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Review article

“Air-sea exchanges of CO₂ in world’s coastal seas”

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Abstract

The air-sea exchanges of CO₂ in the world’s 165 estuaries and 87 continental shelves are evaluated. Generally and in all seasons, upper estuaries with salinities of less than two are strong sources of CO₂ ($39 \pm 56 \text{ mol C m}^{-2} \text{ yr}^{-1}$, negative flux indicates that the water is losing CO₂ to the atmosphere); mid-estuaries with salinities of between 2 and 25 are moderate sources ($17.5 \pm 34 \text{ mol C m}^{-2} \text{ yr}^{-1}$) and lower estuaries with salinities of more than 25 are weak sources ($8.4 \pm 14 \text{ mol C m}^{-2} \text{ yr}^{-1}$). With respect to latitude, estuaries between 23.5 and 50° N have the largest flux per unit area ($63 \pm 101 \text{ mmol C m}^{-2} \text{ d}^{-1}$); these are followed by mid-latitude estuaries (23.5–0° S: $44 \pm 29 \text{ mmol C m}^{-2} \text{ d}^{-1}$; 0–23.5° N: $39 \pm 55 \text{ mmol C m}^{-2} \text{ d}^{-1}$), and then regions north of 50° N ($36 \pm 91 \text{ mmol C m}^{-2} \text{ d}^{-1}$). Estuaries south of 50° S have the smallest flux per unit area ($9.5 \pm 12 \text{ mol C m}^{-2} \text{ d}^{-1}$). Mixing with low-*p*CO₂ shelf waters, water temperature, residence time and the complexity of the biogeochemistry are major factors that govern the *p*CO₂ in estuaries but wind speed, seldom discussed, is critical to controlling the air-water exchanges of CO₂. The total annual release of CO₂ from the world’s estuaries is now estimated to be 0.10 PgC yr^{-1} , which is much lower than published values mainly because of the contribution of a considerable amount of heretofore unpublished or new data from Asia and the Arctic. The Asian data, although indicating high in *p*CO₂, are low in sea-to-air fluxes because the wind speeds are lower than previously determined values, which rely heavily on data from Europe and North America, where *p*CO₂ is lower but wind speeds are much higher, such that the CO₂ fluxes are higher than in Asia. Newly emerged CO₂ flux data in the Arctic reveal that estuaries there mostly absorb, rather than release CO₂.

Most continental shelves, and especially those at high latitude, are under-saturated in terms of CO₂ and absorb CO₂ from the atmosphere in all seasons. Shelves between 0° and 23.5° S are on average a weak source and have a small flux per unit area of CO₂ to the atmosphere. Water temperature, the spreading of river plumes, upwelling, and biological production seem to be the main factors in determining *p*CO₂ in the shelves.

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Wind speed, again, is critical because at high latitudes, the winds tend to be strong. Since the surface water $p\text{CO}_2$ values are low, the air-to-sea fluxes are high in regions above 50°N and below 50°S . At low latitudes, the winds tend to be weak, so the sea-to-air CO_2 flux is small. Overall, the world's continental shelves absorb 0.4PgC yr^{-1} from the atmosphere.

1 Introduction

Carbon is arguably one of the most important elements on earth and understanding the global carbon cycle is fundamental to elucidating the effect of human activities in the Anthropocene era. The oceans are known to have an important role in regulating the climate on annual to millennial scales by absorbing CO_2 and exchanging carbon with various carbon-storing compartments, such as the atmosphere, the land, the biota and the fossil fuel carbon pool. Yet, despite the success of quantifying the air-sea CO_2 exchange and the uptake of anthropogenic CO_2 by the major oceans, effect of the land on these processes is still poorly understood and little discussed (Khatiwala et al., 2012; Le Quéré et al., 2012; Schuster et al., 2012; Wanninkhof et al., 2012).

Coastal waters link the land, the oceans, the atmosphere, biota and sediments. Although they constitute only a little over 7% of the surface area of oceans and less than 0.5% of the volume of the oceans, coastal oceans have a disproportionately large role in primary and new production, remineralization and sedimentation of organic matter (Walsh et al., 1981; Walsh, 1988, 1991; Kempe and Pegler, 1991; Mackenzie et al., 1991, 1998a, b; Chen, 1993; Wollast, 1993, 1998; Gattuso et al., 1998; Carrillo and Karl, 1999; Liu et al., 2000; de Haas et al., 2002; Elliott and McLusky, 2002; Muller-Karger et al., 2005; Thomas, 2010). Coastal waters receive large inputs of terrestrial material, such as suspended sediments and nutrients in solution or in particulate matter, in organic or inorganic forms and through river and groundwater discharge, as well as by exchange with the atmosphere and the open ocean. They therefore tend to show greater temporal and spatial variability than open oceans, and are more affected

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by human activities (Cameron and Pritchard, 1963; Alongi, 1998; Chen and Tsunogai, 1998; Rabouille et al., 2001; Chen, 2002, 2003, 2004; Slomp and Van Cappellen, 2004; Beusen et al., 2005; Chavez et al., 2007; Doney et al., 2007; Radach and Patsch, 2007; Peng et al., 2008; Seitzinger et al., 2010; Durr et al., 2011; Jiang et al., 2012). However, unlike the open oceans, in which millions of observations have been made and the air-sea exchanges of CO_2 have been valued using various developed models (such as by Khatiwala et al., 2012; Schuster et al., 2012; Wanninkhof et al., 2012), coastal waters have been relatively poorly examined.

Although estuaries are known to be generally sources of CO_2 (Frankignoulle et al., 1998; Cai et al., 1999, 2000; Sarma et al., 2001, 2011; Abril et al., 2002; Borges et al., 2003; Dagg et al., 2005; Gao et al., 2005; Dai et al., 2008; Leinweber et al., 2009), only in the last few years have continental shelves been firmly established to absorb CO_2 from the atmosphere. (See, for example, Liu et al., 2000; Chen et al., 2003; Chen, 2004; Abril and Borges, 2005; Borges, 2005; Borges et al., 2005; Cai et al., 2006; Chen and Borges, 2009; Laruelle et al., 2010 and references therein.) Indeed, whether coastal seas are sources or sinks of CO_2 has remained an open question until only recently. The first report of the project on the Land Ocean Interaction in the Coastal Zone under the International Geosphere Biosphere Programme (IGBP) is entitled, "Coastal seas: a net source or sink of atmosphere carbon dioxide" (Kempe, 1995). The first report of LOICZ did not provide any data concerning the air-sea exchanges of carbon in the continental margins, although it concluded that net carbon oxidation in the coastal zone is around $7 \times 10^{12}\text{ mol yr}^{-1}$ (Crossland et al., 2005), implying that the coastal zone is a source of CO_2 to the atmosphere.

Unfortunately, Fasham et al. (2001), summarizing the work of the Joint Global Ocean Flux Study (JGOFS, another IGBP project), concluded that there is a net sea-to-air CO_2 flux from continental margins of 0.5PgC yr^{-1} . They drew this conclusion despite the fact that, at the time, the Joint JGOFS/LOICZ Continental Margins Task Team (Chen et al., 1994) had already gathered sufficient data to demonstrate that, the margins, rather than being a source of CO_2 , are in fact a sink of CO_2 . Indeed, in the same year, Fasham

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published another paper that claimed that the continental shelves are actually a sink of CO₂ of the order of 0.6 PgC yr⁻¹ (Yool and Fasham, 2001). In 2003, the JGOFS also concluded that the shelves take up 0.3 PgC yr⁻¹ of atmospheric CO₂ (Chen et al., 2003). This view however, was not universally accepted (Cai et al., 2003; Cai and Dai, 2004) until more data, especially data obtained in the winter, became available. Many shelves that had been thought to be sources of CO₂ are now known to be sinks of CO₂ when winter data reveal severe under-saturation of CO₂ (Thomas et al., 2004; Cai et al., 2006; Schiettecatte et al., 2007; Jiang et al., 2008b).

Strangely, despite the fact that coastal waters play a major role in the livelihood of humans, and are strongly affected by human activities, our understanding of these waters is mostly semi-quantitative. For example, such basic information as the area of the continental shelf is uncertain. The most recent work of Y. Kang (private communication, 2013) yielded an area of 26.15×10^6 km² for waters shallower than 200 m. This value compares with 26.39×10^6 km² obtained by Laruelle et al. (2012), 24.72×10^6 km² presented by Laruelle et al. (2010), 30.16×10^6 km² obtained by Jahnke (2010), 26×10^6 km² presented by Chen and Borges (2009), 25.83×10^6 km² presented by Cai et al. (2006) and 36×10^6 km² presented by Liu et al. (2000). Merely comparing the total flux across various studies may not be very useful whereas comparing flux per unit area eliminates the problem of an uncertain global shelf area, which varies by as much as 50 % among studies. Even more strangely, despite the fact that rivers export approximately 1 PgC yr⁻¹ (Meybeck, 1982), or roughly half of the carbon that is absorbed by the open oceans each year, this value needs to be confirmed as it was based only on a few studies, and the well regarded study of Meybeck was based on a database of only 27 rivers.

The export of carbon by rivers comprises 40 % organic carbon (0.22 PgC yr⁻¹ of dissolved organic carbon (DOC) and 0.18 PgC yr⁻¹ of particulate organic carbon (POC)) and 60 % inorganic carbon (0.43 PgC yr⁻¹ of dissolved inorganic carbon (DIC) and 0.17 PgC yr⁻¹ of particulate inorganic carbon (PIC)) (Meybeck, 1982; Richey, 2004; IPCC, 2007; Schlunz and Schneider, 2000; Dai et al., 2012; Huang et al., 2012).

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However, estuarine filtering prevents some of the carbon that reaches the estuaries from also entering the oceans (Keil et al., 1997; Kemp et al., 1997; Middelburg and Herman, 2007; Chen et al., 2012; Dai et al., 2012). Whether speciation changes between the organic and inorganic or dissolved and particulate carbon in the estuaries, and how much of each of these forms of carbon actually enters the oceans are yet unknown (Woodwell et al., 1973; Raymond and Bauer, 2000; Wiegner and Seitzinger, 2001).

The above may be summarized by noting that nutrients from land, which may be transported by rivers or submarine groundwater discharge, or may be atmospheric fall-out, markedly affect estuaries and continental shelves (Ittekkot et al., 1991; Cole and Caraco, 2001; Neubauer and Anderson, 2003; Clark et al., 2004; Thomas et al., 2004; Gazeau et al., 2005; Hales et al., 2008; Jiang et al., 2012; Lauerwald et al., 2012). Consequently, estuaries and proximal continental shelves typically sustain high biological productivity (Walsh et al., 1981; Wollast, 1993, 1998; Cai, 2003) which may draw down CO₂. This phenomenon, however, may be more than counteracted by enhanced heterotrophic activity, supported by organic carbon input from rivers (Smith and Hollibaugh, 1993; Heip et al., 1995; Hedges and Keil, 1995; Hedges et al., 1997; Hansell and Carlson, 1998; Bouillon et al., 2006; Jiang et al., 2010). Additionally, direct inorganic carbon input from river water, submarine groundwater discharge and exchanges with tidal marshes and mangroves play an important role in increasing the *p*CO₂ of estuarine and shelf waters (Moran et al., 1991; Miller and Moran, 1997; Neal et al., 1998; Raymond et al., 2000; Raymond and Bauer, 2001; Borges et al., 2003, 2006; Cai et al., 2003; Wang and Cai, 2004; Jahnke et al., 2005; Bouillon et al., 2008; Jiang et al., 2008, 2010; Chen et al., 2012).

Since the above complex and conflicting factors influence the *p*CO₂ of estuarine and shelf waters, the air-sea exchanges of CO₂ in these waters can not yet be estimated by models, and so field data are required. Determinations of the air-sea flux of CO₂ in the world's estuaries and continental shelves, based on direct measurements, are presented below. Data from the literature and some unpublished data from CTA Chen are tabulated. Data for upper, mid and lower estuaries are compared. Seasonal and

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latitudinal variations are discussed and the global flux is presented. Data concerning continental shelves are also considered with reference to season and latitude before the global flux is determined.

2 Air-sea CO₂ exchanges in Estuaries

5 Rivers are the main sources of carbon to the estuaries. Riverine organic carbon is supplied primarily by the erosion of soil organic matter or plant detritus (allochthonous) and by phytoplankton in water (autochthonous). The inorganic carbon is derived mainly from soil and rock erosion, and by the oxidation of organic matter mostly through microbial processes (Odum and Hoskin, 1958; Odum and Wilson, 1962; Probst et al., 1994; 10 Neal et al., 1998; Nelson et al., 1999; Pomeroy et al., 2000). These organic and inorganic forms of carbon in dissolved and particulate phases, reach the estuaries, which are typically wider than river channels. Therefore, particles tend to settle down and decompose, releasing carbon back into the water. Salt marshes, mangroves, and submarine groundwater discharge also export carbon to estuaries, increasing their $p\text{CO}_2$.

15 Rivers are the main sources of nutrients to estuaries. However, high turbidity and limited light cause nutrients rarely to be fully utilized for biological production in rivers or estuaries. Hence, the biological drawdown of CO₂ does not suffice to reduce the estuarine water $p\text{CO}_2$ to below saturation. Consequently, almost all estuaries are sources of CO₂ to the atmosphere. The influence of freshwater from large rivers frequently 20 extends hundreds of kilometers offshore. The enormous discharge of freshwater, sediments and the associated particulate and dissolved organic and inorganic carbon, nitrogen and phosphorus all greatly affect the biological and geochemical processes in the estuary, the plume and the adjacent continental shelf (Chen and Wang, 1999; Gong et al., 2000; Chen et al., 2003). A saline interface normally separates the plume water from the shelf water, with the width of the interface determined by interactions between river discharge and marine driving forces (Shen, 2001; Shen et al., 2003; Chen 25 et al., 2008a). Complex biophysical and geochemical processes govern the direction of

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CO₂ exchange between the plume-affected shelf area and the atmosphere (Kortzinger, 2003; Cooley et al., 2007), but in this investigation, river plumes outside of the estuaries are not considered.

Numerical data are gathered for 165 estuaries. They include 50 heretofore unpublished data from CTA Chen (Fig. 1, Table 1). The Wanninkhof (1992) quadratic equation is used to determine the CO₂ flux per unit area. That is, the flux is a function of the square of the wind speed. Figure 2 presents the $p\text{CO}_2$ and CO₂ fluxes per unit area in the upper, mid and lower estuaries worldwide. Almost all estuaries outside of the Arctic region except for only a few release CO₂ to the atmosphere. 10 Unsurprisingly, upper estuaries, where the riverine effect is the strongest (Kempe, 1979, 1982; Chen et al., 2012), have the highest $p\text{CO}_2$ ($5026 \pm 6190 \mu\text{atm}$) and the highest sea-to-air CO₂ flux ($39.0 \pm 55.7 \text{ mol C m}^{-2} \text{ yr}^{-1}$, where the negative sign indicates that the seawater is losing CO₂); these are followed by the mid estuaries ($p\text{CO}_2 = 2230 \pm 2725 \mu\text{atm}$; flux = $17.5 \pm 34.2 \text{ mol C m}^{-2} \text{ yr}^{-1}$). Lower estuaries have 15 the lowest $p\text{CO}_2$ ($723 \pm 957 \mu\text{atm}$) and CO₂ flux ($8.4 \pm 14.3 \text{ mol C m}^{-2} \text{ yr}^{-1}$). Except for those of the upper estuaries, these $p\text{CO}_2$ values compare favorably with those found by Chen et al. (2012), which were 3033, 2277, and 692 μatm for the upper, mid and lower estuaries, respectively. This study yields much higher $p\text{CO}_2$ values for upper estuaries mainly because new data from Asia are associated with high $p\text{CO}_2$ values. The fluxes obtained by Chen et al. (2012), however, are higher. Their values are 68.5, 37.4 and 20 9.92 $\text{mol C m}^{-2} \text{ yr}^{-1}$ for the upper, mid and lower estuaries, respectively. The seeming inconsistency among results is discussed below.

Figure 3 displays histograms of reported daily CO₂ fluxes per unit area in different seasons and the annual flux per unit area in the world's estuaries. Little seasonality is observed, except that the flux is lower in the winter when the $p\text{CO}_2$ is usually 25 lower, perhaps because the temperature is lower than other seasons. The flux is only marginally higher in summer than in spring or autumn. The numerical average annual flux per unit area is $16.5 \pm 27.7 \text{ mol C m}^{-2} \text{ yr}^{-1}$, which is significantly lower than that, $23.9 \pm 33.1 \text{ mmol C m}^{-2} \text{ d}^{-1}$, obtained by Chen et al. (2012). The numerical average

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annual flux per unit area, however, is not used to calculate the global release of CO₂ because small estuaries dominate the numerical average but they contribute relatively little to the total flux.

5 With respect to latitude, the flux per unit area is the highest, at $63.3 \pm 100.7 \text{ mmol C m}^{-2} \text{ d}^{-1}$ between 23.5 and 50° N, followed by $44.1 \pm 29.3 \text{ mmol C m}^{-2} \text{ d}^{-1}$ between 23.5° S and 0°, followed by $38.8 \pm 55.4 \text{ mmol C m}^{-2} \text{ d}^{-1}$ between 0° and 23.5° N, and $-35.9 \pm 91.2 \text{ mmol C m}^{-2} \text{ d}^{-1}$ north of 50° N. The flux south of 50° S ($9.5 \pm 11.7 \text{ mmol C m}^{-2} \text{ d}^{-1}$) is greatly lower but data are available for only two estuaries. By way of comparison, Chen et al. (2012) obtained $65.5 \pm 78.1 \text{ mmol C m}^{-2} \text{ d}^{-1}$ a slightly higher value than obtained in this study between 23.5° N and 23.5° S. The values of Chen et al. (2012), $67.4 \pm 108 \text{ mmol C m}^{-2} \text{ d}^{-1}$ between 23.5 and 50° N and $59.2 \pm 80 \text{ mmol C m}^{-2} \text{ d}^{-1}$ north of 50° N, are, however, significantly higher than those obtained herein. Notably, most other investigations have presented fluxes higher than those that were presented by Chen et al. (2012).

15 The fact that the annual average flux herein is lower than those reported previously, despite the fact the average $p\text{CO}_2$ is higher, warrants discussion. It follows mainly from the fact that many data from the low latitude bands in Asia have been added, and these areas are mostly areas of low wind energy. Figure 5 plots the wind energy potential which is, like the air-sea gas exchange rate, a quadratic function of wind speed. The areas of high wind energy at low latitudes are concentrated in the dry Middle East and northeastern, northern and northwestern Africa with few rivers, and therefore few estuaries. For example, the total area of the estuaries in the Red Sea region is almost zero (Table 3; Laruelle et al., 2012). Accordingly, the global average CO₂ flux herein is substantially affected by estuaries in areas of low wind energy, and therefore of low CO₂ flux.

20 The 50 newly considered estuaries in Taiwan, southern China and Southeast Asia, all at low latitudes, have lower fluxes than determined from previously obtained results (Table 1), which include many data for European rivers. For instance, only two of the

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19 estuaries that were considered by Abril and Borges (2005), who published perhaps the first global study of CO₂ emissions from estuaries, are outside Europe and the eastern seaboard of the USA. Those authors found a global CO₂ flux per unit area of $35.7 \text{ mol C m}^{-2} \text{ yr}^{-1}$, which is more than triple the value obtained in this study. This finding does not imply that European rivers have higher $p\text{CO}_2$: they do not. Rather, Europe has more windy coasts than elsewhere in the world, and especially Asia. As mentioned above, the wind potential is a quadratic function of wind speed, as is the 1992 Wanninkhof air-sea CO₂ exchange equation. The mean $p\text{CO}_2$ of European estuaries is roughly $1600 \mu\text{atm}$, whereas that of Asian estuaries is much higher, around $4000 \mu\text{atm}$. Yet, the mean wind speed on European coasts is approximately 4 m s^{-1} , compared with about 1.6 m s^{-1} on Asian coasts. The resulting CO₂ fluxes for European estuaries average about $16.9 \text{ mol C m}^{-2} \text{ yr}^{-1}$ vs. a much lower $8.1 \text{ mol C m}^{-2} \text{ yr}^{-1}$ for Asian estuaries (Table 3; Fig. 6) despite their higher $p\text{CO}_2$.

15 In the above calculation, the areas of estuaries are taken from Laruelle et al. (2012), who divided the world into 45 regions, and calculated a total estuarine area of $1.012 \times 10^6 \text{ km}^2$, which is slightly smaller than the value of $1.067 \times 10^6 \text{ km}^2$, given in Laruelle et al. (2010). Table 3 lists the total surface area in each of the 45 regions and the average CO₂ flux per unit area for each region. For regions without data, the mean flux for a similar region is used. Estuaries in North America have the largest total area but the lowest average flux per unit area among all continents, and therefore a low total flux of 10.8 TgC yr^{-1} . That is, a continent with 41 % of world's estuarine area accounts for only 12 % of the world's estuarine CO₂ release (Fig. 6). African, European and South American estuaries have similarly high fluxes per unit area but the areas of the estuaries are only moderate so they are responsible for only 16 % (14.7 TgC yr^{-1}), 26 % (24.1 TgC yr^{-1}) and 12 % (11.6 TgC yr^{-1}), respectively, of the global release. The largest contributor is Asia which has 31.5 % of the world's estuary area and releases almost the same percentage of the world's estuarine released CO₂ (32 % or 30.6 TgC yr^{-1} ; Fig. 6).

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Largely on account of the distribution of data, which include data from high wind regions on both sides of the North Atlantic and around the Arabian Sea in the Indian Ocean, as well as those generally in the low wind regions around the Pacific Ocean, the mean CO_2 flux per unit area is the lowest for estuaries that flow into the Pacific Ocean, with a value of $10.5 \text{ mol C m}^{-2} \text{ yr}^{-1}$ (Fig. 7). This value compares with $12.4 \text{ mol C m}^{-2} \text{ yr}^{-1}$ for estuaries that flow into the Atlantic Ocean and $13.9 \text{ mol C m}^{-2} \text{ yr}^{-1}$ for estuaries that flow into the Indian Ocean. Because the total area of estuaries that enter the Atlantic Ocean exceeds the sum of areas of estuaries that enter the Pacific and Indian Oceans, the total flux of CO_2 released from the estuaries around the Atlantic (54.1 TgC yr^{-1}) exceeds the total flux from estuaries around the Pacific (30.8 TgC yr^{-1}) and the Indian (13.3 TgC yr^{-1}) Oceans. The total area of estuaries that enter the Arctic Ocean is substantial ($324 \times 10^3 \text{ km}^2$), equaling the total areas of the estuaries around the Atlantic and Indian Oceans. Unfortunately, the relevant data are scarce and the available data seem to reveal that the Arctic estuaries absorb, rather than release CO_2 . The flux per unit area and total flux are $-1.1 \text{ mol C m}^{-2} \text{ yr}^{-1}$ and -4.2 TgC yr^{-1} , respectively. The global total release of 94 TgC yr^{-1} is less than half of any previous estimates (Table 2). New data from low wind regions and the Arctic Ocean are responsible for this difference.

3 Air-Sea CO_2 exchanges in continental shelves

Data are available from 87 continental shelves (Table 3 and Fig. 8). Table 3 presents the fluxes in the 45 regions that were identified by Laruelle et al. (2010) and the areas of each region. Figure 9 displays a histogram of the reported daily CO_2 fluxes in different seasons and the annual flux for the world's continental shelves. Respiration rates are higher in summer and fall than in winter and spring (Hopkinson, 1985, 1988; Griffith et al., 1990; Hopkinson and Smith, 2005; Jiang et al., 2010). However, as with estuaries, no seasonality of flux per unit area on continental shelves is evident, and the values fall between -4.0 and $-5.5 \text{ mmol C m}^{-2} \text{ d}^{-1}$, except in autumn, when

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the flux is only $-0.5 \text{ mmol C m}^{-2} \text{ d}^{-1}$. The numerical annual mean air-to-sea flux is $-1.09 \pm 2.9 \text{ mol C m}^{-2} \text{ yr}^{-1}$. Multiplying this value by the total global area of the shelves yields a global flux of $-0.40 \text{ PgC yr}^{-1}$, which is slightly less than the published value (Table 5). A positive value indicates that the shelves absorb CO_2 .

Figure 10 presents a histogram of the reported daily fluxes of CO_2 in different latitude bands. Most shelves absorb CO_2 from the atmosphere (negative fluxes) while shelves at low latitudes have a slight tendency to release CO_2 (positive fluxes). This finding is consistent with the work of Cai et al. (2006), who found that shelves at low latitudes between 30° N and 30° S are a source of CO_2 of the order of 0.11 PgC yr^{-1} , whereas those in temperate and high-latitude regions are sinks of CO_2 of the order of 0.33 PgC yr^{-1} . The CO_2 flux per unit area is highest on the South American shelves ($-3.6 \text{ mol C m}^{-2} \text{ yr}^{-1}$) but since their total area is moderate, the South American shelves absorb the second largest amount of CO_2 from the atmosphere annually at $-103.5 \text{ TgC yr}^{-1}$, or 26 % of the global shelf absorption.

Asian shelves have the highest total area but their flux per unit area ($-0.13 \text{ mol C m}^{-2} \text{ yr}^{-1}$) is the lowest of all, primarily because of the generally low wind speed and because some shelves release rather than absorb CO_2 . The total annual flux from Asian shelves is only -22 TgC yr^{-1} , or 5 % of the global absorption by all shelves. North American shelves rank second in terms of both flux per unit area ($-2.1 \text{ mol C m}^{-2} \text{ yr}^{-1}$) and shelf area. Accordingly, North American shelves absorb the most CO_2 from the atmosphere at -156 TgC yr^{-1} , or 39 % of the global absorption by all shelves. Shelves around the Antarctica have the third highest flux per unit area ($-2.0 \text{ mol C m}^{-2} \text{ yr}^{-1}$) and the third largest total shelf area, resulting in the third highest total annual flux at -70 TgC yr^{-1} , or 18 % of the global absorption (Fig. 11). Unfortunately, data are available for only two such shelves.

Figure 12 shows the total CO_2 flux per unit area and the total CO_2 flux from shelves in different oceans. Two shelves in the Southern Ocean have the highest flux per unit area ($-2 \text{ mol C m}^{-2} \text{ yr}^{-1}$) with a total annual flux of -70 TgC yr^{-1} , or 18 % of the global shelf absorption. The second highest flux per unit area is that of shelves in the Arctic Ocean

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($-1.8 \text{ mol C m}^{-2} \text{ yr}^{-1}$), which also have the second highest total flux at -129 TgC yr^{-1} , or 33 % of the global absorption. Shelves in the Atlantic Ocean have the highest total absorption (-130 TgC yr^{-1} , or 33 % of the global absorption), the third highest flux per unit area ($-1.2 \text{ mol C m}^{-2} \text{ yr}^{-1}$) and the second highest total shelf area. The largest shelf area is that of the shelves around the Pacific Ocean but since the flux per unit area is low ($-0.4 \text{ mol C m}^{-2} \text{ yr}^{-1}$), their total absorption is only -49 TgC yr^{-1} , or 12 % of global absorption. Shelves around the Indian Ocean have the least total area and the second lowest flux per unit area ($-0.6 \text{ mol C m}^{-2} \text{ yr}^{-1}$), resulting in the lowest total flux (-18 TgC yr^{-1} , or only 4 % of the global absorption). In total, the world's shelves absorb 396 TgC yr^{-1} or $0.396 \text{ PgC yr}^{-1}$.

The shift from the sinking of CO_2 at higher latitudes to acting as a weak source at lower latitudes is explained by four major factors. The first is that waters on continental shelves are mostly dominated by the open oceans, as revealed simply by the salinity of most shelves, which is only slightly lower than that of the open ocean waters, except close to the estuaries. For example, for a shelf with 10 % input from rivers with a salinity of 0.5 and a $p\text{CO}_2$ of $1000 \mu\text{atm}$, and 90 % input from open oceans with a salinity of 35 and a $p\text{CO}_2$ of $300 \mu\text{atm}$, the resulting salinity (S) is 31.55. For the sake of argument, the $p\text{CO}_2$ of this $S = 31.55$ shelf water is approximately $370 \mu\text{atm}$, depending on the alkalinity of the river water. Restated, mixing with open ocean waters with low $p\text{CO}_2$ causes the $p\text{CO}_2$ of river water with high $p\text{CO}_2$ be reduced to below saturation. Notably, open ocean waters at high latitudes are frequently under-saturated and open ocean waters at low latitudes are frequently super-saturated (Takahashi et al., 2002; Kaltin et al., 2002; Kaltin and Anderson, 2005; Chen et al., 2006a, b, 2008a, b; Ciais et al., 2008). Therefore, mixing with open ocean waters at high latitudes helps shelf waters become under-saturated whereas mixing with open ocean waters at low latitudes frequently yields shelf waters that are still super-saturated (Hidalgo-Gonzalez et al., 1997; Ito et al., 2005; Cai et al., 2006; Chen et al., 2008a, 2012).

The second factor that contributes to the super-saturation of shelf waters at low latitudes is temperature because $p\text{CO}_2$ increases by 4.3 % for an increase of a degree

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Celcuis (Bakker et al., 1999; Takahashi et al., 2002). Simply increasing by 15°C the temperature of the shelf water with a $p\text{CO}_2$ of $370 \mu\text{atm}$ in the example given above would result in a $p\text{CO}_2$ of above $600 \mu\text{atm}$, if all other factors are held constant. Notably, the difference between the temperatures of shelves at high latitude shelves and those at low latitude commonly exceeds 15°C . Temperature similarly affects open ocean water so not only do warm temperatures increase the $p\text{CO}_2$ of shelf waters but also these waters also mix with open ocean waters with higher $p\text{CO}_2$, mainly because they are hotter than open oceans at high latitudes. The proximal shelves in waters with a depth of, say, less than 40 m, typically exhibit a greater seasonal range of water temperatures than the distal shelves with a water depth of between 40 and 200 m. The effect of temperature on the $p\text{CO}_2$ of proximal shelf waters is thus greater than that of distal shelf waters. Unfortunately, the readily available $p\text{CO}_2$ data do not suffice for a meaningful synthesis. As a matter of fact, for navigational or geopolitical reasons, $p\text{CO}_2$ is rarely measured along the coast or the data are frequently not disclosed.

The third factor in affecting $p\text{CO}_2$ on shelves is the fact that the discharge of organic matter by rivers is higher at lower latitudes. As much as 60 % of the riverine organic carbon discharge to the shelves occurs between 0° – 30° (Walsh, 1988; Ludwig et al., 1996a, b; Borges et al., 2005). The total amount is approximately -0.3 PgC yr^{-1} , most of which is decomposed in the continental margins (McKee, 2003; Cai et al., 2006). Importantly, however, the cited studies did not identify the recipient of the riverine export. As indicated above, a significant fraction of the export is decomposed in the estuaries and does not reach the shelves.

The fourth factor that is responsible for the higher $p\text{CO}_2$ in shelves at lower latitudes involves lower biological productivity. Shelves at mid and high latitudes are generally highly productive whereas those at low latitudes, especially the non-upwelling shelves, are typically oligotrophic. The more effective biological pumping in the shelves at mid and high latitudes causes these shelves to have lower $p\text{CO}_2$.

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Table 1. Seasonal and annual air-to-sea fluxes of CO₂ in world's estuaries.

type	lon.(°)	lat.(°)	spring flux ^c (mmol C m ⁻² d ⁻¹)	summer flux (mmol C m ⁻² d ⁻¹)	autumn flux (mmol C m ⁻² d ⁻¹)	winter flux (mmol C m ⁻² d ⁻¹)	annual flux (mol C m ⁻² yr ⁻¹)	References
1-1 (fjord) (US) ^b	-152.5	57.7	-1.8		1.8		0.001	Takahashi et al. (2012) (LDED database)
11-1 (fjord) (CA)	-55.8	52.3		-2.1			-0.8	Takahashi et al. (2012) (LDED database)
14-1 (fjord) (IC)	-23.2	66.2	-0.7	-7.0	-12.9	-4.8	-2.3	Takahashi et al. (2012) (LDED database)
14-2 (fjord) (IC)	-23.6	66.1		-7.7			-2.8	Takahashi et al. (2012) (LDED database)
14-3 (fjord) (IC)	-23.7	65.7			5.4		2.0	Takahashi et al. (2012) (LDED database)
14-4 (fjord) (IC)	-24.1	65.6	-0.3				-0.1	Takahashi et al. (2012) (LDED database)
14-5 (fjord) (IC)	-18.6	66.0	-48.2	-7.8	-11.2	-9.0	-7.0	Takahashi et al. (2012) (LDED database)
Aby lagoon (CI)	-3.3	5.4	-10.1	1.2	-11.3	-4.1	-2.7	Kone et al. (2009)
Altamaha Sound (US)	-81.3	31.3	57.8	127.0	79.7	28.5	26.8	Jiang et al. (2008a)
Ambalayaar (IN)	79.3	10.0		-0.02			-0.007	(Sarma et al., 2012)
Amur River (RU)	141.1	52.9			0.1		0.3	Johnson et al. (2009) (WOD09 database)
Ason (ES)	-3.5	43.3		-3.0			-1.1	Ortega et al. (2005)
Aveiro lagoon (PT)	-8.7	40.7					12.4	Borges and Frankignoulle (unpublished)
Baitarani (IN)	86.9	20.5		20.7			7.6	Sarma et al. (2012)
Bancal (PH)	115.0	5.0	2.2				0.8	Chen (unpublished)
Bebar River (MY)	103.4	3.1			17.7		6.5	Chen (unpublished)
Bellamy (US)	-70.9	43.1	-11.0	43.0	6.0		4.6	Hunt et al. (2011)
Betsiboka (MG)	46.3	-15.7					3.3	Ralison et al. (2008)
Bharatakulza (IN)	76.0	11.2		11.7			4.3	Sarma et al. (2012)
Bothnian Bay (FI)	21.0	63.0					3.5	Algesten et al. (2004)
Brazos River (US)	-95.4	28.9					0.033	Zeng et al. (2011)
Brunei River (BN)	96.4	16.5		53.7			19.6	Chen (unpublished)
Cauvery (IN)	79.89	11.26		2.23			0.8	Sarma et al. (2012)
Chalakudi (IN)	76.18	10.69		12.86			4.70	Sarma et al. (2012)
Changjiang (Yantze) (CN)	120.5	31.5	23.5	65.5	33.7	37.8	14.6	Zhai et al. (2007)
Chi Shui River (TW)	120.11	23.29		176		68.5	44.6	Chen (unpublished)
Chilka (lagoon) (IN)	85.5	19.1	9.8	141.0			27.5	Gupta et al. (2008)
Cho Shui River (TW)	120.3	23.9	651.0	13.4			121.0	Chen (unpublished)
Chung Kang River (TW)	120.8	24.7	45.8	53.4	28.8	144.0	24.8	Chen (unpublished)
Churchill River (CA)	-94.2	58.8		1.2	-3.6		-0.4	Stainton (2009)
Citanduy-Mangalit (ID)	108.8	-7.7	25.7 ^d				9.4	Chen (unpublished)
Citujung-Kragjilan (ID)	106.4	-6.0	36.9 ^d				13.5	Chen (unpublished)
Cocheco (US)	-70.8	43.1	2.0	26.0	2.0		3.7	Hunt et al. (2011)
Cochin (IN)	76.0	9.5			267.0	65.0	60.6	Gupta et al. (2008)
Cross Sound (fjord) (US) (LDED database)	-134.1	56.6		-0.2	45.1		8.2	Takahashi et al. (2012)

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Table 1. Continued.

type	lon.(°)	lat.(°)	spring flux ^c (mmol C m ⁻² d ⁻¹)	summer flux (mmol C m ⁻² d ⁻¹)	autumn flux (mmol C m ⁻² d ⁻¹)	winter flux (mmol C m ⁻² d ⁻¹)	annual flux (mol C m ⁻² yr ⁻¹)	References
Doboy Sound (US)	-81.3	31.4	15.2	47.4	51.0	16.0	11.9	Jiang et al. (2008a)
Douro (PT)	-8.7	41.1			240.0		87.6	Frankignoulle et al. (1998)
Duplin River (US)	-81.3	31.5	53.4	83.0	73.2	23.4	21.3	Wang and Cai (2004)
Ebríe lagoon (CI)	-4.3	5.5	56.4	109.0	61.9	47.9	26.6	Kone et al. (2009)
Elbe (DE)	8.8	53.9	180.0				65.7	Frankignoulle et al. (1998)
Erms (DE)	6.9	53.4		110.0			40.2	Frankignoulle et al. (1998)
Endau River (MY)	103.6	2.7			1.0		0.4	Chen (unpublished)
Erii Jen River (TW)	120.2	22.9				26.5	12.9	Chen (unpublished)
Florida Bay (US)	-80.8	25.0	68.5	11.1			1.7	Millero et al. (2001)
Fong Kang River (TW)	120.7	22.2	6.7	-17.9		18.0	0.8	Chen (unpublished)
Gaderu creek (IN)	82.3	16.8					20.4	Borges et al. (2003)
Gironde (FR)	-1.1	45.6	110.0	110.0	65.0	50.0	30.6	Frankignoulle et al. (1998)
Godavari (IN)	82.3	16.7					8.0	Bouillon et al. (2003), Sarma et al. (2012)
Godthåbsfjord (GL) ^e	-51.9	64.1					-7.25	Flysgaard et al. (2012)
Golfo Almirante Montt (fjord) (CL)	-72.0	-52.1			-17.7 ^d		-6.5	Takahashi et al. (2012) (LDED database)
Great Bay (US)	-70.9	43.1					3.6	Hunt et al. (2011)
Guadalquivir (ES)	-6.0	37.4		104.0			37.9	de la Paz et al. (2007)
Haldia (IN)	88.2	21.9		12.3			4.5	Sarma et al. (2012)
Hanjiang (CN)	116.8	23.4				0.9	0.3	Chen (unpublished)
Ho Ping River (TW)	121.8	24.3	5.3	22.0		68.5	11.7	Chen (unpublished)
Hooghly (IN)	88.0	22.0	31.8	-1.1	16.7	2.5	4.9	Mukhopadhyay et al. (2002)
Hou Lung River (TW)	120.8	24.6	72.9	9.3	7.6	21.0	10.1	Chen (unpublished)
Hsiu Ku Luan River (TW)	121.5	23.5	26.5	41.9		19.2	10.7	Chen (unpublished)
Hua Lien River (TW)	121.6	23.9	93.4	75.3		4.8	21.1	Chen (unpublished)
Hudson River Estuary (US)	-74.0	40.7					5.9	Raymond et al. (1997)
Isla Gordon (fjord) (CL)	-68.9	-55.2			-1.2 ^d		-0.4	Takahashi et al. (2012) (LDED database)
Itacuraca creek Sepetiba (Bay)(BR)	-44.0	-23.0					41.4	Ovalle et al. (1990), Borges et al. (2003)
Jiulong Jiang (Xiamen Bay) (CN)	118.1	24.5				4.3	0.5	Dai et al. (2009)
Jiulongjiang (CN)	118.0	24.5					1.6	Chen (unpublished)
Johor River (MY)	104.0	1.5			2.3		0.8	Chen (unpublished)
Kakinada Bay (IN)	82.3	16.7					3.0	Bouillon et al. (2003)
Kali (IN)	74.2	14.8		3.2			1.2	Sarma et al. (2012)
Kaneohe Bay and stream (US)	-157.8	21.5					1.5	Fagan and Mackenzie (2007)
Kao Ping River (TW)	120.4	22.5	98.1	51.8	30.5	12.4	17.6	Chen (unpublished)
Kapuas River (ID)	109.1	0.1				148.3	54.1	Chen (unpublished)

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Table 1. Continued.

type	lon.(°)	lat.(°)	spring flux ^c (mmol C m ⁻² d ⁻¹)	summer flux (mmol C m ⁻² d ⁻¹)	autumn flux (mmol C m ⁻² d ⁻¹)	winter flux (mmol C m ⁻² d ⁻¹)	annual flux (mol C m ⁻² yr ⁻¹)	References
Kennebec River (US)	-69.8	43.8	22.5	22.0	-0.2	-49.6	-0.5	Takahashi et al. (2012) (LDED database)
Khura River estuary (TH)	98.3	9.2					35.7	Miyajima et al. (2009)
Kidogweni creek (Gazi Bay) (KE)	39.5	-4.4				154.4 ^d	21.8	Bouillon et al. (2007b)
Kien Vang creeks (VN)	105.1	8.7	32.2		154.7		34.2	Kone and Borges (2008)
Klang River (MY)	101.4	3.0			7.7		2.8	Chen (unpublished)
Kobbe fjord (GL)	-51.5	64.2	-2.7		-136.6	-2.6	-17.3	Ruiz-Halpern et al. (2010)
Kochi back waters (IN)	76.4	10.0		8.1			2.9	Sarma et al. (2012)
Kola Bay (RU)	33.4	69.1	-2.5	-0.2	-3.5	-3.9	-0.9	Johnson et al. (2009) (WOD09 database)
Krishna (IN)	81.1	15.8		6.8			2.5	Sarma et al. (2012)
Lan Yang River (TW)	121.8	24.7	65.5	66.0		23.2	18.8	Chen (unpublished)
Liminganlahti Bay (FI)	25.4	64.9		-0.9			-0.9	Silvennoinen et al. (2008)
Lin Pien River (TW)	120.5	22.4	44.4	54.5		49.0	18.0	Chen (unpublished)
Little Bay (US)	-70.9	43.1	-5.1	33.9	3.9		4.0	Hunt et al. (2011)
Loire (FR)	-2.2	47.2			155.0		64.4	Abril et al. (2003)
Luohe (CN)	115.6	22.9				0.1	0.022	Chen (unpublished)
Mahanadi (IN)	86.6	20.0		3.1			1.1	Sarma et al. (2012)
Mahisagar (IN)	72.6	22.1		10.2			3.7	Sarma et al. (2012)
Mandovi (IN)	73.8	15.7		18.1			6.6	Sarma et al. (2012)
Mandovi-Zuari (IN)	73.5	15.3		0.2			14.2	Sarma et al. (2001)
Matolo creek (KE)	40.1	-2.1					21.2	Bouillon et al. (2007a)
Mekong (VN)	106.5	10.0					30.8	Borges (unpublished)
Mempawah River (ID)	89.0	22.0		23.2			8.5	Chen (unpublished)
Mtoni (TZ)	39.3	-6.9					2.4	Kristensen et al. (2008)
Nagada creek (Papua New Guinea) (ID)	145.8	-5.2				43.6 ^d	15.9	Borges et al. (2003)
Nagavaii (IN)	84.0	18.2		0.2			0.1	Sarma et al. (2012)
Nalounghe (CN)	112.0	21.8				10.1	3.7	Chen (unpublished)
Narmada (IN)	73.0	20.2		8.8			3.2	Sarma et al. (2012)
Netravathi (IN)	75.0	12.7		70.7			25.8	Sarma et al. (2012)
Norman's Pond (BS)	-76.1	23.8				13.8	5.0	Borges et al. (2003)
Orinoco River (VE) (LDED database)	-62.3	8.6	31.8				11.6	Takahashi et al. (2012)
Oyster (US)	-70.9	43.1	-17.2	51.5	2.5		4.5	Hunt et al. (2011)
Pa Chang River (TW)	120.1	23.3	29.9	94.2		34.8	19.3	Chen (unpublished)
Pahang River (MY)	103.5	3.5			3.5		1.3	Chen (unpublished)
Palau lagoon (PW)	134.5	7.5	0.03		-1.0		-0.2	Watanabe et al. (2006)
Parker River estuary (US) Hopkinson (2003)	-70.8	42.8		3.2	2.9		1.1	Raymond and
Pei Kang River (TW)	120.2	23.5	27.3	80.0	35.1	28.8	15.6	Chen (unpublished)
Pei Nan River (TW)	121.2	22.8	155.0			147.0	48.4	Chen (unpublished)
Penna (IN)	80.2	14.4		5.2			1.9	Sarma et al. (2012)
Piaui River estuary (BR)	-37.5	-11.5					15.0	Souza et al. (2009)

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Table 1. Continued.

type	lon.(°)	lat.(°)	spring flux ^c (mmol C m ⁻² d ⁻¹)	summer flux (mmol C m ⁻² d ⁻¹)	autumn flux (mmol C m ⁻² d ⁻¹)	winter flux (mmol C m ⁻² d ⁻¹)	annual flux (mol C m ⁻² yr ⁻¹)	References
Po Tzu River (TW)	120.1	23.4		85.5		89.9	32.0	Chen (unpublished)
Ponnayaar (IN)	80.3	12.4		96.3			35.2	Chen (unpublished)
Potou lagoon (CI)	-3.8	5.6	40.3	186.0	45.5		36.8	Kone et al. (2009)
Qiantang River (CN)	122.0	30.1				6.3	0.1	Chen (unpublished)
Qinjiang (CN)	108.6	21.7					2.3	Chen (unpublished)
Rajang River (MY)	115.5	2.1			7.1		2.6	Chen (unpublished)
Randers Fjord (DK)	10.3	56.6	-5.0	52.9			8.7	Gazeau et al. (2005)
Ras Dege creek (TZ)	39.3	-6.9					12.0	Kristensen et al. (2008), Bouillon et al. (2007c)
Rhine (NL)	4.1	52.0		160.0	75.1		21.9	Frankignoulle et al. (1998)
Ria de Vigo (FR)	8.6	42.1	-0.1	-0.5	0.5	-0.6	-0.1	Álvarez-Salgado et al. (1999)
Rio San Pedro (ES)	-6.1	36.4					39.4	Ferron et al. (2007)
Rompin River (MY)	103.5	2.8			1.5		0.6	Chen (unpublished)
Rongjiang (CN)	116.7	23.3				14.0	5.1	Chen (unpublished)
Rushikulya (IN)	85.2	19.3		-0.02			-0.01	Sarma et al. (2012)
S. Muar (MY)	102.6	2.0			3.2		1.2	Chen (unpublished)
Sabarmathi (IN)	72.8	21.6		13.8			5.1	Sarma et al. (2012)
Sado (PT)	-8.9	38.5			396.0		145.0	Frankignoulle et al. (1998)
Saja-Besaya (ES)	-4.0	43.4		446.0			163.0	Ortega et al. (2005)
São Francisco Estuary (US)	-122.3	37.7		1.8		0.5	0.4	Peterson (1979)
Sapelo Sound (US)	-81.3	31.6	19.1	41.1	47.1	16.8	10.5	Jiang et al. (2008a)
Saptamukhi creek (IN)	89.0	22.0					20.7	Ghosh et al. (1987), Borges et al. (2003)
Satilla River (US)	-81.5	31.0			116.0		42.5	Cai and Wang (1998)
Scheldt (BE/NL)	3.5	51.4	175.0	233.0	326.0	240.0	94.1	Frankignoulle et al. (1998)
Sodih Besar (MY)	104.1	1.9			12.6		4.6	Chen (unpublished)
Sentosa River (MY)	104.1	1.9			17.2		6.3	Chen (unpublished)
Sharavathi (IN)	74.5	14.4		10.2			3.7	Sarma et al. (2012)
Shark River (US)	-81.1	25.2					16.0	Kone and Borges (2008)
Skeena River (US)	-130.1	53.9			65.6		23.9	Takahashi et al. (2012)
Subarnalekha (IN)	87.6	21.5		0.03			0.01	Sarma et al. (2012)
Szu Chung River (TW)	120.7	22.1	12.9	50.4		-0.8	7.6	Chen (unpublished)
Ta An River (TW)	120.6	24.4	-0.4	3.4	27.3	17.0	4.3	Chen (unpublished)
Ta Chia River (TW)	120.6	24.3	-6.3	25.3	-29.2		-1.2	Chen (unpublished)
Tagba lagoon (CI)	-5.0	5.4	18.1	114.0	28.5	13.2	18.5	Kone et al. (2009)
Tam Giang creeks (VN)	105.2	8.8	141.5	128.5			49.3	Kone and Borges (2008)
Tamar (UK)	-4.2	50.4	90.1	120.0			38.3	Frankignoulle et al. (1998)
Tan Shui River (TW)	121.5	25.1	168.0	160.0	214.0	3.3	49.8	Chen (unpublished)
Tana (KE)	40.1	-2.1					21.2	Bouillon et al. (2007a)
Tapti (IN)	72.7	21.1		362.5			132.4	Sarma et al. (2012)

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Table 1. Continued.

type	lon.(°)	lat.(°)	spring flux ^c (mmol C m ⁻² d ⁻¹)	summer flux (mmol C m ⁻² d ⁻¹)	autumn flux (mmol C m ⁻² d ⁻¹)	winter flux (mmol C m ⁻² d ⁻¹)	annual flux (mol C m ⁻² yr ⁻¹)	References
Tendo lagoon (CI)	-3.2	5.3	-17.7	75.6	-4.9	-3.0	7.0	Kone et al. (2009)
Thames (UK)	0.9	51.5			250.0		91.3	Frankignoulle et al. (1998)
Tou Chien River (TW)	120.9	24.8	55.9	10.5	7.2	46.6	11.0	Chen (unpublished)
Trang River estuary (TH)	99.4	7.2					30.9	Miyajima et al. (2009)
Tseng Wen River (TW)	120.1	23.1	93.2	-1.8	12.4		34.6	Chen (unpublished)
Tung Kang River (TW)	120.4	22.5	114.0		48.9	121.0	40.5	Chen (unpublished)
Urdabai (ES)	-2.7	43.4			22.8		8.3	Ortega et al. (2005)
Vaigai (IN)	78.9	9.3		0.2			0.1	Sarma et al. (2012)
Vamsadhara (IN)	84.7	18.9		0.4			0.1	Sarma et al. (2012)
Vellar (IN)	79.9	11.7		17.0			6.2	Sarma et al. (2012)
Wadden Sea estuary (NL)	4.8	53.0	-160.0				-58.4	Zemmelink et al. (2009)
Wailoa river-estuary (US) ^d	-159.5	22.2	1032		422	607	251	Paquay et al. (2007)
Wailuku River (US)	-155.08	19.72	5.73				5.73	Paquay et al. (2007)
Wu River (TW)	120.5	24.2	44.4	92.1			24.9	Chen (unpublished)
Yangon (MM)	121.8	31.3				5.4	2.0	Chen (unpublished)
Yen Shui River (TW)	120.2	23.0	50.1	125.0		14.4	23.1	Chen (unpublished)
Yenisey (RU)	82.7	71.8	29.7	16.7	3.5	27.5	7.1	Johnson et al. (2009)
York River (US)	-76.4	37.2	10.0	29.0	16.7	6.5	5.6	Raymond et al. (2000)
Zhujiang (Pearl River) (CN)	113.5	22.5	60.2	70.7	47.0	22.2	6.9	Guo et al. (2009)
Zuari (IN)	74.0	-15.3		6.4			2.3	Sarma et al. (2012)

^a Positive fluxes indicate an emission of CO₂ from water to the atmosphere;^b BE: Belgium; BN: Brunei; BR: Brazil; BS: Bahamas; CI: Côte d'Ivoire; CL: Chile; CN: China; DE: Germany; DK: Denmark; ES: Spain; FI: Finland; FR: France; GL: Greenland; IC: Iceland; ID: Indonesia; IN: India; KE: Kenya; MG: Repoblikan'i Madagasikara; MM: Myanmar; MY: Malaysia; NL: Netherlands; PH: Philippines; PT: Portugal; PW: Palau; RU: Russia; TH: Thailand; TW: Taiwan; TZ: Tunisia; UK: United Kingdom; US: United States; VE: Venezuela; VN: Vietnam;^c Spring: March–May; Summer: June–August; Fall: September–November; Winter: December–February;^d Austral seasons;^e not used in the calculation.

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Table 2. Summary of reported total air-to-sea fluxes of CO₂ in world's estuaries.

	Unit area flux (mol C m ⁻² yr ⁻¹)	Area (10 ⁶ km ²)	Total flux (PgC yr ⁻¹)	References
Estuaries (n = 19)	35.71	1.40	0.60	Abril and Borges (2005)
Estuaries (n = 16)	38.12	0.94	0.43	
Non-estuarine salt marshes (n = 1)	23.45	0.14	0.04	
Mangroves	13.66	0.20	0.04	Borges (2005)
Ave/Total	33.20	1.28	0.51	
Estuaries (n = 16)	28.62	0.94	0.32	
Non-estuarine salt marshes	21.40	0.14	0.036	
Mangroves	18.66	0.15	0.033	Borges et al. (2005)
Ave/Total	26.42	1.23	0.39	
Estuaries (n = 32)	32.10	0.943	0.36	
Non-estuarine salt marshes	30.40	0.384	0.09	
Mangroves	27.10	0.147	0.05	Chen and Borges (2009)
Ave/Total	28.27	1.474	0.50	
Small deltas and estuaries	25.7 ± 15.8	0.084	0.026 ± 0.016	
Tidal systems and embayments	28.5 ± 24.9	0.276	0.094 ± 0.082	
Lagoons	17.3 ± 16.6	0.252	0.052 ± 0.050	
Fjords and fjards	17.5 ± 14.0	0.456	0.096 ± 0.077	Laruelle et al. (2010)
Ave/Total (n=60)	21.0 ± 17.6	1.067	0.268 ± 0.225	
Estuaries (including both river-dominated and nonriverine coastal lagoons)	20.83	1.05	0.25	Cai (2011)
Estuaries (n = 106)	23.9 ± 33.1	1.07	0.26	Chen et al. (2012)
Estuaries (n = 165)	7.74	1.01	0.094	This study

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Table 3. Areas and air-sea fluxes of CO₂ in estuaries and continental shelves by biogeochemical provinces.

MARCATS Segments Number	continent	ocean	System Name	Class	Estuarine Surface (10 ³ km ²)	average CO ₂ flux (mol C m ⁻² yr ⁻¹)	CO ₂ flux (TgC yr ⁻¹)	Shelf Surface (10 ³ km ²)	average CO ₂ flux (mol C m ⁻² yr ⁻¹)	CO ₂ flux (TgC yr ⁻¹)
1	NA	PA	North Eastern Pacific	Subpolar	33.9	10.71 (n = 3)	4.36	461	-3.51 (n = 3)	-19.40
2	NA/OC	PA	Californian Current	EBC	8.9	0.93 (n = 3)	0.10	214	-2.22 (n = 3)	-5.69
3	NA	PA	Tropical Eastern Pacific	Tropical	6.2	14.47	1.08	198	-0.05 (n = 2)	-0.13
4	SA	PA	Peruvian Upwelling Current	EBC	4.2	34.71	1.75	143	-0.62 (n = 4)	-1.07
5	SA	AT	Southern America	Subpolar	22	-3.46 (n = 2)	-0.91	1230	-3.25 (n = 3)	-47.98
6	SA	AT	Brazilian Current	WBC	26.3	28.20 (n = 2)	8.90	521	3.97 (n = 1)	24.81
7	SA	AT	Tropical Western Atlantic	Tropical	13.4	11.60 (n = 1)	1.87	517	-12.78 (n = 1)	-79.26
8	NA	AT	Caribbean Sea	Tropical	26.2	5.04 (n = 1)	1.58	344	0.66 (n = 1)	2.74
9	NA	AT	Gulf of Mexico	Marginal Sea	31.9	8.02 (n = 2)	3.07	544	-0.19 (n = 2)	-1.26
10	NA	AT	Florida Upwelling	WBC	34	9.81 (n = 15)	4.00	858	-1.10 (n = 4)	-11.27
11	NA	AT	Sea of Labrador	Subpolar	36.1	-0.76 (n = 1)	-0.33	395	-2.11 (n = 1)	-10.02
12	NA	AT	Hudson Bay	Marginal Sea	39	-0.44 (n = 1)	-0.20	1064	0.84 (n = 1)	10.73
13	NA	AR	Canadian Archipelagos	Polar	163.7	-1.08	-2.11	1177	-4.06 (n = 2)	-57.34
14	NA	AR	Northern Greenland	Polar	24.1	-2.05 (n = 5)	-0.59	614	-6.14 (n = 1)	-45.20
15	NA	AR	Southern Greenland	Polar	8.8	-1.08	-0.11	270	-5.95 (n = 1)	-19.29
16	EU	AR	Norwegian Basin	Polar	17	-17.30 (n = 1)	-3.53	171	-3.83 (n = 1)	-7.45
17	EU	AT	North Eastern Atlantic	Marginal Sea	37.6	37.73 (n=8)	17.02	1112	-1.04 (n = 2)	-13.88
18	EU	AT	Baltic Sea	Marginal Sea	26.3	1.28 (n = 2)	0.40	383	-1.95 (n = 1)	-8.96
19	EU	AT	Iberian Upwelling	EBC	12.7	58.75 (n = 10)	8.95	283	-1.33 (n = 5)	-4.51
20	EU	AT	Mediterranean Sea	Marginal Sea	15.1	-0.06 (n = 1)	-0.01	580	1.47 (n = 3)	10.21
21	EU	AT	Black Sea	Marginal Sea	10.3	10.00	1.24	172	-0.79	-1.63
22	AF	AT	Moroccan Upwelling	EBC	5.6	34.71	2.33	225	3.02 (n = 1)	8.15
23	AF	AT	Tropical Eastern Atlantic	Tropical	26.6	17.25 (n = 5)	5.51	284	0.29 (n = 1)	0.99
24	AF	AT	Southern Western Africa	EBC	1.7	34.71	0.71	308	-2.41 (n = 1)	-8.91
25	AF	IN	Aguilhas Current	WBC	28.4	14.52	4.95	254	-4.03 (n = 1)	-12.28
26	AF	IN	Tropical Western Indian	Tropical	5.8	15.73 (n = 5)	1.09	72	1.03 (n = 1)	0.89
27	AF	IN	Western Arabian Sea	Indian Margins	2	3.32 (n = 1)	0.08	102	-0.32 (n = 2)	-0.40
28	AF	IN	Red Sea	Marginal Sea	0.04	10.00	0.005	190	0.12 (n = 2)	0.28
29	AS	IN	Persian Gulf	Marginal Sea	2.3	10.00	0.28	233	-0.79	-2.20
30	AS	IN	Eastern Arabian Sea	Indian Margins	14.5	9.02 (n = 25)	1.57	342	0.01 (n = 1)	0.06
31	AS	IN	Bay of Bengal	Indian Margins	10.1	19.82 (n = 10)	2.40	230	-0.22 (n = 1)	-0.60
32	AS	IN	Tropical Eastern Indian	Indian Margins	16.2	13.73 (n = 6)	2.67	809	-0.28 (n = 4)	-2.74

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Table 4. Continued.

type	Lon.(°)	Lat.(°)	spring fluxes ^b (mmol C m ⁻² d ⁻¹)	summer fluxes (mmol C m ⁻² d ⁻¹)	autumn fluxes (mmol C m ⁻² d ⁻¹)	winter fluxes (mmol C m ⁻² d ⁻¹)	annual flux (mol C m ⁻² yr ⁻¹)	References
Baltic Sea	20; 13.9	57; 54.9	-92.9	-66.5	-3.6	-34.4	-1.95	Thomas and Schneider (1999), Kuss et al. (2006)
Bass Strait	148.0	-38.8		-0.11 ^c	-0.73 ^c			Hydes et al. (2012)
Bay of Biscay (Northern)	-7.9	49						Borges et al. (2006)
Bay of Biscay (Southern)	-3.5	46.5						de la Paz et al. (2010)
Beaufort Shelves	-155	72		-2.81				Murata and Takizawa (2003), Cai et al. (2006)
Bering Sea Shelf	-165	57	-1.2	-0.66				-6.15 Nedashkovsky et al. (1995), Codispoti et al. (1986), Walsh and Dieterle (1994)
Bering Sea Shelf	-165.4	56.7						-8 Codispoti et al. (1986)
Bristol Bay	-164	58						-0.2 Borges et al. (2005) Kelley and Hood (1971), Codispoti et al. (1986), Chen (1993), Murata and Takizawa (2003)
Canterbury Bight	170.7	-45.8	-0.64 ^c	-0.43 ^c	-0.41 ^c	-0.37 ^c	-0.17	Guilerson et al. (2005)
Chukchi Sea	-165	72.5	-0.05	-2.3	-2.47	-0.04	-5.33	Bates (2006)
Coastal Calif. (Monterey Bay)	-121.9	36.9						0.05 Friederich et al. (2002)
East China Sea (Middle)	124	31	-8.8	-4.9	2.9	-10.4	-1.9	Zhai and Dai (2009)
East China Sea (Northern)	126	33	-5.04	-2.52	1.9		-0.79	Shim et al. (2007)
East China Sea (Southern Eastern)	125	30	-4.87	-3.32	-5.14	-8.57	-1.45	Wang et al. (2000)
English Channel	-1.2	50.2						-0.15 Borges and Frankignoulle (2003), Thomas et al. (2007)
Funka Bay	140.6	42.3						-7 Nakayama et al. (2000)
Gray's Reef	-80.9	31.4	0.28	-0.35	-0.01	-1.72	-0.16	Sabine et al. (2012)
Great Barrier Reef	145.5	-15						0.33 Kawahata et al. (1999)
Gulf of Biscay	-6.5	49	-6.98	-15.08	-1.43	0.94	-2.88	Frankignoulle and Borges (2001)
Gulf of Cadiz	-6.5	36.75	-0.85	1.45	-0.4	-1.75	-0.16	Ribas-Ribas et al. (2011), Huertas et al. (2006) ^b
Gulf of Lion	4	43						7.1 de Madron et al. (2010)
Gulf of Mexico Shelf (Northwest)	-88.6	30.0	-1.35	-0.16	-0.31		-0.22	Sabine et al. (2012)
Gulf of Nicoya	-84.9	9.6			-0.05			-0.02 Pfeil et al. (2012) (SOCAT database)
Gulf of Trieste	13.6	45.7		5.43	0.77			-2.5 Turk et al. (2010)
Hudson Bay	-85	59						0.84 Eise et al. (2008)
Ishigaki Island ^d	124.3	24.4	-27		55	25	6.45	Kayanne et al. (2005)
Java Sea	112.9	-5.6	0.26 ^c	-0.01 ^c	0.07 ^c	0.23 ^c	0.05	Hydes et al. (2012)
Jiaozhou Bay	120.3	36.15	4.14	19.47	17.07	-0.15	3.7	Li et al. (2007)
Kaneohe Bay	-157.8	21.5						1.45 Fagan and Mackenzie (2007)
Kara Sea	74.0	74.0		-1.62	0.14		0.01	Fransson et al. (2001)
Lá Push	-125.0	48.0						-0.27 Sabine et al. (2011)
Laptev Sea	130.0	74.0						0.01 Fransson et al. (2001)
Malacca Strait	101.6	2.4	-0.10		0.63		0.10	Hydes et al. (2012)
Moorea ^d	-149.9	-17.5		1.5 ^c		-1.2 ^c	0.05	Frankignoulle et al. (1996), Gattuso et al. (1993)
New Jersey Coast	-74.2	39.4						-0.68 Boehme et al. (1998)

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Table 4. Continued.

type	Lon.(°)	Lat.(°)	spring fluxes ^b (mmol C m ⁻² d ⁻¹)	summer fluxes (mmol C m ⁻² d ⁻¹)	autumn fluxes (mmol C m ⁻² d ⁻¹)	winter fluxes (mmol C m ⁻² d ⁻¹)	annual flux (mol C m ⁻² yr ⁻¹)	References
North Coastal of California	-123.8	39.0		2.52			0.92	Pfeil et al. (2012) (SOCAT database)
North Sea	2.6	56.7						-1.38 Thomas et al. (2004)
North Sea (Northern and Middle)	2.5	52.0	-12.47	6.8	4.35	-0.35	-0.7	Schiettecatte et al. (2007), Hoppema (1991) ^d
North Sea (Southern)	2.5	52.0	-12.47	6.8	4.35	-0.35	-0.7	Takahashi et al. (2012) (LDED database)
Northeast Coastal of Australia	151.5	-23.5	-0.16 ^c	0.28 ^c	0.04 ^c		0.02	Hydes et al. (2012), Chen (unpublished)
NorthEast Sunda Shelf	105.7	0.7	-0.04		0.28	0.01	0.03	Chen et al. (2003), Otsuki et al. (2003), Wakita et al. (2003)
Okhotsk Sea	143.5	44.5		-4.1				-1.67 Goyet et al. (1998)
Omani coast	59.0	20.0	0.75	-7.13	-0.95	-1.17	-0.9	Hales et al. (2005)
Oregon Coast	-124.5	44.5		-20				-0.78 Sakamoto et al. (2008)
Olaru Bay	141.0	43.3	-8.8	-8.9	7.4	-6.9	-0.78	Sakamoto et al. (2008)
Palau Islands ^d	134.4	7.4		33	49		15.0	Kayanne et al. (2005)
Patagonian shelf	-85.0	-45.0	-7 ^c	-3.8 ^c	-2.9 ^c	-1 ^c	-1.35	Bianchi and Allison (2009)
Prydz Bay	78.9	-68.6				-75 ^c	-2.45	Gibson and Trull (1999), Borges et al. (2005), Wang et al. (1998)
Red Sea	42.8	13.4			0.04		0.01	Hydes et al. (2012)
Ross Sea	180.0	-75.0				-13 ^c	-1.5	Sweeney (2003), Wang et al. (1998), Bates et al. (1998)
Scotian shelf	-63.0	44.0	1.6	-3.1	-5.9	-8.3	-1.42	Shadwick et al. (2011)
Southeast Coastal of Australia	152.4	-32.8	-0.74 ^c	-0.57 ^c			-0.24	Takahashi et al. (2012) (LDED database)
South China Sea (Northern)	116.0	22.0	2.7	7.5	1.4		0.86	Zhai et al. (2005, 2007)
Sydney Coast (Port Hacking time series station)	151.2	-34.1						-0.17 McNeil (2010)
Taiwan St. ^d	120.3	25.0	-17.6					-6.4 Ma et al. (1999)
Vancouver Is. Coast	-126.0	49.0						-0.5 Ianson and Allen (2002)
West Coastal of India	74.0	14.1	0.06		0.03	0.03	0.01	Hydes et al. (2012)
Yellow Sea	122.0	35.5	-4.4	1.8	-4.4	-13	-2.2	Oh et al. (2000), Wang et al. (2001)
Yellow Sea (Northern)	122.5	38.5	1.88	3.38	1.39	0.24	1.68	Xue et al. (2012)
Yellow Sea (Southern)	122.0	34.5	4.47	1.56	4.85		1.99	Xue et al. (2011)

^a Positive fluxes indicate an emission of CO₂ from water to the atmosphere;^b Spring: March–May; Summer: June–August; Fall: September–November; Winter: December–February;^c Austral seasons;^d not used in the calculation.

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Table 5. Summary of reported annual global air-sea CO₂ fluxes in world's continental shelves.

CO ₂ sink in the coastal ocean (PgC yr ⁻¹)	References
-1.00	Tsunogai et al. (1999)
-0.10	Liu et al. (2000)
0.50	Fasham et al. (2001)
-0.60	Yool and Fasham (2001)
-0.24	Rabouille et al. (2001)
-0.30	Chen et al. (2003)
-0.36	Chen (2004)
-0.40	Thomas et al. (2004)
-0.90	Ducklow and McCallister (2004)
-0.37	Borges (2005)
-0.45	Borges et al. (2005)
-0.22	Cai et al. (2006)
-0.33 to -0.36	Chen and Borges (2009)
-0.21	Laruelle et al. (2010)
-0.25	Cai (2011)
-0.40	This study

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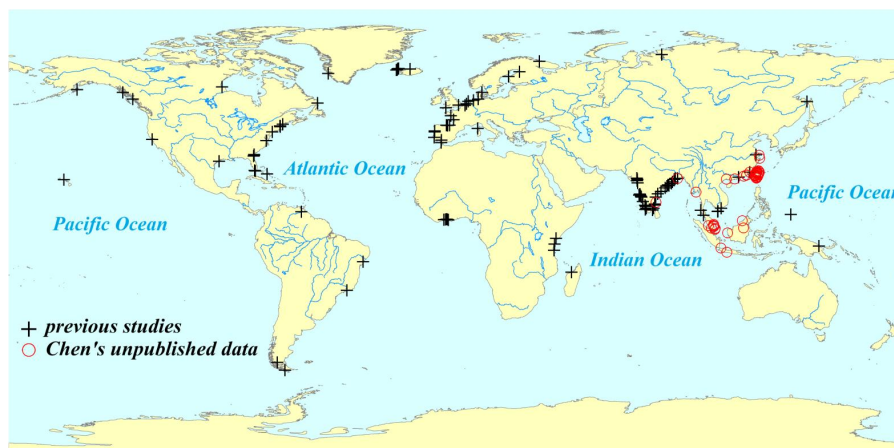


Fig. 1. Distribution of estuaries studied.

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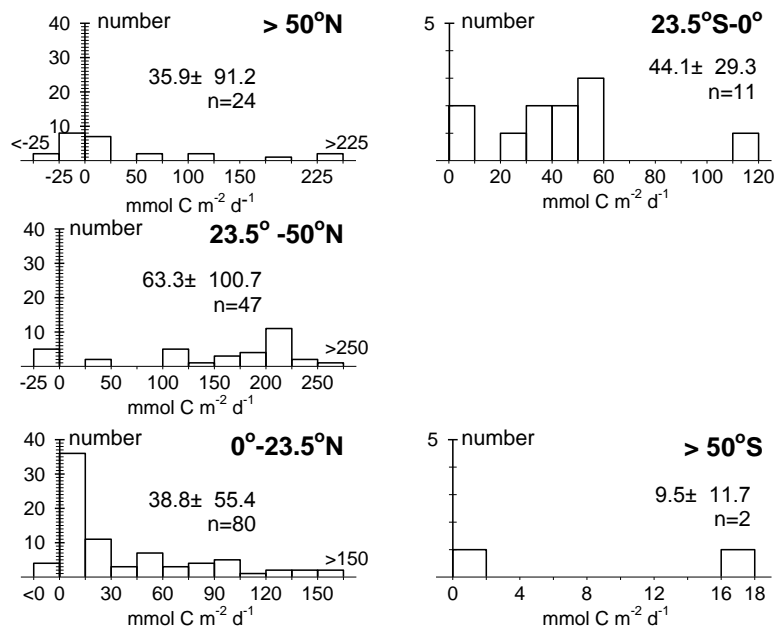


Fig. 4. Histogram of reported annual CO₂ fluxes of world's estuaries in various latitude bands.

5097

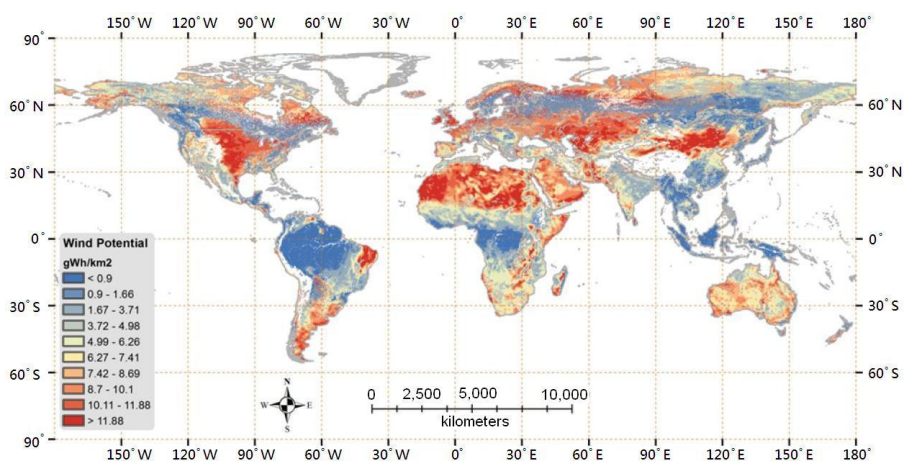


Fig. 5. Global wind potential (courtesy Zhou et al., 2012).

5098

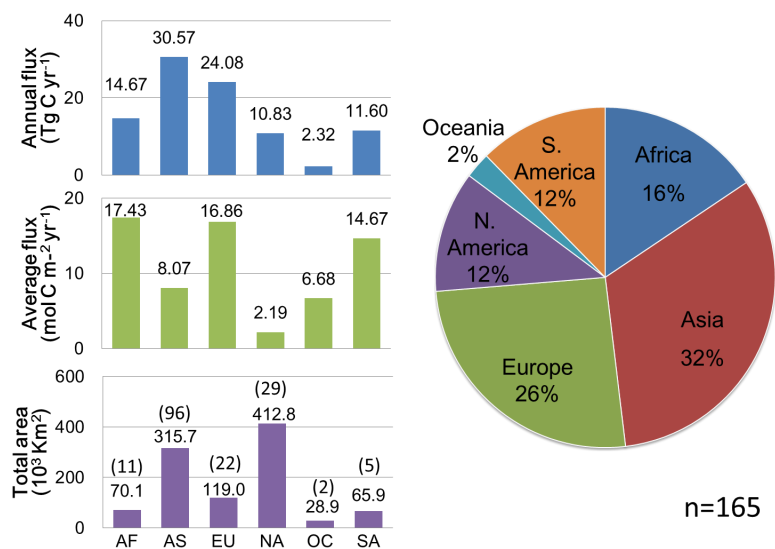


Fig. 6. Total annual CO₂ flux and CO₂ flux per unit area from estuaries in each continent.

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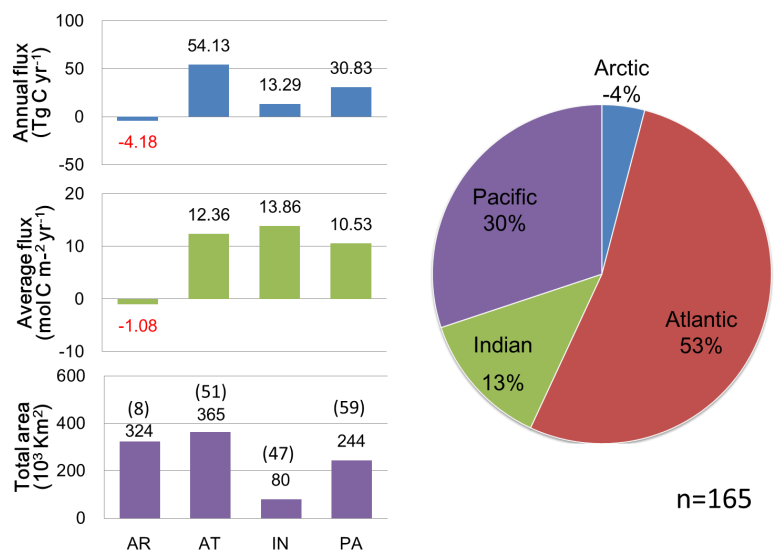


Fig. 7. Total annual CO₂ flux and CO₂ flux per unit area from estuaries around each ocean.

5100

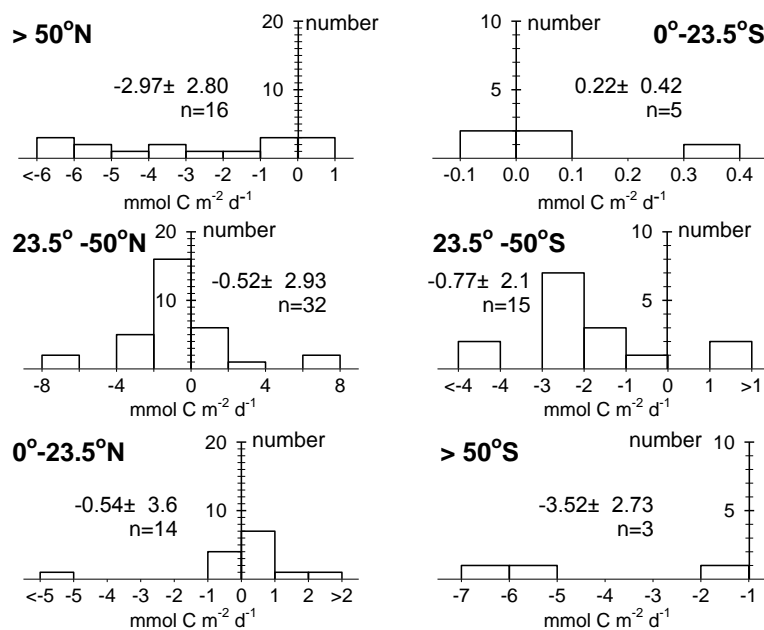


Fig. 10. Histogram of reported annual CO₂ fluxes of continental shelves in various latitude bands.

5103

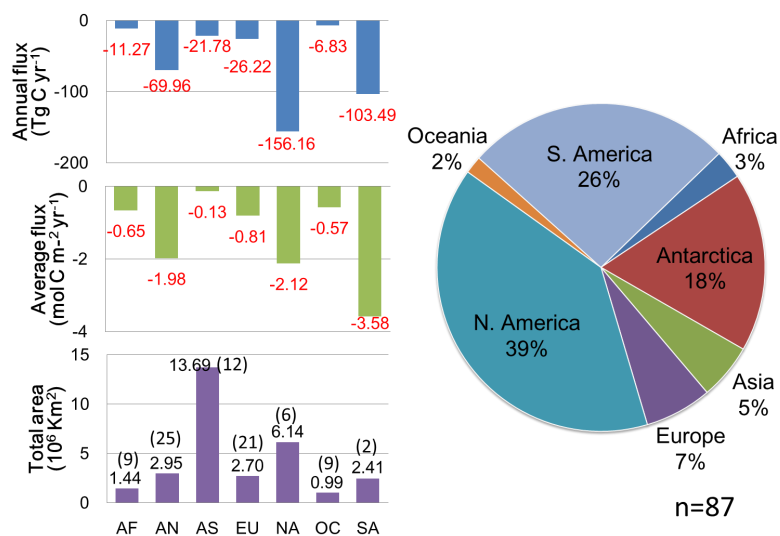


Fig. 11. Total annual CO₂ flux and CO₂ flux per unit area of continental shelves in different continents.

5104

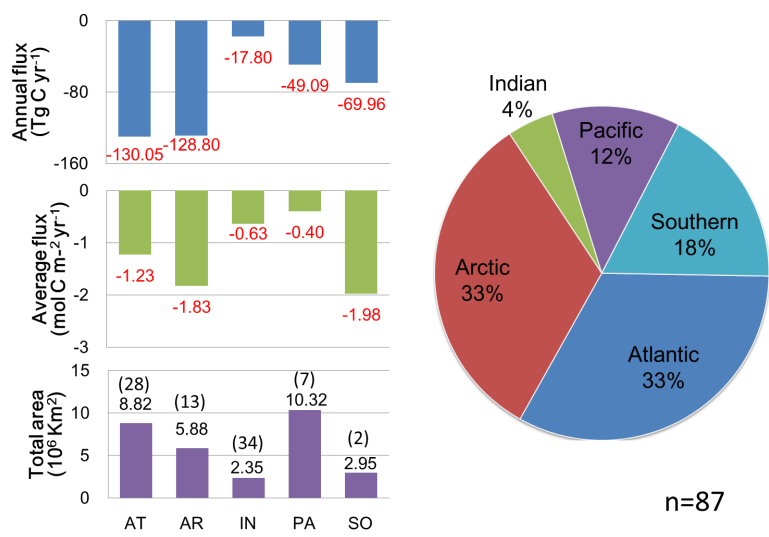


Fig. 12. Total annual CO₂ flux and CO₂ flux per unit area of continental shelves in different oceans.