Interactive comment on “Review article “Air-sea exchanges of CO$_2$ in world’s coastal seas”” by C.-T. A. Chen et al.

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We appreciated the through and constructive comments which helped strengthening the manuscript.

Review of “Air-sea exchanges of CO$_2$ in world’s coastal seas” by Chen et al. This is a very well written and thorough review of literature pertaining to gas transfer and CO$_2$ fluxes in estuaries and the coastal shelf. The authors have compiled a vast amount of published CO$_2$ air-sea flux data and supplemented it with important new data from SE Asian waters. Readers should find this a valuable resource.

I think the paper would benefit from a few minor revisions. I also have some questions that I think need to be clarified prior to publication.

C4290

Reply: Thanks for the penetrating questions.

Introduction-
The introductory review of carbon fluxes from the land through the estuaries then through the coastal shelf zone is succinct and informative. I was a little surprised that Tranvik et al.’s (2009) estimate of riverine C flux to the ocean was not covered as I think this is one of the more definitive analyses from freshwater scientists of the composition and quantity of river fluxes.

Reply: Thanks for the suggestion, we have added some discussion about this brilliant article. The revised paragraph is as follows:

In the above calculation, the areas of groups of estuaries are taken from the most recent and comprehensive work of Laruelle et al. (2013), which divided the world into regions and calculated a total estuarine area of $1.012 \times 10^6$km$^2$, slightly smaller than the value of $1.067 \times 10^6$km$^2$ given in Laruelle et al. (2010). Table 3 lists the total surface area in each of the 45 regions and the numerically averaged CO$_2$ flux per unit area for each region. Our global flux calculation is based on the sum of regional fluxes for these 45 zones (area multiplied by zonal average CO$_2$ flux (molCm$^{-2}$ yr$^{-1}$)). These 165 estuaries are compartmentalized into 35 regions, and the numerically averaged CO$_2$ flux per unit area is calculated. For 10 regions without data, the mean flux for the same classification region is used (Table 3). The outgassing of pCO$_2$ in global estuaries is 0.094PgC yr$^{-1}$, and is about 31% of the global riverine organic carbon flux (Seitzinger et al., 2010). This compares with the 48% of organic carbon released as CO$_2$ from estuaries and inland waters (Tranvik et al., 2009).

The main thrust of the paper is the presentation of air-sea CO$_2$ flux data. I assume most of the reported values compiled from the literature are computed using the thin
boundary layer (TBL) method (aka stagnant film method), i.e. multiplying a wind, speed dependent gas transfer velocity by the air, water $\Delta pCO_2$. Given the essential importance of the TBL method, I think a little more introductory discussion of the calculation is warranted, especially the uncertainty associated with the gas transfer velocity, wind speed relation (time of day of measurement, wind speed averaging periods, etc). Relevant literature has been cited but I think in a review of this sort it is helpful to more directly present this material.

Reply: Indeed most reported values compiled from the literature are computed using the thin boundary layer method but a few are based on the floating chamber method. The method used is now given in new Table 2. Also listed now are the source of the gas exchange coefficient and the wind speed.

Calculations and data presentation-
Not enough information is provided in the paper to allow assessment of the computed air, sea $CO_2$ fluxes and the authors’ interpretation of them.

Reply: We have now added the method of calculating $pCO_2$ flux (Table 2) and the global flux as follows:

"Numerical data are gathered for 165 estuaries (Table 1), of which 99 are from literature. Unpublished data from 50 estuaries and 16 from data banks are also included, and the Wanninkhof (1992) quadratic equation is used to determine the flux. The method used to calculate the flux, as well as sources of the gas exchange coefficient and wind speed are listed in Table 2. Of note is that using different $pCO_2$ flux method and gas transfer velocity causes disparity in flux estimations (Borges et al., 2004; Ferron et al., 2007; Jiang et al., 2008a; Zappa et al., 2007). However, there is still not a consensus on the most suitable coefficient to use in estuaries. Factors affecting gas exchange coefficients include wind speed, tidal current and bottom stress, whereas the wind speed is the most considered. It is important to point out that this paper deals mostly with published results. It is not possible to re-do the flux calculations, say, based on the same gas exchange coefficient, as the original data were not provided in the papers cited. Important to note is that there is a lack of temporal coverage in most of the data sets although previous studies (Bozec et al., 2011; Dai et al., 2009; Kitidis et al., 2012) have demonstrated short term changes in $pCO_2$ at scales of days or less. Yet, typically data on such a scale are limited to only a few cruises. The lack of seasonality in the numerically averaged fluxes is almost certainly an artefact influenced by averaging all available data."

In the above calculation, the areas of groups of estuaries are taken from the most recent and comprehensive work of Laruelle et al. (2013), which divided the world into regions and calculated a total estuarine area of $1.012 \times 10^6 \text{km}^2$, 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 numerically averaged $CO_2$ flux per unit area for each region. Our global flux calculation is based on the sum of regional fluxes for these 45 zones (area multiplied by zonal average $CO_2$ flux ($\text{molCm}^{-2} \text{yr}^{-1}$)). These 165 estuaries are compartmentalized into 35 regions, and the numerically averaged $CO_2$ flux per unit area is calculated. For 10 regions without data, the mean flux for the same classification region is used (Table 3). The outgassing of $pCO_2$ in global estuaries is $0.094 \text{PgC yr}^{-1}$, and is about 31% of the global riverine organic carbon flux (Seitzinger et al., 2010). This compares with the 48% of organic carbon released as $CO_2$ from estuaries and inland waters (Tranvik et al., 2009).

Please include the equation used to compute the gas transfer velocity. Wanninkhof 1992 is cited as the source but that paper makes clear a couple of things: 1) the choice of a quadratic function is arbitrary not based on any underlying theoretical con-
siderations; 2) flux enhancement at low wind speeds is important and temperature, dependent. Furthermore, plots in Wanninkhof (1992) suggest a very large low bias at low wind speeds which may have a major bearing on the author’s conclusion that globally, fluxes are less than previously reported because of the addition of new data from Asian waters where average wind speed is 1.6 m/s. I would have thought the cubic equation proposed by Wanninkhof et al. (2012) and fit to the GasEx, 2001 data set would have been a better choice for the present work. If Wanninkhof (1992) Eq 3 has been used without adjustment then I would expect calculated fluxes in low wind areas to be biased low by a factor of 3 to 4.

Reply: Thanks for the valuable suggestion. When we choose the equation of gas transfer velocity, we only follow the same equation most authors used in our cited literature. Wanninkhof (1992) is the most used, followed by different equations of Raymond and Cole (2001). For the CO2 flux in global estuaries, our Asian calculation constitutes 7% of surface area and 13% of CO2 flux in global estuaries. Therefore, most part of global estimation is based on published articles. In this study, we try to emphasize that the high wind speed will result in high CO2 flux. We have revised the paragraphs as follows:

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 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 mol C m⁻² yr⁻¹, which is more than triple the value obtained in this study. This finding does not imply that European rivers have higher pCO2; they do not. Rather, Europe has more windy coasts than elsewhere in the world, and especially Asia. Parts of these higher fluxes may have resulted from higher wind speed. As mentioned above, the

wind potential is a quadratic function of wind speed, as is the 1992 Wanninkhof air-sea CO2 exchange equation. It is important to point out, however, that the water turbulence is an importance factor for gas transfer velocity in low wind speed regions but little data is available. We have compared the Wanninkhof (1992) quadratic equation \( U_{500} = 0.31 \times U_{10}^2 \) with other equations such as Raymond and Cole (2001), Borges et al. (2004), Ho et al. (2011), and Jiang et al. (2008a). Using Wanninkhof’s (1992) quadratic equation may underestimate flux, although the value is similar with Ho et al. (2011) at low wind speed (<5 m s⁻¹). Note that there is no theoretical basis for the above equations as most are based on curve fitting techniques. Since we do not have data to show which equation is the best we have chosen the Wanninkhof quadratic equation which most references we cited used. Due to the fact that using different air-sea exchange equations results in large uncertainties, and that there is no universally accepted equation the above conclusion can only be deemed preliminary. The mean pCO₂ of European estuaries is roughly 1600 µatm, whereas that of Asian estuaries is much higher, around 4000 µatm. 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 mol C m⁻² yr⁻¹ vs. a much lower 8.1 mol C m⁻² yr⁻¹ for Asian estuaries (Table 3; Fig. 6) despite their higher pCO₂.

Please include the source of the wind speed data used in any calculations. I am a little uneasy about using global wind potential as a surrogate for u² because a number of spatially variable considerations other than wind speed are factored into Zhou et al’s (2012) calculation. Also, my understanding is that wind power potential varies as u³ and I note that Zhou et al do not provide the equation they used for their calculation (I am relying on lecture notes for wind power calculations). Zhou et al’s Fig 1 is reproduced with permission as Fig 5 in this paper. More generally, I did not find Fig 5 particularly helpful because the relevant wind speed information (estuaries and coastal
(shelves) tends to get lost in the land mass when, in fact, winds along the coast are the
relevant consideration for estuarine and coastal shelf flux calculations.

Reply: In our calculation, most of wind speed data are collected from WindSat Data
and field measurements, however, a few early data are taken from NCEP/NCAR
reanalysis monthly mean wind data. We do not use global wind potential as wind
speed data although we have included Fig. 5 to get a clear picture of global wind
patterns.

It was not clear to me which fluxes in Tables 1 and 4 were reproduced from the cited
literature and which involved new calculations. Are all values recomputed from reported
$pCO_2$ and using a consistent wind speed data source?

Reply: Most CO$_2$ flux data are adopted from published articles although we have
calculated some flux data collected from $pCO_2$ data banks (a few are estimated from
pH and total alkalinity) and our unpublished data. We have now listed sources of data
in the new tables 2 and 6.

I would find a table listing the $pCO_2$ measurements very useful. Perhaps as supple-
mentary material.

Reply: Thanks for the suggestion. We have now listed these details in Tables 2 and 6.

p 5045 line 20 - I think the discrepancies between continental shelf area estimates is
exaggerated a bit. If one discounts the $36 \times 10^6$ value of Liu et al (2000) as an outlier
all the other results fall by and large within $26 \pm 1$, which is really pretty good.

Reply: Thanks for the opinion. We have listed these published continental shelf area
values in order for the readers to get an idea. We have only adopted area data from
Laruelle et al., 2013 (Table 3; $30 \times 10^6 km^2$). We have now modified the comparison by
adding "which may seem an outlier" after .....Liu et al. (2000). Note Jahnke’s value of
30 is also high.

p 5026 line 23 , Jaing et al. 2008 citation , is this 2008a or 2008b?

Reply: Thanks. It should have been “2008a”.

Exchanges in estuaries-

p 5047 , The roles of light and nutrients vis a vis biological production is discussed.
Perhaps a comment about the role of residence time would be in order as well. Primary
production in inland waters requires light (controls the rate of growth) and nutrients
SETS the maximum achievable biomass) and the amount of production depends on the
time available to grow, i.e. short, fast rivers will experience less C transformation than
long, slow rivers given the same light and nutrient availability. Residence time is also
relevant to leaching of organic matter to produce DOC and microbial transformation of
DOC.

Reply: Thanks for suggestion. We have added some discussion as follows:

Generally, net ecosystem production in estuaries tends to be net heterotrophic,
that is, respiration is larger than production (Battin et al., 2008). Various
complex biogeochemical processes in estuaries are affected by the topography
and river flow. As small deltas and large rivers’ estuaries have short residence
time (Durr et al., 2011), physical mixing is the major factor affecting carbonate
parameters. On the other hand, with longer residence time the transformation
between inorganic and organic material becomes more active. This is because
now suspended particles have more time to settle and aquatic organisms have
more time to grow, and leach dissolved organic carbon, when light becomes
more available in the nutrient-abundant estuaries. On the other hand, dissolved
organic carbon decomposes more when the residence time is longer compared
with physical force-dominant estuaries.

Is the role of tidal forcing on estuarine mixing worth a comment as this may have bearing on sediment burial, etc.

Reply: Thanks a lot. It is now added to the text as follows:

Tidal forcing on estuarine mixing affects submarine groundwater discharge, sediment burial and disturbance, the pCO$_2$ in the surface water as well as the air-to-sea CO$_2$ exchange. These, however, have not been evaluated in a quantitative way.

p 5048- Flux results are categorized on upper, mid and lower estuaries. Can you provide a functional definition used to delineate estuarine systems? For example, is the criterion simply a specified salinity. If so, what values were used?

Reply: We have revised the paragraphs as follows:

Figure 2 presents the pCO$_2$ and CO$_2$ fluxes per unit area in the upper, mid and lower estuaries worldwide. Upper, mid, and lower estuaries are defined as those areas of estuaries with salinities below 2, between 2 and 25, and above 25, respectively, as salinity data are the most readily available. Otherwise, divisions are made based approximately on one-thirds of the distance from the point where the river starts to widen to the river mouth. Almost all estuaries outside of the Arctic region except for only a few release CO$_2$ to the atmosphere. Unsurprisingly, upper estuaries, where the riverine effect is the strongest (Kempe, 1979, 1982;Chen et al., 2012), have the highest pCO$_2$ (numerical average=5026 ± 6190 µatm) and the highest sea-to-air CO$_2$ flux (numerical average=39.0 ± 55.7 molC m$^{-2}$ yr$^{-1}$, where the positive sign indicates that the seawater is losing CO$_2$); these are followed by the mid estuaries (numerical averaged pCO$_2$ = 2230 ± 2725 µatm; numerical averaged flux=17.5 ± 34.2 molC m$^{-2}$ yr$^{-1}$). Lower estuaries have the lowest pCO$_2$ (numerical average=723 ± 957 µatm) and CO$_2$ flux (numerical average= 8.4 ± 14.3 molC m$^{-2}$ yr$^{-1}$). Except for those of the upper estuaries, these pCO$_2$ 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 pCO$_2$ values for upper estuaries mainly because new data from Asia are associated with high pCO$_2$ values. The fluxes obtained by Chen et al. (2012), however, are higher. Their values are 68.5, 37.4 and 9.92 molC m$^{-2}$ yr$^{-1}$ for the upper, mid and lower estuaries, respectively. The seeming inconsistency among results is discussed below.

River plumes outside of estuaries are neglected. Is it possible to estimate their relative contribution to the overall estuary + shelf flux to justify their exclusion, i.e. are they sufficiently rare as to be unimportant (although I imagine when they occur they must carry a fair amount of C with them).

Reply: River plumes outside of estuaries are not specifically discussed but will be the subject of another study.

Not much seasonality is reported for the fluxes yet individual estuaries in Table 1 for which values are reported for all 4 seasons show large differences between seasons. Has the reported lack of seasonality been influenced by averaging all available data or were only data from estuaries with data for all seasons considered? The discussion left me feeling that seasonality isn’t a big deal, but when I look at individual estuaries it seems to be highly relevant on a case by case basis. Can you reassure me that the lack of seasonality is ‘real’ rather than being an artefact of the statistical method applied? I would not want the reader to come away thinking that they could measure the flux at a single time of year and assume that is representative of the mean annual
Some published articles only reported data for one season, and some only provided annual flux. The seasonal variation indeed should not be ignored as mentioned. We have revised the paragraphs as follows:

Numerical data are gathered for 165 estuaries (Table 1), of which 99 are from literature. Unpublished data from 50 estuaries and 16 from data banks are also included, and the Wanninkhof (1992) quadratic equation is used to determine the flux. The method used to calculate the flux, as well as sources of the gas exchange coefficient and wind speed are listed in Table 2. Of note is that using different $pCO_2$ flux method and gas transfer velocity causes disparity in flux estimations (Borges et al., 2004; Ferron et al., 2007; Jiang et al., 2008a; Zappa et al., 2007). However, there is still not a consensus on the most suitable coefficient to use in estuaries. Factors affecting gas exchange coefficients include wind speed, tidal current and bottom stress, whereas the wind speed is the most considered. It is important to point out that this paper deals mostly with published results. It is not possible to re-do the flux calculations, say, based on the same gas exchange coefficient, as the original data were not provided in the papers cited. Further, there is a lack of temporal coverage as previous studies (Bozec et al., 2011; Dai et al., 2009; Kitidis et al., 2012) have demonstrated short term changes in $pCO_2$ at scales of days or less. Yet, typically data on such a scale are limited to only a few cruises. The lack of seasonality in the numerically averaged fluxes is almost certainly an artefact influenced by averaging all available data.

Can you quantify how small the contribution of small estuaries is? What is the definition of a small estuary? Does the difference between northern and southern hemispheres reflect the much larger terrestrial catchment area supplying organic matter in the northern hemisphere?

Small estuaries are identified as surface areas < 1,000 km$^2$ (Durr et al., 2011). The surface areas of small estuaries add up to 7.8% of global estuaries area. The total flux is about 10% of global flux because the small estuaries have higher value of $CO_2$ flux per square meter (Laruelle et al., 2010).

I am quite concerned that the quadratic wind speed function, rather than real changes in gas transfer velocity, is responsible for the low fluxes reported for Asian low latitude regions. I know from lots of personal experience that it is actually penetrative convection prior to sunrise that governs mixed, layer depth in low wind speed lakes and reservoirs. I presume the same might be the case for tropical estuaries. The implication of this is that the turbulent velocity scale in the surface layer of the water column computed from heat transfer considerations is often greater than that computed from wind speed. Vachon et al. (2010, Vachon, D., Prairie, Y ., T., Cole, J., J. (2010). The relationship between near-surface turbulence and gas transfer velocity in freshwater systems and its implications for floating chamber measurements of gas exchange. Limnology and Oceanography, 55(4), 1723-1732.) have shown that water turbulence is a much better indicator of gas transfer than wind speed. Could it be that the calculation of gas exchange in low-latitude Asian waters has a strong low bias because wind speed is not the correct parameter to be considering for such calculations? (I recommend, also, Schladow, S. G., Lee, M., Hurzeler, B. E., Kelly, P. B. (2002). Oxygen transfer across the air-water interface by natural convection in lakes. Limnology and Oceanography, 47(5), 1394-1404.)

Again, I think it is important that the reader understands that the choice of a quadratic function is arbitrary and has no basis in theory. Because it is simply a curve fitting technique, it is important that the equation used for this work fits the available field data on gas transfer velocities well at low wind speeds. I just need some reassurance that this is the case.
the water turbulence is an importance factor for gas transfer velocity in low wind speed region. We agonized about choosing the equation of gas transfer velocity. We compared the Wanninkhof (1992) equation \( k_{660} = 0.31 \times U_{10}^2 \) with the other equations such as Raymond and Cole (2001), Borges et al. (2004), Ho et al. (2011), and Jiang et al. (2008a). Using Wanninkhof (1992) equation may underestimate flux, although the value is similar with Ho et al. (2011) at low wind speed \(< 5 \text{ m s}^{-1}\). As you mentioned, "it is simply a curve fitting technique", but we do not have data to show which equation is the best and have decided to choose the Wanninkhof quadratic equation which most references we cited used. The above has been added as a new paragraph as follows:

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 19 estuaries that were considered by Abril and Borges (2005), who published perhaps the first global study of \( \text{CO}_2 \) emissions from estuaries, are outside Europe and the eastern seaboard of the USA. Those authors found a global \( \text{CO}_2 \) flux per unit area of \( 35.7 \text{molC m}^{-2} \text{yr}^{-1} \), 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. Parts of these higher fluxes may have resulted from higher wind speed. As mentioned above, the wind potential is a quadratic function of wind speed, as is the 1992 Wanninkhof air-sea \( \text{CO}_2 \) exchange equation. It is important to point out, however, that the water turbulence is an importance factor for gas transfer velocity in low wind speed regions but little data is available. We have compared the Wanninkhof (1992) quadratic equation \( k_{660} = 0.31 \times U_{10}^2 \) with other equations such as Raymond and Cole (2001), Borges et al. (2004), Ho et al. (2011), and Jiang et al. (2008a). Using Wanninkhof’s (1992) quadratic equation may underestimate flux, although the value is similar with Ho et al. (2011) at low wind speed \(< 5 \text{ m s}^{-1}\).

Note that there is no theoretical basis for the above equations as most are based on curve fitting techniques. Since we do not have data to show which equation is the best we have chosen the Wanninkhof quadratic equation which most references we cited used. Due to the fact that using different air-sea exchange equations results in large uncertainties, and that there is no universally accepted equation the above conclusion can only be deemed preliminary. 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 \( \text{s}^{-1} \), compared with about 1.6 m \( \text{s}^{-1} \) on Asian coasts. The resulting \( \text{CO}_2 \) fluxes for European estuaries average about 16.9 molC \( \text{m}^{-2} \text{yr}^{-1} \) vs. a much lower 8.1 molC \( \text{m}^{-2} \text{yr}^{-1} \) for Asian estuaries (Table 3; Fig. 6) despite their higher \( p\text{CO}_2 \).

**p 5050 line 19 - What is the criterion for defining a similar region? Is it based on area, latitude, terrestrial catchment area, etc?**

*b* Reply: We have modified "the similar region" to "the same classification region" (Table 3). The classifications according to Laruelle et al. (2013) are Eastern Boundary Current (EBC), Indian Margins, Marginal Sea, Polar, Subpolar, Tropical, and Western Boundary Current (WBC).

**p 5056 lines 1-7 - This discussion depends on the definition of the system, i.e. where the boundaries are drawn and the time scale over which the assessment is made. Presumably, cooling effects leading to undersaturation in the surface layer are offset by warming effects in the surface layer at other times of day or year? Do you have an example of such a system? How frequently does it occur?**

*b* Reply: We don’t have a good example to show that the deep layer may become super saturated simply because it is warmer although temperature inversions frequently
occur along the Chinese coasts in winter. We have deleted the related sentence.

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/10/C4290/2013/bgd-10-C4290-2013-supplement.pdf

Interactive comment on Biogeosciences Discuss., 10, 5041, 2013.