and rivers and by high sea surface temperature [*Cai et al.*, 2003]. Further south, the west Florida shelf and the Gulf of Mexico also appear as sources of CO_2 (Table S1). Similarly, tropical and subtropical shelves in the western South Atlantic Ocean (except the Amazon plume) are sources of CO_2 to the atmosphere (Table S1). Elsewhere, the shelf and upper slope of the northern South China Sea in the western Pacific Ocean [*Cai and Dai*, 2004] and the Arabian Sea [*Goyet et al.*, 1998] are annual sources of CO_2 to the atmosphere. In contrast, in the Caribbean Sea, an area integrated CO_2 flux is nearly zero (Table S1) perhaps due to the lack of terrestrial inputs of OC. An area-weighted mean sea-air CO_2 flux in low-latitude western boundary current shelves is estimated to be 12 ± 5 g C $m^{-2}a^{-1}$ (i.e., 1.0 mol C $m^{-2}a^{-1}$ or a total flux of 98 Tg C a^{-1}) (Table 1 and Table S1).

3.3. Polar Ocean Margins

[7] High latitude (>60°) shelf systems are classified as phototrophic-Arctic and -Antarctic shelves because their

Table 1. Sea-Air CO_2 Fluxes and Areas of Various Continental Shelf Provinces[a]

Province	Shelf Area, 10^6 km^2	Sea-to-Air CO_2 Flux: g C $m^{-2}a^{-1}$, Cai	Sea-to-Air CO_2 Flux: g C $m^{-2}a^{-1}$, Borges	Sea-to-Air CO_2 Flux: Tg C a^{-1}, Cai
Eutrophic, 30°–60°	3.61	−24	−22	−86.6
Mesotrophic, 30°–60°	7.82	−24	−22	−188
WBC, 0°–30°	8.16	12	22	97.9
Arctic, 60°–90°	4.36	−12	−23	−52.3
Antarctic, 60°–90°	0.39	−12	−23	−4.7
EBC, 30°–60°	0.23	−12	−1.3	−2.8
EBC, 0°–30°	1.26	12	1.3	15.1
Global total or mean	25.83	−8.6	-	−221

[a]WBC: Western Boundary Current Shelves; EBC: Eastern Boundary Current Shelves. Total flux is given as per shelf province (negative: CO_2 uptake from the atmosphere; positive: CO_2 release to the atmosphere). Shelf areas are taken from *Walsh* [1988]. CO_2 fluxes from comparable systems in *Borges et al.* [2005] (i.e., marginal seas and coastal upwelling in their Table 1) are listed for comparison. Their original data are listed in mol C $m^{-2}a^{-1}$ and 1 mol C = 12 g C. Thus, for example, for our western boundary current shelf province (0°–30°), their corresponding name is "marginal seas at 0°–30°" and the flux is 1.84 mol C $m^{-2}a^{-1}$ (i.e., 22 g C $m^{-2}a^{-1}$).

biological production is often limited by available light [*Walsh*, 1988]. The Arctic shelves are affected by terrestrial inputs and have experienced rapid global warming changes. The Antarctic shelves have an upwelling feature, and thus are a separate province from the Arctic. From inorganic carbon mass balance [*Anderson et al.*, 1998] and pCO_2 data, an average sea-air CO_2 flux is estimated as -12 ± 4 g C $m^{-2}a^{-1}$ for the Arctic shelves (Table 1 and Table S1). Based on recent work in the Ross Sea, the same sea-air CO_2 flux of -12 g C $m^{-2}a^{-1}$ is tentatively assigned to the Antarctic coastal oceans (Table 1 and Table S1). The apparently small areal flux in the polar shelves is due to the ice coverage which blocks sea-air CO_2 flux most of the year. Thus the Arctic shelves may become a large CO_2 sink as the ice-free period lengthens under future global warming conditions. However, enhanced terrestrial OC input may have an opposite effect as the climate warms and permafrost melts (see references in Text S1).

3.4. Upwelling-Dominated Shelves

[8] The final two classifications for shelf systems are upwelling-dominated systems. Such regions are usually associated with eastern boundary currents, narrow shelves, and upwelling-favorable winds [*Walsh*, 1988]. Major upwelling systems located at low latitude are a source of CO_2 to the atmosphere due to intense and relatively permanent upwelling that brought high pCO_2 deep-water to the sea surface and the rapid warming of the surface water. The annual sea-air flux is about 12 g C $m^{-2}a^{-1}$ (or 1.0 mol C $m^{-2}a^{-1}$) based on data from the Omani coast [*Goyet et al.*, 1998], north [*Lefèvre et al.*, 2002] and central Chile margins and from the central California coast (Table 1 and Table S1). In contrast, upwelling systems located at mid-high latitudes are relatively weak and seasonally variable. They often appear to be a sink of atmospheric CO_2 due to the strong biological consumption resulting from the upwelling of nutrient-rich subsurface water and the cold surface temperature [*Borges and Frankignoulle*, 2002; *Hales et al.*, 2005]. But these systems are extremely dynamic and highly variable. For example, the Iberian Peninsula and the Galician coast of the North Atlantic eastern boundary upwelling system are moderate-to-strong sinks of CO_2 (flux = -6 to -26 g C $m^{-2}a^{-1}$ [*Borges and Frankignoulle*, 2002] and Table S1). However, although the Oregon coast is a strong sink of atmospheric CO_2 [*Hales et al.*, 2005], upwelling systems to its north (i.e., Vancouver) and south (Northern and central California) are not (Table S1). For purposes of budgetary estimates, a sea-air CO_2 flux of -12 g C $m^{-2}a^{-1}$ is assigned to mid-latitude upwelling shelves (Table 1).

3.5. Net Global Sea-Air CO_2 Flux in Ocean Margins

[9] The net global continental shelf sea-air CO_2 flux and associated standard error are thus estimated as $-(0.22 \pm 0.16)$ Pg C a^{-1} (Table 1, Table S1, and Supplemental Note 1 in Text S1). It is emphasized here that most shelf provinces, with the exception of, perhaps, the eutrophic shelves, are greatly undersampled and, hence, substantial uncertainty remains that warrants great attention. The net global continental shelf CO_2 uptake flux derived here is lower than previous estimates that were extrapolated from single shelf studies (-0.4 Pg C a^{-1} [*Thomas et al.*, 2004], -1.0 Pg C a^{-1} [*Tsunogai et al.*, 1999] or based on an individual shelf area-averaged method (-0.9 Pg C a^{-1} [*Ducklow and McCallister*, 2004]) that did not consider CO_2 release from low latitude shelves. However, when flux values from low latitude shelves are included, their estimated global flux is similar to ours (H. Ducklow, personal communication, 2005). Our result is also similar to an estimate based on a mixture of data (uptake) and an educated-guess (release) [*Chen et al.*, 2003]. A recent synthesis suggests that the global shelf is a sink of CO_2 (sea-air flux = -0.37 Pg C a^{-1}) if inner estuaries and salt marshes are not included, but otherwise a source of CO_2 (0.12 Pg C a^{-1}) [*Borges et al.*, 2005]. CO_2 emission rate from estuarine and salt marsh (including mangrove) waters estimated here (Supplemental Note 2 in Text S1) and by *Borges et al.* [2005] is 0.4–0.5 Pg C a^{-1}. However, it was also estimated that marsh and mangrove vegetation had a net CO_2 fixation rate of about 0.5 Pg C a^{-1} [*Woodwell et al.*, 1973]. Thus, net CO_2 exchange with the atmosphere in these inshore systems is an unresolved but potentially important budget issue that need be addressed before further partition of CO_2 sink within "terrestrial biosphere" can be made (Supplemental Note 2 in Text S1).

[10] The current work distinguishes from that of *Borges et al.* [2005] in the following aspects. Firstly, our work focuses exclusively on continental shelves. CO_2 fluxes from more shelves are synthesized in this work than that given by *Borges et al.* [2005] (i.e., 31 vs. 17 shelves), resulting in significant flux differences in some shelf provinces (Table 1). Secondly and more importantly, these shelves are classified, synthesized and extrapolated based on marginal provinces advocated in earlier works [*Ducklow and McCallister*, 2004; *Walsh*, 1988; *Wollast*, 1998]. Finally, it should be pointed out that a much smaller total shelf area (1.46×10^6 km^2) was adopted for the low latitude non-upwelling shelves by *Borges et al.* [2005] than that used by us (8.16×10^6 km^2, both cited [*Walsh*, 1988]) which reduces the difference between us in the final total flux. Thus updating of basic geographic information on marginal systems is in great need.

4. Broader Implications

[11] Sea-air CO_2 flux data from various shelves are often in conflict if they are not viewed with an ocean margin classification such as the one presented here. A striking latitudinal contrast in shelf sea-air CO_2 flux emerges from this analysis (Figure 1 and Table 1). Present day shelves located between 30° and 90° (i.e., eutrophic, mesotrophic, Arctic, Antarctic, and mid-latitude upwelling shelves) are sinks of atmospheric CO_2 with a total sea-air flux of -0.33 Pg C a^{-1}. In contrast, those shelves located from 0 to 30° (low-latitude western boundary current and major upwelling shelves) are sources of CO_2 to the atmosphere with a total release of 0.11 Pg C a^{-1}. Because of the geographical distribution of continental shelves, most of the shelf CO_2 sinks are in the mid- to high-latitude northern hemisphere and the sources are in the tropical and subtropical zone (30°N to 30°S). This sink/source distribution pattern is consistent with the observation of a smaller north to south atmospheric CO_2 gradient than is expected from anthropogenic CO_2 emission between the two hemispheres

and within the Northern Hemisphere [*Keeling et al.*, 1996; *Prentice*, 2001].

[12] The sea surface temperature increase from high to low latitude shelves is an important factor controlling this latitudinal distribution in a manner similar to the open ocean as the marine carbon dioxide equilibrium has a direct response to temperature (i.e., 4.3%/°C) [*Takahashi et al.*, 2002]. Sea surface temperature at 25°N is about 15°C higher than that at 50°N. This temperature difference would raise the pCO_2 value of the surface water from 80 μatm undersaturated with respect to the atmospheric value (~375 μatm) at 50°N to 100 μatm supersaturated at 25°N everything else being equal. In addition, strong seasonal sea surface temperature variation in the temperate zone (i.e., eutrophic and mesotrophic shelves) may promote CO_2 uptake and export via the so–called continental shelf pump mechanism [*Thomas et al.*, 2004; *Tsunogai et al.*, 1999; *Yool and Fasham*, 2001]. The latitudinal contrast in shelf sea-air CO_2 flux may also be associated with the differences in terrestrial inputs of OC (total of ~0.5 Pg C a^{-1}) and freshwater with latitude. These inputs are much greater on low latitude non-upwelling shelves with 60% of the inputs on the 0–30° zone shelves (i.e., 0.3 Pg C a^{-1}) [*Borges et al.*, 2005; *Walsh*, 1988]. It has been believed that a majority of the terrestrial OC is decomposed in continental margins [*McKee*, 2003]. If only $^1/_2$ of the terrestrial OC supplied to the low latitudes is decomposed in the shelf, it is sufficient to support the CO_2 release there.

[13] Sea surface CO_2 uptake or release is often taken as an indicator of system level net autotrophy or heterotrophy [*Ducklow and McCallister*, 2004; *Mackenzie et al.*, 2004; *Smith and Hollibaugh*, 1993; *Walsh et al.*, 1981]. While our analysis confirms that the global continental shelf system has crossed a threshold of changing from its pre-industrial state, during which ocean margins are widely viewed as having been heterotrophic and a CO_2 source (0.4 Pg C a^{-1}) [*Smith and Hollibaugh*, 1993], to a current or future state as a CO_2 sink (model predicted current sea-air flux is −0.1 to 0.3 Pg C a^{-1} [*Mackenzie et al.*, 2004]), it remains to be determined whether this shift is largely a result of passive CO_2 uptake due to a higher pCO_2 in today's atmosphere, or as has been suggested by [*Mackenzie et al.*, 2004], is an indicator of a shift in ecosystem metabolism from heterotrophy to autotrophy.

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