Available online at www.sciencedirect.com

SciVerse ScienceDirect

Current Opinion in Environmental Sustainability

Strong sources of CO_2 in upper estuaries become sinks of CO_2 in large river plumes

Chen-Tung Arthur Chen[1,2], Ting-Hsuan Huang[1], Yu-Han Fu[1], Yan Bai[2] and Xianqiang He[2]

An extensive search of the literature and data banks identified studies of water-to-air CO_2 exchange in 106 estuaries. Generally, pCO_2 in upper estuaries is highly supersaturated with respect to the atmospheric CO_2, and so a large amount of CO_2 is released to the atmosphere per unit surface area. Wider mid and lower estuaries are associated with slower river flow and lower turbidity, and therefore greater biological productivity. Further, mixing with low-pCO_2 seawater reduces pCO_2 and, thereby, the water-to-air CO_2 flux on the ocean side. All of the globe's estuaries release 0.26 Pg C/y to the atmosphere. However, nutrients that are provided by large rivers, such as the Amazon and Changjiang (Yangtze), and those entrained by the river plumes promote photosynthesis to such an extent that the water becomes undersaturated. Accordingly, the large river plumes become a CO_2 sink even many hundred kilometers beyond the river mouth.

Addresses
[1] Institute of Marine Geology and Chemistry, National Sun Yat-sen University, Kaohsiung 804, Taiwan
[2] State Key Laboratory of Satellite Ocean Environment Dynamics, Second Institute of Oceanography, SOA, Hangzhou, China

Corresponding author: Chen, Chen-Tung Arthur (ctchen@mail.nsysu.edu.tw)

Current Opinion in Environmental Sustainability 2012, **4**:179–185

This review comes from a themed issue on Carbon and nitrogen cycles
Edited by Chen-Tung Arthur Chen and Dennis Peter Swaney

Received 6 October 2011; Accepted 10 February 2012
Available online 8th March 2012

1877-3435/$ – see front matter

DOI 10.1016/j.cosust.2012.02.003

Introduction

Rivers are the major conduits of water, nutrients, minerals and carbon from land to the oceans. Within river basins, atmospheric CO_2-saturated rainwater falls on rocks and soils, and CO_2 is converted into plant tissue by photosynthesis. Yet, most CO_2 enters the terrestrial carbon cycle when rainwater percolates through carbonates and silicates. Particularly in soils, bacterial oxidation decomposes photosynthetically generated organic carbon. Respiration in roots is an equally important source of CO_2 in soil. Soil water, groundwater, and runoff slowly find their way into rivers, and carbon is thereafter transported by rivers to the oceans in the form of dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), particulate inorganic carbon (PIC) and particulate organic carbon (POC). Denudation and mud slides are another source of ancient carbon in river water [1–3].

In most aquatic systems, respiration exceeds autochthonous gross primary production, with net heterotrophy sustained by the input of organic carbon from the catchment. Mostly owing to the decomposition of organic matter, the partial pressure of CO_2 (pCO_2) in soil water and river water is supersaturated with respect to CO_2 in the atmosphere. Moreover, remineralization of DOC and POC that are carried by rivers typically makes river and estuary ecosystems highly heterotrophic. Consequently, most rivers, and therefore estuaries, are sources of CO_2 to the atmosphere [2,4–12,13••,14••,15–17]. Since most studies of the riverine transport of carbon to oceans have really considered only the amount transported by rivers, and have ignored the amount released from estuaries [18], the amount that actually enters the oceans must be smaller than they have determined.

Although some individual estuaries have been analyzed in detail, general patterns of the global distribution of the water-to-air CO_2 fluxes in estuaries are still not well understood, because of a lack of data. Fortunately, a huge number of studies have recently been published around the globe. For example, the summary of Chen and Borges [13••] concerned 32 estuaries, while that of Laruelle *et al.* [14••] covered 60. The present investigation considers 106 estuaries for which pCO_2 data are available in either the literature or various data banks. For the first time, the water-to-air fluxes of CO_2 in the upper, mid and lower estuaries worldwide are systematically analyzed.

Following Elliott and McLusky [19] and Jiang *et al.* [20], this work adopts perhaps the most widely applied definition of an estuary, which was originally offered by Cameron and Pritchard [21], as 'a semi-enclosed coastal body of water, which has a free connection with the open sea and within which seawater is measurably diluted with freshwater derived from land drainage'. However, large bodies of semi-enclosed coastal seas such as the Baltic or the Bohai, are not regarded as estuaries. Upper/mid/lower estuaries are operationally defined as those areas of estuaries with salinities below 2, between 2 and 25, and above 25, respectively, whenever salinity data are available. Otherwise, divisions are artificially made based approximately on one-thirds of the distance from the point where the river starts to widen to the river mouth.

General patterns

Although relationships between pCO_2 and river hydrography, changes in land use, fertilizer and waste water discharges, atmospheric deposition, water-to-air CO_2 exchange, the turbidity and biological productivity of estuarine water and tidal motions, or the interaction between the water and the bottom sediments is not always evident, some general patterns of the saturation state of CO_2 in estuarine waters seem to exist. The narrowness of upper estuaries causes the flow rate to be high, such that incoming turbid river water remains turbid. Strong flow also disturbs bottom sediments, increasing turbidity. As a result, a lack of light limits biological productivity, and so the photosynthetic draw-down of CO_2 is weak. However, organic matter that is carried by the rivers is regenerated and high-pCO_2 outflow from salt marshes, mangroves and submarine groundwater discharge (SGD) help keep pCO_2 high, causing CO_2 to be released to the atmosphere [9,20,22–32]. On average, upper estuaries around the world have a pCO_2 of 3033 ± 1078 μatm and a water-to-air flux of 68.5 ± 25.6 mol C/m^2/y (Figure 1).

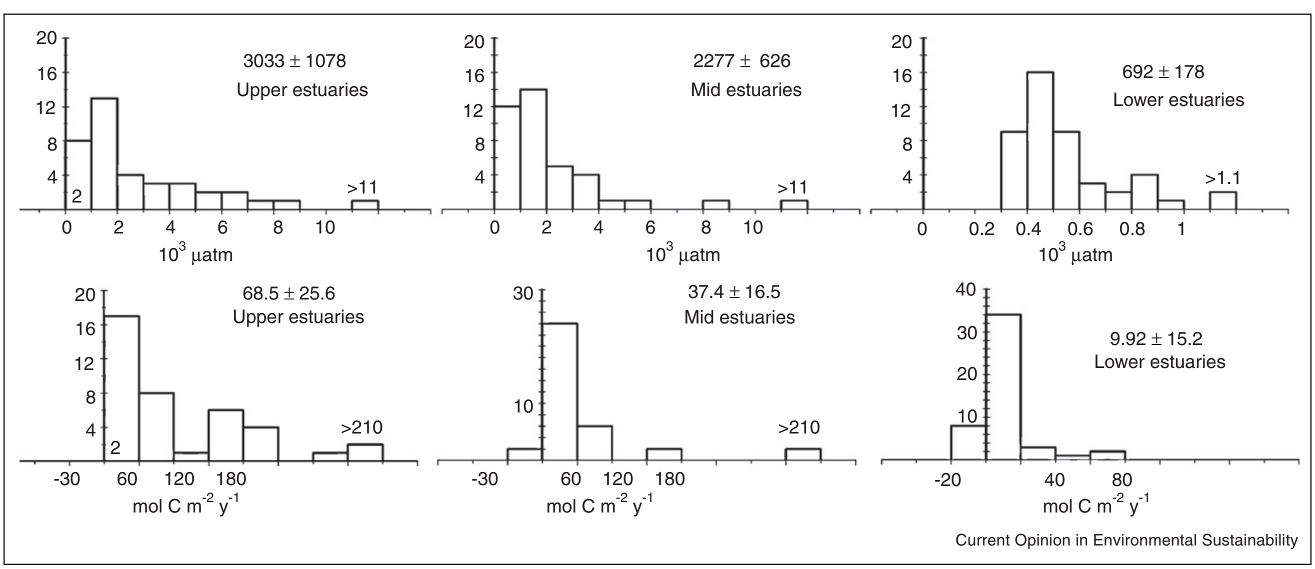
In mid estuaries, pCO_2 is normally lower than in upper estuaries because some of the CO_2 in the water has already been lost to the atmosphere. Additionally, currents and resuspension of bottom sediments become weaker, so the transparency is higher. Consequently, photosynthesis is enhanced, and the supply of abundant nutrients from rivers and SGD results in a higher biological draw-down of CO_2. Additionally, per unit estuarine surface area, the input of high pCO_2 outflows from salt marshes, mangroves and SGD is smaller. Furthermore, mixing with low-pCO_2 ocean water is more extensive than in upper estuaries. Accordingly, pCO_2, and hence the water-to-air flux of CO_2 in mid estuaries usually declines rapidly as salinity increases [33,34•,35•,36]. On average globally, mid estuaries have a pCO_2 value of 2277 ± 626 μatm and a water-to-air flux of 37.4 ± 16.5 mol C/m^2/y (Figure 1).

The values of pCO_2, and therefore the water-to-air fluxes of CO_2, are usually lowest in the lower estuaries, because incoming water from the mid estuary has lost more CO_2 to the atmosphere. Enhanced photosynthesis in the relatively clear water draws down more CO_2. More mixing with low-pCO_2 ocean water and lower inputs per unit estuarine surface area from sediments, salt marshes, mangroves and SGD than in the upper and mid estuaries cause pCO_2 to be lowest in the lower estuary. In fact, photosynthesis may draw down enough CO_2 from waters that is already relatively low in pCO_2 to make the water undersaturated, at times turning the edges of the lower estuary or the river plume into a sink of CO_2 [34•,35•,37•,38,39]. Available data demonstrate that the pCO_2 in lower estuaries, excluding river plumes, is reduced to only 692 ± 178 μatm (a global average), and that lower estuaries release only 9.92 ± 15.2 mol C/m^2/y to the atmosphere (Figure 1).

Large river plumes

Major rivers provide a disproportionately important link between terrestrial and marine materials: the world's 10

Figure 1



Histogram of water-to-air CO_2 fluxes in upper, mid and lower estuaries worldwide ([14••] and references therein, [30,58,63–67], Chen, unpublished data).

largest rivers transport around 40% of the fresh water and the particulate materials that enter the oceans. Furthermore, around 40% of the organic matter in the global oceans is buried in the deltas of large rivers [40]. A case in point is the Changjiang (Yangtze) River, which is the longest and largest river in China in terms of discharge. The Changjiang River is the third longest in the world, after the Nile and Amazon Rivers, but in terms of discharge, it ranks fourth behind the Amazon, Zaire and Orinoco Rivers. The Changjiang has a pCO_2 of about 1200 μatm in the downstream region all-year-round, which declines abruptly when seawater is encountered close to the river mouth. Notably, the East China Sea (ECS) water, at a salinity of around 33, is usually slightly undersaturated and seawater with a salinity of 30 contains only 10% river water. The 10-fold dilution of the Changjiang water by ECS water reduces the pCO_2 of the river water to near the saturation value.

Since Changjiang has a large discharge, the salinity in the summer is commonly less than 30 in the middle of the ECS. At this location, however, the turbidity of the plume is sufficiently low for phytoplankton to bloom, given enough light and abundant of nutrients. Therefore, pCO_2 is further reduced to as low as 200 μatm or lower in the river plume for most of the year, even many hundred kilometers from the river mouth [34•,39,41].

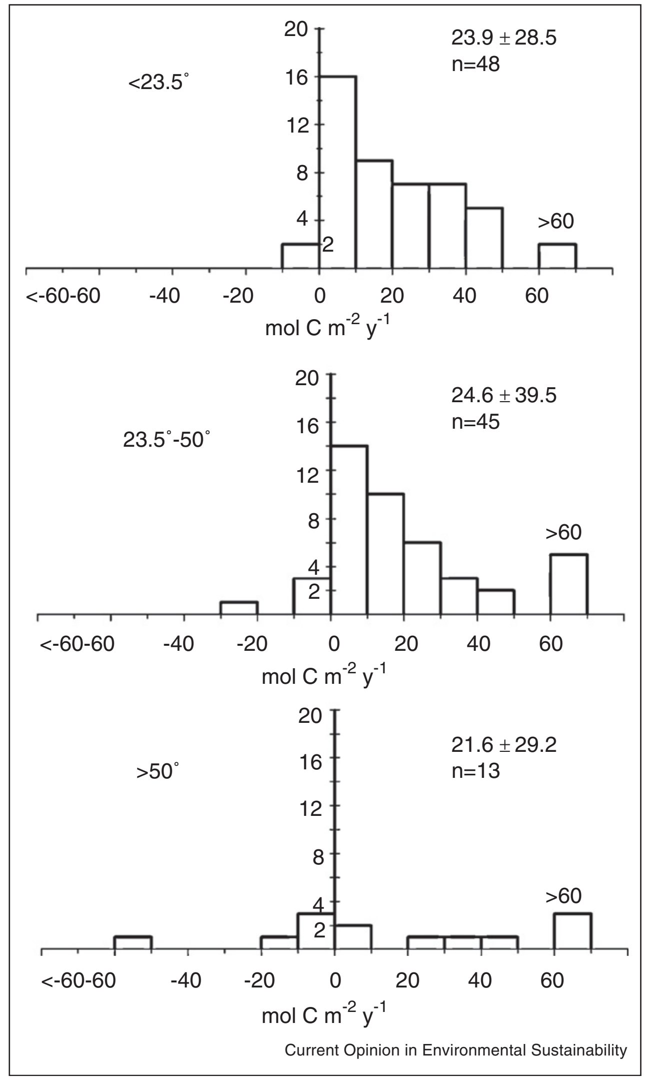
Significant river plume-induced water-to-air fluxes of CO_2 have also been found in the Amazon, Mississippi, Congo, Ganges and Pearl River plumes [37•,42–48].

Geographical variations

Unlike continental shelves in temperate (23.5–50°) and high-latitude (>50°) regions where seas typically act as sinks for atmospheric CO_2 [13••], the estuaries in these regions mostly release CO_2 to the atmosphere (Figure 2). This contrast reflects the fact that open oceanic waters are generally undersaturated in CO_2 in temperate and high-latitude regions [49], and, the continental shelves are highly productive, promoting the open-ocean CO_2 undersaturation. Incoming river water to the estuaries is usually highly supersaturated with respect to CO_2, loaded with terrestrial organic matter that regenerates in the estuaries, and exhibits a high turbidity that impedes productivity. Therefore, CO_2 remains supersaturated.

In tropical regions, open ocean waters are typically oversaturated with CO_2, and nonupwelling continental shelves are normally oligotrophic; they, therefore, exhibit low productivity and relatively high pCO_2. However, these regions receive up to 60% of the global riverine organic carbon inputs [50–52], promoting the supersaturation on the continental shelves [13••]. Naturally, all of the above factors make tropical estuaries generally sources of CO_2 to the atmosphere [53•]. In summary, estuaries in all three latitude bands are generally sources of CO_2. Interestingly,

Figure 2



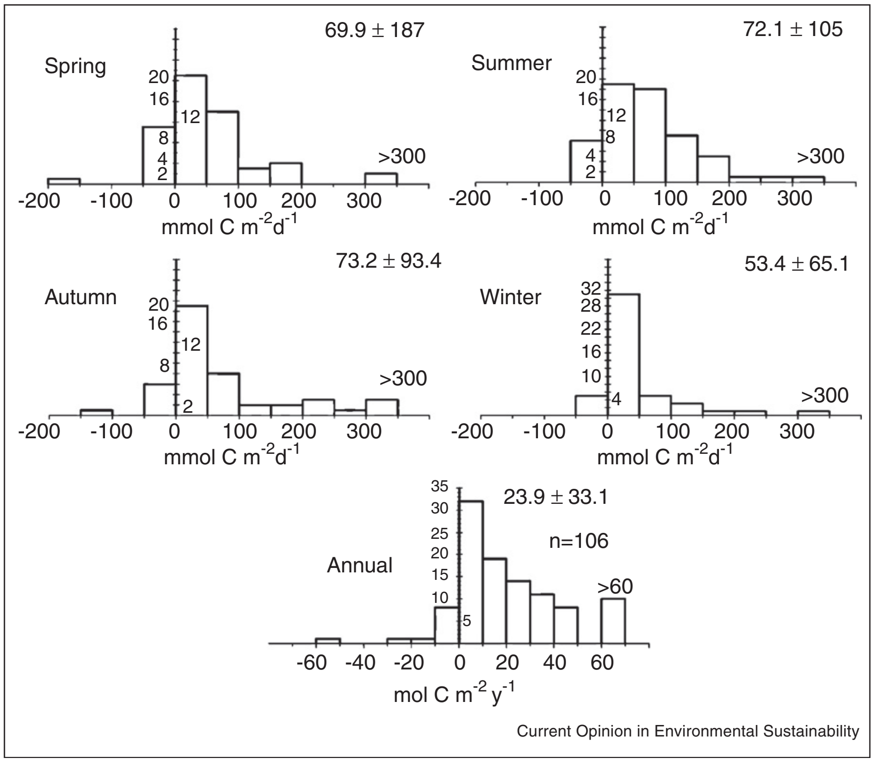
Histogram of water-to-air CO_2 flux in regions between 23.5°N and 23.5°S, 23.5–50°, and >50° ([14••] and references therein, [29,30,58,63–78], Chen, unpublished data).

water-to-air fluxes do not significantly vary geographically, and all fall around 24 mol C/m^2/y although the flux is slightly lower at high latitudes (Figure 2).

Seasonal variations

Although relevant data vary greatly, most continental shelves are generally sinks for CO_2 during most of the year, with the possible exception of summer (June–August in the northern hemisphere) because the warming of seawater thermodynamically increases pCO_2 [13••]. Most data reveal that, generally, the water in estuaries releases CO_2 in all seasons although the flux seems to be highest in autumn (September–November; 73.2 ± 93.4 mmol C/m^2/d) and lowest (53.4 ± 65.1 mmol C/m^2/d) in winter (December–February; Figure 3). The numerical average

Figure 3



Histogram of water-to-air flux in four seasons and the annual flux for estuaries worldwide ([14••] and references therein, [29,30,58,63–68,70,71,76,78], Chen, unpublished data).

of the annual water-to-air flux of CO_2 is 23.9 ± 33.1 mol C/m^2/y, which yields a global estuarine flux of 0.26 Pg C/y when the global estuarine surface area is taken to be 1.07×10^6 km^2 [54]. Notably, this total flux is subject to large uncertainty because few field expeditions cover the entire tidal cycle. Further, measurements frequently do not cover various wind mixing and stratification conditions of the water column. Contribution from coastal vegetation is also poorly studied [26,55]. Finally, the global average flux is likely to be an overestimate because upper estuaries have high fluxes but have a much smaller surface area than the lower estuaries, which have a low flux. By way of comparison, Chen and Borges [13••] provided a global estuarine CO_2 emission value of up to 0.5 Pg C/y, Laruelle *et al.* [14••] gave 0.27 ± 0.23 Pg C/y, and Cai [55] gave 0.25 ± 0.25 Pg C/y. Importantly, the IPCC [18] report provided a riverine input of 0.8 Pg C/y to the oceans, but at least a third of this is released to the atmosphere in estuaries.

Conclusions

Rivers are the major conduits for transporting terrestrial material toward the oceans, but not all transported material reaches the oceans. Upper estuaries are found usually to be highly supersaturated in terms of pCO_2, while mid estuaries are less so and lower estuaries are the least supersaturated. They together release some of the carbon that is transported by the rivers to the atmosphere. However, large river plumes are often found to be sinks of CO_2 because of a high rate of photosynthesis.

Predicting the future trend is not easy because the driving forces and feedback systems in estuaries are complex, as they are subject to intense anthropogenic disturbance. Increasing loadings of inorganic nutrients for biological production in estuaries reduces pCO_2 especially in the lower estuaries where suspended particles have sufficiently settled to allow enough light for photosynthesis. The construction of dams around the world will also reduce the downstream transport of sediments, increasing the transparency of water but reducing the degree of respiration by reducing the POC load [56–58]. Additionally, the atmospheric CO_2 will continue to rise. Consequently, those lower estuaries that are now small sources of atmospheric carbon will probably become net sinks of CO_2 in the future. Considering only the increase in nutrient delivery by rivers, Borges [59••] has suggested that by 2100, the negative feedback (reduction of atmospheric CO_2) will be of the order of magnitude of the present day sink of atmospheric CO_2 by the coastal oceans. Added to this effect is a small negative feedback that is associated with increased limestone weathering [58] and the dissolution of $CaCO_3$ in sediments that is caused by ocean acidification [59••]. However, increased loadings of detrital organic matter, mostly due to agricultural practices, will increase respiration rates and the production of CO_2. Consequently, most upper and mid estuaries are likely to remain as sources of CO_2 for at least the next few centuries. Increased river basin nutrient management procedures could lead to a decreased nutrient and DOC loads to the estuaries [60,61]. Yet, complicated feedback that is related to changes such as land use patterns and hydrological cycles remains to be investigated [62].

Acknowledgements

This research was partially supported by the National Science Council of Taiwan (NSC 98-2621-M-110-001-MY3; 99-2611-M-110-002-MY3) and Aim for the Top University Plan. The manuscript was completed while C.T.A. Chen was on leave at the Second Institute of Oceanography, Hangzhou. Y.C. Chang of IMGC, NSYSU helped with preparing the manuscript. W.J. Cai, A. Borges and two anonymous reviewers provided valuable comments which helped strengthening the manuscript.

References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- • of special interest
- •• of outstanding interest

1. Kempe S: **Carbon in the freshwater cycle**. In *The Global Carbon Cycle.* Edited by Bolin B, Degens ET, Kempe S, Ketner P. 1979:317-342. (Scope 13).

2. Schlunz B, Schneider RR: **Transport of terrestrial organic carbon to the oceans by rivers: re-estimating flux- and burial rates**. *Int. J. Earth Sci.* 2000, **88**:599-606 doi: 10.1007/s005310050290.

3. Cole JJ, Caraco NF: **Carbon in catchments: connecting terrestrial carbon losses with aquatic metabolism**. *Mar. Freshw. Res.* 2001, **52**:101-110.

4. Cai WJ, Wang Y: **The chemistry, fluxes, and sources of carbon dioxide in the estuarine waters of the Satilla and Altamaha Rivers, Georgia**. *Limnol Oceanogr* 1998, **43**:657-668.

5. Gattuso JP, Frankignoulle M, Wollast R: **Carbon and carbonate metabolism in coastal aquatic ecosystems**. *Annu Rev Ecol Syst* 1998, **29**:405-434 doi: 10.1146/annurev.ecolsys.29.1.405.

6. Frankignoulle M: **Carbon dioxide emission from European estuaries**. *Science* 1998, **282**:434-436 doi: 10.1126/science.282.5388.434.

7. Raymond PA, Bauer JE, Cole JJ: **Atmospheric CO_2 evasion, dissolved inorganic carbon production, and net heterotrophy in the York River estuary**. *Limnol Oceanogr* 2000, **45**:1707-1717.

8. Abril G, Nogueira M, Etcheber H, Cabecadas G, Lemaire E, Brogueira MJ: **Behaviour of organic carbon in nine contrasting European estuaries**. *Estuar. Coast. Shelf Sci.* 2002, **54**:241-262 doi: 10.1006/ecss.2001.0844.

9. Borges AV, Djenidi S, Lacroix G, Theate J, Delille B, Frankignoulle M: **Atmospheric CO_2 flux from mangrove surrounding waters**. *Geophys Res Lett* 2003, **30**:1558 doi: 10.1029/2003gl017143.

10. Crossland C, Kremer HH, Lindeboom HJ, Crossland JIM, Le Tissier MDA (Eds). *Coastal Fluxes in the Anthropocene: The Land-Ocean Interactions in the Coastal Zone Project of the International Geosphere-Biosphere Programme*. Berlin; 2005.

11. Middelburg JJ, Herman PMJ: **Organic matter processing in tidal estuaries**. *Mar Chem* 2007, **106**:127-147 doi: 10.1016/j.marchem.2006.02.007.

12. Ciais P, Borges AV, Abril G, Meybeck M, Folberth G, Hauglustaine D, Janssens IA: **The impact of lateral carbon fluxes on the European carbon balance**. *Biogeosciences* 2008, **5**:1259-1271.

13. •• Chen CTA, Borges AV: **Reconciling opposing views on carbon cycling in the coastal ocean: continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO_2**. *Deep-Sea Res. II-Top. Stud. Oceanogr.* 2009, **56**:578-590 doi: 10.1016/j.dsr2.2009.01.001.

A synthesis of worldwide measurements of the pCO_2 indicates that most open shelves in the temperate and high-latitude regions are undersaturated with respect to atmospheric CO_2 during all seasons but the low-latitude shelves seem to be oversaturated. This paper compiles the most extensive data sets for estuaries and continental shelves in the world. It was concluded that estuaries, salt marshes and mangroves emit up to 0.5 Pg C/y based on direct measurements of CO_2 to the atmosphere. On the other hand, CO_2 measurement and mass-balance calculations reveal that continental shelves absorb about 0.33–0.36 Pg C/y of CO_2 from the atmosphere.

14. •• Laruelle GG, Durr HH, Slomp CP, Borges AV: **Evaluation of sinks and sources of CO_2 in the global coastal ocean using a spatially-explicit typology of estuaries and continental shelves**. *Geophys Res Lett* 2010, **37**:L15607 doi: 10.1029/2010gl043691.

This paper builds upon the database of Chen and Borges [13••], and increased the number of estuaries from 32 to 60. Using a spatially explicit global typology of estuaries the computed emission of CO_2 to the atmosphere (0.27 ± 0.23 Pg C/y) is ~26% to ~55% lower than previous estimates. On the other hand, the CO_2 enters the continental shelf seas at a rate of 0.21 ± 0.36 Pg C/y. The flux per surface area over continental shelf seas ($-0.7/-1.2$ mol C/m^2/y) is the double of the value in the open oceans.

15. Kempe S: **Long-term records of CO_2 pressure fluctuations in fresh waters**. *Mitt Geol Palaeontol Inst Univ Hamburg* 1982, **52**:91-332.

16. Kempe S: **Sinks of the anthropogenically enhanced carbon cycle in surface fresh waters**. *J Geophys Res* 1984, **89**:4657-4676.

17. Lauerwald R, Hartmann J, Ludwig W, Moosdorf N: **Assessing the non-conservative fluvial fluxes of dissolved organic carbon in North America**. *J Geophys Res* 2012. in press.

18. Intergovernmental Panel on Climate C: *IPCC Fourth Assessment Report Climate Change 2007*. Geneva: Intergovernmental Panel on Climate Change; 2007.

19. Elliott M, McLusky DS: **The need for definitions in understanding estuaries**. *Estuar Coast Shelf Sci* 2002, **55**:815-827 doi: 10.1006/ecss.2002.1031.

20. Jiang LQ, Cai WJ, Wang YC: **A comparative study of carbon dioxide degassing in river- and marine-dominated estuaries**. *Limnol Oceanogr* 2008, **53**:2603-2615 doi: 10.4319/lo.2008.53.6.2603.

21. Cameron WM, Pritchard Dw: **Estuaries**. In *The Sea.* Edited by Hill MN. John Wiley and Sons; 1963:306-324.

22. Alvarez M, Fernandez E, Perez FF: **Air–sea CO_2 fluxes in a coastal embayment affected by upwelling: physical versus biological control**. *Oceanol Acta* 1999, **22**:499-515.

23. Cai WJ, Pomeroy LR, Moran MA, Wang YC: **Oxygen and carbon dioxide mass balance for the estuarine-intertidal marsh complex of five rivers in the southeastern US**. *Limnol Oceanogr* 1999, **44**:639-649.

24. Cai WJ, Wiebe WJ, Wang YC, Sheldon JE: **Intertidal marsh as a source of dissolved inorganic carbon and a sink of nitrate in the Satilla River-estuarine complex in the southeastern US**. *Limnol Oceanogr* 2000, **45**:1743-1752.

25. Raymond PA, Bauer JE: **Use of C-14 and C-13 natural abundances for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: a review and synthesis**. *Org Geochem* 2001, **32**:469-485 doi: 10.1016/s0146-6380(00)00190-x.

26. Borges AV: **Do we have enough pieces of the jigsaw to integrate CO_2 fluxes in the coastal ocean?** *Estuaries* 2005, **28**:3-27 doi: 10.1007/bf02732750.

27. Zhai W, Dai M, Guo X: **Carbonate system and CO_2 degassing fluxes in the inner estuary of Changjiang (Yangtze) River, China**. *Mar Chem* 2007, **107**:342-356 doi: 10.1016/j.marchem.2007.02.011.

28. Leinweber A, Gruber N, Frenzel H, Friederich GE, Chavez FP: **Diurnal carbon cycling in the surface ocean and lower atmosphere of Santa Monica Bay, California**. *Geophys Res Lett* 2009, **36**:L08601 doi: 10.1029/2008gl037018.

29. Zemmelink HJ, Slagter HA, van Slooten C, Snoek J, Heusinkveld B, Elbers J, Bink NJ, Klaassen W, Philippart CJM, de Baar HJW: **Primary production and eddy correlation measurements of CO_2 exchange over an intertidal estuary**. *Geophys Res Lett* 2009, **36**:L19606 doi: 10.1029/2009gl039285.

30. Dai MH, Lu ZM, Zhai WD, Chen BS, Cao ZM, Zhou KB, Cai WJ, Chen CTA: **Diurnal variations of surface seawater pCO_2 in contrasting coastal environments**. *Limnol Oceanogr* 2009, **54**:735-745 doi: 10.4319/lo.2009.54.3.0735.

31. Peng TR, Chen CTA, Wang CH, Zhanc J, Lin YJ: **Assessment of terrestrial factors controlling the submarine groundwater discharge in water shortage and highly deformed island of Taiwan, western Pacific Ocean**. *J Oceanogr* 2008, **64**:323-337 doi: 10.1007/s10872-008-0026-0.

32. Cai WJ, Wang YC, Krest J, Moore WS: **The geochemistry of dissolved inorganic carbon in a surficial groundwater aquifer in North Inlet, South Carolina, and the carbon fluxes to the coastal ocean**. *Geochim Cosmochim Acta* 2003, **67**:631-639 doi: 10.1016/s0016-7037(02)01167-5.

33. Hopkinson CJ, Smith EM, del Giorgio PA, Williams PJL: **Estuarine respiration: an overview of benthic, pelagic and whole system respiration**. In *Respiration in Aquatic Ecosystems.* Edited by del Giorgio PA, Williams PJL. Oxford University Press; 2005:122-146.

34. • Chen CTA, Zhai W, Dai M: **Riverine input and air–sea CO_2 exchanges near the Changjiang (Yangtze River) estuary: status quo and implication on possible future changes in metabolic status**. *Cont Shelf Res* 2008, **28**:1476-1482 doi: 10.1016/j.csr.2007.10.013.

Because of anthropogenic activities the nutrient loadings of the Changjiang are on the rise. Yet, river water is still supersaturated in the upper estuary but decreases quickly in the mid estuary due to mixing with low pCO_2 waters from offshore. In addition, settling of particles in the estuary results in better light conditions so that phytoplankton bloom, driving down pCO_2 to about 200 μatm outside of the river mouth.

35. • Chen CTA, Wang SL, Lu XX, Zhang SR, Lui HK, Tseng HC, Wang BJ, Huang HI: **Hydrogeochemistry and greenhouse gases of the Pearl River, its estuary and beyond**. *Quat Int* 2008, **186**:79-90 doi: 10.1016/j.quaint.2007.08.024.

All three major tributaries of the Pearl River are highly eutrophicated in the region of the Pearl River Delta because of the high nutrient and sediment loading. At places, the dissolved oxygen saturation level becomes as low as 2%, resulting in high pCO_2. Yet, largely as a result of mixing with the open ocean water but partly because of biological consumption, pCO_2 quickly reduces to near saturation only tens of kilometers off the mouth of the estuary.

36. Guo XH, Dai MH, Zhai WD, Cai WJ, Chen BS: **CO_2 flux and seasonal variability in a large subtropical estuarine system, the Pearl River Estuary, China**. *J Geophys Res-Biogeosci* 2009, **114** doi: 10.1029/2008jg000905.

37. • Kortzinger A: **A significant CO_2 sink in the tropical Atlantic Ocean associated with the Amazon River plume**. *Geophys Res Lett* 2003, **30** doi: 10.1029/2003gl018841.

A strong undersaturation of surface seawater with respect to atmospheric CO_2 was found in the Amazon River plume which is advected into the surface circulation of the tropical Atlantic. A conservative estimate of the plume-related CO_2 sink yields a net air-to-sea flux of 0.014 Pg C/y.

38. Ortega T, Ponce R, Forja J, Gomez-Parra A: **Fluxes of dissolved inorganic carbon in three estuarine systems of the Cantabrian Sea (north of Spain)**. *J Mar Syst* 2005, **53**:125-142 doi: 10.1016/j.marsys.2004.06.006.

39. Zhai WD, Dai MH: **On the seasonal variation of air–sea CO_2 fluxes in the outer Changjiang (Yangtze River) Estuary, East China Sea**. *Mar Chem* 2009, **117**:2-10 doi: 10.1016/j.marchem.2009.02.008.

40. Hedges JI, Keil RG: **Sedimentary organic-matter preservation — an assessment and speculative synthesis**. *Mar Chem* 1995, **49**:81-115 doi: 10.1016/0304-4203(95)00008-f.

41. Chen CTA, Wang SL: **Carbon, alkalinity and nutrient budgets on the East China Sea continental shelf**. *J Geophys Res-Oceans* 1999, **104**:20675-20686 doi: 10.1029/1999jc900055.

42. Kumar MD, Naqvi SWA, George MD, Jayakumar DA: **A sink for atmospheric carbon dioxide in the northeast Indian Ocean**. *J Geophys Res-Oceans* 1996, **101**:18121-18125 doi: 10.1029/96jc01452.

43. Bakker DCE, de Baar HJW, de Jong E: **The dependence on temperature and salinity of dissolved inorganic carbon in East Atlantic surface waters**. *Mar Chem* 1999, **65**:263-280 doi: 10.1016/s0304-4203(99)00017-1.

44. Ternon JF, Oudot C, Dessier A, Diverres D: **A seasonal tropical sink for atmospheric CO_2 in the Atlantic ocean: the role of the Amazon River discharge**. *Mar Chem* 2000, **68**:183-201 doi: 10.1016/s0304-4203(99)00077-8.

45. Cai WJ: **Riverine inorganic carbon flux and rate of biological uptake in the Mississippi River plume**. *Geophys Res Lett* 2003, **30**:1032 doi: 10.1029/2002gl016312.

46. Lohrenz SE, Cai WJ: **Satellite ocean color assessment of air–sea fluxes of CO_2 in a river-dominated coastal margin**. *Geophys Res Lett* 2006, **33** doi: 10.1029/2005gl023942.

47. Cooley SR, Coles VJ, Subramaniam A, Yager PL: **Seasonal variations in the Amazon plume-related atmospheric carbon sink**. *Global Biogeochem Cycl* 2007, **21** doi: 10.1029/2006gb002831.

48. Dai MH, Zhai WD, Cai WJ, Callahan J, Huang BQ, Shang SL, Huang T, Li XL, Lu ZM, Chen WF *et al.*: **Effects of an estuarine plume-associated bloom on the carbonate system in the lower reaches of the Pearl River estuary and the coastal zone of the northern South China Sea**. *Cont Shelf Res* 2008, **28**:1416-1423 doi: 10.1016/j.csr.2007.04.018.

49. Takahashi T, Sutherland SC, Wanninkhof R, Sweeney C, Feely RA, Chipman DW, Hales B, Friederich G, Chavez F, Sabine C: **Corrigendum to "Climatological mean and decadal change in surface ocean pCO_2, and net sea–air CO_2 flux over the global oceans" [Deep Sea Res II 56 (2009) 554–577]**. *Deep Sea Res I: Oceanogr Res Pap* 2009, **56**:2075-2076 doi: 10.1016/j.dsr.2009.07.007.

50. Ludwig W, AmiotteSuchet P, Probst JL: **River discharges of carbon to the world's oceans: determining local inputs of alkalinity and of dissolved and particulate organic carbon**. *CR Acad Sci I Fasc a-Sci Terre Planet* 1996, **323**:1007-1014.

51. Huang T-H, Fu Y-H, Pan P-Y, Chen C-TA: **Fluvial carbon fluxes in tropical rivers**. *Curr Opin Environ Sustain* 2012, **4** doi: 10.1016/j.cosust.2012.02.004 this issue.

52. Dai M, Yin Z, Meng F, Liu Q, Cai W-J: **Spatial Distribution of Riverine DOC Inputs to the Ocean: An Updated Global Synthesis**. *Curr Opin Environ Sustain* 2012, **4** this issue.

53. • Zhai WD, Dai MH, Cai WJ, Wang YC, Wang ZH: **High partial pressure of CO_2 and its maintaining mechanism in a subtropical estuary: the Pearl River estuary, China**. *Mar Chem* 2005, **93**:21-32 doi: 10.1016/j.marchem.2004.07.003.

Distributions of surface water pCO_2, dissolved oxygen and associated carbonate parameters in the Pearl River estuary were investigated. It was concluded that aerobic respiration is the most important process in maintaining high pCO_2 in this large subtropical estuary under increasing anthropogenic pressure in China.

54. Durr HH, Laruelle GG, van Kempen CM, Slomp CP, Meybeck M, Middelkoop H: **Worldwide typology of nearshore coastal systems: defining the estuarine filter of river inputs to the oceans**. *Estuar Coasts* 2011, **34**:441-458 doi: 10.1007/s12237-011-9381-y.

55. Cai W-J: **Estuarine and coastal ocean carbon paradox: CO_2 sinks or sites of terrestrial carbon incineration?** *Annu Rev Mar Sci* 2011, **3**:123-145 doi: 10.1146/annurev-marine-120709-142723.

56. Syvitski JP, Vorosmarty CJ, Kettner AJ, Green P: **Impact of humans on the flux of terrestrial sediment to the global coastal ocean**. *Science* 2005, **308**:376-380 doi: 10.1126/science.1109454.

57. Seitzinger SP, Mayorga E, Bouwman AF, Kroeze C, Beusen AHW, Billen G, Van Drecht G, Dumont E, Fekete BM, Garnier J *et al.*: **Global river nutrient export: a scenario analysis of past and future trends**. *Global Biogeochem Cycl* 2010, **24**:Gb0a08 doi: 10.1029/2009gb003587.

58. Zeng FW, Masiello CA, Hockaday WC: **Controls on the origin and cycling of riverine dissolved inorganic carbon in the Brazos River, Texas**. *Biogeochemistry* 2011, **104**:275-291 doi: 10.1007/s10533-010-9501-y.

59. Borges AV: *Present Day Carbon Dioxide Fluxes in the Coastal* •• *Ocean and Possible Feedbacks Under Global Change*. 2011 doi: 10.1007/978-90-481-9821-4_3:. 47–77.

The author asserts that the potential feedbacks on increasing atmospheric CO_2 from changes in carbon flows in the coastal ocean could be disproportionately higher than that in the open ocean. The changes could be driven by three main processes: first, changes in coastal physics; second, changes in land-use pattern, waste water inputs, agricultural fertilizers and changes in hydrological cycle; third, changes in seawater carbonate chemistry such as ocean acidification.

60. Macpherson GL, Roberts JA, Blair JM, Townsend MA, Fowle DA, Beisner KR: **Increasing shallow groundwater CO_2 and limestone weathering, Konza Prairie, USA**. *Geochim Cosmochim Acta* 2008, **72**:5581-5599 doi: 10.1016/j.gca.2008.09.004.

61. Feely RA, Chen CTA: **The effect of excess CO_2 on the calculated calcite and aragonite saturation horizons in the Northeast Pacific**. *Geophys Res Lett* 1982, **9**:1294-1297 doi: 10.1029/GL009i011p01294.

62. Radach G, Patsch J: **Variability of continental riverine freshwater and nutrient inputs into the North Sea for the years 1977–2000 and its consequences for the assessment of eutrophication**. *Estuar Coasts* 2007, **30**:66-81.

63. Álvarez-Salgado XA, Doval MD, Pérez FF: **Dissolved organic matter in shelf waters off the Ría de Vigo (NW Iberian upwelling system)**. *J Mar Syst* 1999, **18**:383-394 doi: 10.1016/s0924-7963(97)00114-0.

64. Paquay FS, Mackenzie FT, Borges AV: **Carbon dioxide dynamics in rivers and coastal waters of the "Big Island" of Hawaii, USA, during baseline and heavy rain conditions**. *Aquat Geochem* 2007, **13**:1-18 doi: 10.1007/s10498-006-9005-5.

65. Watanabe A, Kayanne H, Hata H, Kudo S, Nozaki K, Kato K, Negishi A, Ikeda Y, Yamano H: **Analysis of the seawater CO_2 system in the barrier reef-lagoon system of Palau using total alkalinity-dissolved inorganic carbon diagrams**. *Limnol Oceanogr* 2006, **51**:1614-1628.

66. Sutherland SC, Newberger T, Takahashi T, Sweeney C: *Report of Underway pCO_2 Measurements in Surface Waters and the Atmosphere during July–August 2005*. 2006/03/13. Carbon Dioxide Information Analysis Center; 2005.

67. Dagg MJ, Bianchi TS, Breed GA, Cai WJ, Duan S, Liu H, McKee BA, Powell RT, Stewart CM: **Biogeochemical characteristics of the lower Mississippi River, USA, during June 2003**. *Estuaries* 2005, **28**:664-674 doi: 10.1007/bf02732905.

68. Delille B, Borges AV, Delille D: **Influence of giant kelp beds (*Macrocystis pyrifera*) on diel cycles of pCO_2 and DIC in the Sub-Antarctic coastal area**. *Estuar Coast Shelf Sci* 2009, **81**:114-122 doi: 10.1016/j.ecss.2008.10.004.

69. Fagan KE, Mackenzie FT: **Air–sea CO_2 exchange in a subtropical estuarine-coral reef system, Kaneohe Bay, Oahu, Hawaii**. *Mar Chem* 2007, **106**:174-191 doi: 10.1016/j.marchem.2007.01.016.

70. Ghosh S, Jana TK, Singh BN, Choudhury A: **Comparative study of carbon dioxide system in virgin and reclaimed mangrove waters of Sundarbans during freshet**. *Mahasagar-Bull Natl Inst Oceanogr* 1987, **20**:155-161.

71. Millero FJ, Hiscock WT, Huang F, Roche M, Zhang JZ: **Seasonal variation of the carbonate system in Florida Bay**. *Bull Mar Sci* 2001, **68**:101-123.

72. Ovalle ARC, Rezende CE, Lacerda LD, Silva CAR: **Factors affecting the hydrochemistry of a mangrove tidal creek, sepetiba bay, Brazil**. *Estuar Coast Shelf Sci* 1990, **31**:639-650 doi: 10.1016/0272-7714(90)90017-l.

73. Peterson DH: In *Sources and Sinks of Biologically Reactive Oxygen, Carbon, Nitrogen, and Silica in Northern San Francisco Bay*. Edited by Conomos TJ. San Francisco, CA: Pacific Division of the American Association for the Advancement of Science; 1979:175-193.

74. Raymond PA, Caraco NF, Cole JJ: **Carbon dioxide concentration and atmospheric flux in the Hudson River**. *Estuaries* 1997, **20**:381-390 doi: 10.2307/1352351.

75. Ruiz-Halpern S, Sejr MK, Duarte CM, Krause-Jensen D, Dalsgaard T, Dachs J, Rysgaard S: **Air–water exchange and vertical profiles of organic carbon in a subarctic fjord**. *Limnol Oceanogr* 2010, **55**:1733-1740 doi: 10.4319/lo.2010.55.4.1733.

76. Sarma V, Kumar NA, Prasad VR, Venkataramana V, Appalanaidu S, Sridevi B, Kumar BSK, Bharati MD, Subbaiah CV, Acharyya T *et al.*: **High CO_2 emissions from the tropical Godavari estuary (India) associated with monsoon river discharges**. *Geophys Res Lett* 2011, **38**:L08601 doi: 10.1029/2011gl046928.

77. Sutherland SC, Takahashi T, Sweeney C: *Report of Underway pCO_2 Measurement in Surface Waters and the Atmosphere during March–July 2002*. 2002/11/21. Carbon Dioxide Information Analysis Center; 2002.

78. Kristensen E, Flindt MR, Ulomi S, Borges AV, Abril G, Bouillon S: **Emission of CO_2 and CH_4 to the atmosphere by sediments and open waters in two Tanzanian mangrove forests**. *Mar Ecol-Progr Ser* 2008, **370**:53-67 doi: 10.3354/meps07642.