On some biases of estimating the global distribution of air-sea CO$_2$ flux by bulk parameterizations

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[1] It is important to examine the parameterizations used in calculating air-sea exchange fluxes as they are essential in developing global carbon models and in carbon budget calculations. We quantify the potential biases involved in the parameterizations. Adopting a non-zero gas transfer velocity for low wind areas results in a significant increase in the CO$_2$ flux in equatorial regions with a net increase of +0.2 Pg C yr$^{-1}$ in the total sea-air global flux. The ocean “cool skin temperature” effect on CO$_2$ flux estimation is found to be an order of magnitude smaller than early estimations. The previously unknown salty-skin effect has an opposite contribution that cancels the cool-skin effect. Comparing different wind speeds derived from satellite data and Global Circulation Models (GCM), the most significant divergence is found at the low wind equatorial regions regarding the CO$_2$ flux estimation. Citation: Zhang, X., and W.-J. Cai (2007), On some biases of estimating the global distribution of air-sea CO$_2$ flux by bulk parameterizations, Geophys. Res. Lett., 34, L01608, doi:10.1029/2006GL027337.

1. Introduction

[2] Quantifying the sea-to-air (hereafter sea-air) gas fluxes has been difficult due to complicated sea surface dynamical processes that still are inadequately understood. The net CO$_2$ flux, $F$, through the sea-air interface depends, in the first order approximation bulk formula, on three quantities: partial pressure difference across the sea surface $\Delta$pCO$_2$, (which is linked to the concentration gradient of aqueous CO$_{2w}$ across the surface mass diffusive layer), the CO$_2$ gas transfer velocity or piston velocity $k$, and the gas solubility $\alpha$,

$$ F = -k (\alpha_w pCO_{2w} - \alpha_a pCO_{2a}) $$

$$ = -k (\alpha_w \Delta pCO_2 + \Delta \alpha pCO_{2a}) \approx -k \alpha_w \Delta pCO_2 $$

(1)

where subscript $w$ indicates the water side at the bottom of the diffusive layer, $a$ indicates air side at the surface of the water, $\Delta$pCO$_2 = pCO_{2w} - pCO_{2a}$ and $\Delta \alpha = \alpha_w - \alpha_a$. Assuming negligible changes in temperature, salinity and other physical and chemical properties across the diffusive layer, the solubility constant is assumed to be constant (i.e., $\alpha_a = \alpha_w$) and is determined by temperature and salinity in the bulk water as in work by Weiss [1974].

[3] The piston velocity is controlled by surface dynamical processes and has a strong wind-speed dependence. However $\Delta$pCO$_2$ depends on other factors such as sea surface temperature, total CO$_2$ concentration, and alkalinity. The geographical and seasonal variations are quite different among these quantities and thus the global CO$_2$ flux budget should not be considered to be proportional to any single of the three quantities. For example, piston velocity and CO$_2$ flux in equatorial region are uncorrelated over the period from 1985 to 1999 [Feely et al., 2002].

[4] The oceanic CO$_2$ uptake can be calculated directly on the basis of monthly averaged wind speeds, climatological surface $\Delta$pCO$_2$, seasonal biological and temperature effects [Takahashi et al., 2002]. Takahashi’s current calculations show that the ocean total CO$_2$ uptake is about $-1.63$ or $-2.34$ Pg C yr$^{-1}$ respectively by using the squared and cubic bulk parameterizations for the wind speed dependence on gas transfer rates [Wanninkhof, 1992; Wanninkhof and McGillis, 1999] (referred to herein as W92 and WandMC99) (http://www.ldeo.columbia.edu/res/pi/CO2/). These empirical relationships are also used in current global carbon numerical models to determine the air-sea interface exchanges of CO$_2$ [Matsumoto et al., 2004; Wetzel et al., 2005]. The regional sea-air fluxes at a variety of latitudes are listed by different parameterization schemes in Table 1. Here a negative sign denotes transport from atmosphere to ocean (at high to middle latitudes) and a positive sign denotes the reverse (at low latitudes). Low wind situations, which correspond to very small gas transfer velocities in these parameterizations, are frequently found at low latitudes. Although underestimated as we will argue, this region still contributes a substantial part of the global CO$_2$ flux (outgassing) due to high $\Delta$pCO$_2$ and enormous areas (Table 1).

[5] The parameterizations of gas transfer velocity with wind speed have been mainly based on curve fitting of field and laboratory observations and some simple physical arguments [Monahan and Spillane, 1984; Liss and Merlivat, 1986, Wanninkhof, 1992; Woolf, 1997; Asher and Wanninkhof, 1998; Wanninkhof and McGillis, 1999; Nightingale et al., 2000; McGillis et al., 2004]. Significant scatter exists when the measured gas transfer velocities are plotted against wind speeds. The uncertainty is due both to measurement errors and other factors besides wind speed that affect gas transfer, such as sea state, unsteady wind, surface films, convections, and evaporation. While many studies have focused on high wind contributes to a large part of oceanic CO$_2$ flux [Woolf, 2005], this study considers the other cases that complement the high wind air-sea exchange study. Here, we address the possible bias in estimating the global CO$_2$ flux budget introduced by artificially setting a zero flux at the zero wind condition in parameterization of gas transfer velocity with...
wind speed. While it is doubtful that a single wind speed parameter can cover all spatial scales and environmental conditions, the practical advantage is that wind is currently the most robust parameter available with global coverage. To test sensitivity of using different global wind products, air-sea CO₂ fluxes are estimated from both satellite-derived (SSM/I) and GCM analysis wind (NCEP/NCAR). Recently, McGillis and Wanninkhof [2006] pointed out that the effect of the cool skin layer on the air-sea CO₂ flux appears to be overestimated because the difference in the thickness of the diffusive boundary layer and thermal boundary layer were not taken into account. In this paper the effects of the ocean’s cool skin layer, as well as the effect of ocean’s salty skin layer, on global flux are further evaluated.

2. Data and Methods

[6] The climatological distribution of the surface ocean pCO₂ for each month over the global oceans has been computed by Takahashi et al. [2002] based on nearly one million measurements made since 1956. The data with a spatial resolution of 4° × 5° for the year 1995 (a reference year) represents our current state of knowledge about the global surface ocean pCO₂. The anomalies associated with El Niño periods are excluded in this data set. The response time of CO₂ chemistry in ocean is rather slow when compared with gas exchange and a monthly mean adequately captures the seasonal variability.

[7] Two global wind products are used here: 10-m wind speed from a GCM model of the NCEP/NCAR reanalysis project, and 10-m wind speed retrievals from the satellite microwave radiometers (SSM/I). Another variable, SST from NCEP/NCAR analysis and from AVHRR, is also used. Space based products of monthly-mean ocean wind and SST used are from POA/AC at JPL (http://podaac-www.jpl.nasa.gov/). All the data are interpolated onto a 4° × 5° low-resolution space grid to conform to the surface pCO₂ data resolution. While winds are available from different satellite sensors, only winds with the global coverage from SSM/I radiometers are used here because they have the longest time coverage starting since 1989. The averaged wind speed, u₄₀, has a typically smaller speed range than the short-term steady wind speed, u, missing low and high winds. To bridge the difference between global data of the spatial-and-temporal means and local-and-instantaneous gas transfer velocity, a wind speed probability density function (PDF) of Rayleigh distribution, p(uₜ), is adopted. This distribution function is fully specified by the mean value and has been shown to be a reasonable approximation for a global ocean wind speed frequency distributions [Wentz et al., 1984]. The gas transfer velocity at each grid point is thus a distribution function of wind speeds, k(uₜ)p(uₜ), depending on a particular choice of parameterization models. Following equation 1, the CO₂ flux at each grid point equals –aₜₕ₂pCO₂ₜₕ₂k(uₜ)p(uₜ).

[8] Various gas transfer velocity models parameterized with wind speed will be examined here. Wanninkhof’s wind-speed square and cubic models are chosen as the baseline estimation of global gas flux, in particular, the short-term formulae which give a better representation of global gas flux distribution as a function of wind. At low wind speed situations, however, wind speed may not even be the most dominant parameter for gas transfer velocity. To quantify the range of bias due to the single parameter models at low wind speed, some perturbations are introduced. The simplest is to set piston velocity to a constant value at low wind while keeping the values unchanged otherwise (auxiliary material Figure S1a). The constant 10 cm/hr is chosen from published papers [Monahan and Spillane, 1984; Soloviev and Schlüschel, 2001; Asher et al., 2004; McGillis et al., 2004].

[9] In the approximation of equation 1, it is assumed that CO₂ solubility is constant within the surface boundary layer. Robertson and Watson [1992] argued that due to the ocean’s cool skin layer, the change of the CO₂ solubility across the thermal layer can be significant so as to produce an increased oceanic global uptake of about 0.7 Pg C yr⁻¹. However, the thickness of the molecular diffusive layer is proportional to the (diffusivity)¹/² or equally in Schmidt number, Sc¹/². The thermal diffusive layer is an order of magnitude deeper than the mass diffusive layer. For example, at 20°C, the Schmidt number for heat, CO₂, and NaCl in water are approximately 7.5, 600, and 780 respectively. Thus the excess uptake enhanced by the cool skin effect is overestimated when it is calculated with the temperature across the thermal layer, Tₜₕ₂ – Tₚ₁, instead of the mass diffusive layer, ΔTₘₕ₂. The temperature across a mass

Table 1. Global Oceanic CO₂ Uptakes Estimated From Different Parameterizations of Piston Velocity

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<tbody>
<tr>
<td>Liss and Merlivat [1986]</td>
<td>–0.17</td>
<td>–0.39</td>
<td>0.48</td>
<td>–0.62</td>
<td>–0.19</td>
<td>–0.88</td>
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<tr>
<td>W92</td>
<td>–0.28</td>
<td>–0.67</td>
<td>0.82</td>
<td>–1.07</td>
<td>–0.32</td>
<td>–1.52</td>
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<tr>
<td>WandMC98</td>
<td>–0.33</td>
<td>–0.84</td>
<td>0.71</td>
<td>–1.32</td>
<td>–0.42</td>
<td>–2.21</td>
</tr>
<tr>
<td>Nightingale et al. [2000]</td>
<td>–0.23</td>
<td>–0.54</td>
<td>0.71</td>
<td>–0.87</td>
<td>–0.26</td>
<td>–1.20</td>
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<tr>
<td>Monahan and Spillane [1984]</td>
<td>–0.18</td>
<td>–0.36</td>
<td>0.78</td>
<td>–0.59</td>
<td>–0.17</td>
<td>–0.53</td>
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<tr>
<td>McGillis et al. [2001]</td>
<td>–0.35</td>
<td>–0.84</td>
<td>0.88</td>
<td>–1.33</td>
<td>–0.42</td>
<td>–2.07</td>
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*Note that, for example, k = max(5, 0.306(Uₜₕ₂)²) means k = 5 when 0.306(Uₜₕ₂)² < 5, and k = 0.306(Uₜₕ₂)² when 0.306(Uₜₕ₂)² > 5.*

*The parameterization schemes are used for the comparison calculations shown in this paper.*
Figure 1. Seasonal correlation of ocean surface $pCO_2$ and wind. The global distributions of climatological ocean surface wind [Young, 1999] and $CO_2$ in surface water [Takahashi et al., 2002] are very different. The surface $CO_2$ and wind are negatively coupled seasonally in high latitude regions on average (in red). While in the mid-latitude areas that SST is regulated by subtropical gyres, the seasonal coupling is in phase with the wind (blue). Since the seasonal change of wind speed is weak in the equatorial regions of the Pacific and Atlantic, the phase difference is of little meaningful and not shown (black). Land surface and ice covered sea surface are marked as green.

diffusive layer should be scaled down by a factor of $(S_{Sc}/Sc_{ma})^n$ based on similar arguments of scaling the piston velocity by $Sc^n$. Here, we chose $n = 1/2$:

$$\Delta T_{max} = (S_{Sc}/Sc_{ma})(T_{ik} - T_B)$$

[10] The $CO_2$ solubility is also a function of salinity, $S$, and both $\partial S/\partial T < 0$ and $\partial S/\partial S < 0$. The depth of the salty skin layer, due to evaporation, is at the same order of magnitude as that of the gas diffusion layer. Neglecting surface radiative heat flux, it can be shown (see details in the auxiliary material) that the salinity difference across the boundary, $S_{ik} - S_B$, is a function of skin temperature:

$$S_{ik} - S_B = \frac{2}{\sqrt{\pi}}S_B H(G(T_B - T_{ik}))$$

$$= S_B G(T_B - T_{ik}) + O(G^2(T_B - T_{ik})^2)$$

where $G = c_p L^{-1} k_T k_S^{-5} \approx 0.02(\degree C)^{-1}$ for sea water, $c_p$ and $L$, are the specific heat of constant pressure and latent heat of sea water, and $k_T$ and $k_S$ are the thermal and saline diffusivities. Since the ocean salinity is generally fairly constant, the salinity difference across the saline skin in $psu$ is roughly 70% of the negative skin temperature in $\degree C$.

[11] There are various models and parameterizations for cool skin temperatures [Saunders, 1967; Fairall et al., 1996; Liu et al., 1979; Soloviev and Schlüssel, 1994]. Here we adopt a simple empirical relationship between cool skin temperature and wind speed, $u$, from different field studies [Donlon et al., 2002; Horrocks et al., 2003]:

$$T_{sk} - T_B = -a - be^\left(-\frac{u}{u_o}\right).$$

The empirical constants, $a$, $b$, and $u_o$, are slightly different given by different authors, but have little effect on our flux calculation. The increased $CO_2$ flux due to the ocean skin layer is:

$$\Delta F_{sk} = \left(\frac{\partial T}{\partial T} + \frac{\partial T}{\partial S}(S_{sk} - S_B)\right) \cdot k \cdot pCO_{2a}$$

The other term of bias of the flux estimation is from errors in calculating solubility due to the uncertainty of the water bulk temperature and salinity used (also see equation 1):

$$\Delta F_{\alpha w} = \Delta \alpha_w \cdot k \Delta pCO_{2a}.$$
wind speeds are, in decreasing order: S. of 50°S, N. of 50°N, 14°S–50°S, 14°N–50°N, and 14°N–14°S (Figure 2a). There is large out gassing in equatorial regions where the most probable wind speed is a little over 3 m/s. Therefore, a significant underestimation of regional CO₂ outgassing flux in the equatorial areas and thus an overestimation of global CO₂ uptake can be caused by the uncertainty in gas transfer velocity parameterizations at low wind speeds.

Systematic field measurements of gas transfer velocities in regions of strong atmospheric CO₂ sources with consistently lower winds and strong surface currents have only now become available through GasEx-2001. Early GasEx-1998 occurred in a strong atmospheric CO₂ sink region with prevailing intermediate to high winds. The GasEx-2001 results show a weak wind speed - gas transfer dependence [McGillis et al., 2004]. This is in sharp contrast with previous field studies of air-sea gas exchange that have shown that wind was the dominating force in gas transfer velocities. Any change in the incident radiation, phytoplankton biomass, surface films, and surface ocean stratification may have significant impact on the amount and variability of air-sea gas exchanges. A regression for the gas transfer data with wind speed found by McGillis et al. [2004] is: \( k_{660} = 8.2 + 0.014 U_{10N} \) (cm/hr), i.e., an elevated gas transfer velocity at wind speeds less than 6 ms⁻¹ as compared to the finding based on data from GasEx-1998: \( k_{660} = 3.3 + 0.026 U_{10N} \) [McGillis et al., 2001]. The coefficient of cube term is of less significant since the data are mostly collected under low wind conditions. Elevated gas transfer velocities at low wind speeds have also been observed in other field experiments (see auxiliary material Figure S1 and Text S1). Field measurements of Air-sea Interactions and Remote Sensing (FAIRS) are consistent with GasEx-2001 [Asher et al., 2004]. CO₂ fluxes directly measured by the bell-jar method in turbulent areas such as coral reef systems [Frankignoulle et al., 1996] strongly support a non-zero gas flux of about 15 cm/hr at near-zero wind conditions. Gas transfer velocities calculated by an analytic model that is capable of capturing some daily variability also show scatter within the 5 to 10 cm/hr range at low wind speeds under the GasEx-1998 condition [Soloviev and Schlüssel, 2001]. The model includes the convective forced [Soloviev and Schlüssel, 1994].

The effect on global and regional CO₂ gas flux for different parameterizations of gas transfer velocities with wind can be demonstrated by its wind speed dependency as shown in Figures 2b–2e. It is known that there are net gains in CO₂ uptake throughout all regions by changing from the square windspeed – gas transfer velocity to the cubic windspeed – gas transfer velocity with an accumulated \(-0.7 \text{ Pg C yr}^{-1}\) gain in global CO₂ flux (i.e., the total uptake flux increases from \(-1.52\) to \(-2.21 \text{ Pg C yr}^{-1}\)). As listed in Table 1, the global CO₂ uptake is reduced by as much as 0.12–0.16 Pg C yr⁻¹ by a simple modification of gas transfer velocity to a constant value at low wind speed. This is due to a larger out gassing in the 14°N–14°S equatorial region (\(0.25–0.38 \text{ Pg C yr}^{-1}\)) and a less of an increase in CO₂ uptake in other regions (\(-0.13–0.22 \text{ Pg C yr}^{-1}\)). Most observations indicate a smaller constant non-zero adjustment (~3 cm/hr) for non-equatorial regions [Donelan and Wanninkhof, 2001], this will yield a low bound of flux.

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**Figure 2.** Dependency of mean annual air-sea flux on wind speeds. (a) Global wind distributions, the bars are for averaged wind (41 year NCAR/NCEP), and the curves are for the derived short-term wind. The red, green, blue, magenta, and cyan solid curves are noted for latitude bands of N of 50°N, 14°N–50°N, 14°N–14°S, 14°S–50°S, and S of 50°S respectively. (b, c, d, and e) The global CO₂ average flux distributions with short-term steady wind calculated by Wanninkhof’s wind-speed square and cubic models with or without a simple non-zero adjustment of 10 cm/hr.
estimate of about 0.2 Pg C yr\(^{-1}\) due to the low wind adjustment.

[16] The total regional flux budgets from both northern and southern high latitudes are a relatively small part of the total budget, even where the extremely high gas transfer velocity (by 1–2 order magnitude) and the extremely low surface water \(pCO_{2w}\) occur (but not concurrently there). For example, at northern high latitudes, the CO\(_2\) air-sea flux per unit area is only 2–3 times larger than the rest of regions due to a seasonal phase delay in extreme wind and extreme low \(pCO_{2w}\). In addition, the ice-free sea surface area at high latitudes is only a small percentage of the global ocean surface. The latitudinal maxima in the oceanic CO\(_2\) uptake are located around 40\(^\circ\)N and 45\(^\circ\)S (Figure 3).

[17] The global CO\(_2\) sea-air flux is also calculated using satellite SSM/I derived wind. Averaged over the same period from 1989 to 2001, the ocean uptake is on average about 0.2 Pg C yr\(^{-1}\) less than that from CDC model wind based on several parameterizations (for example, .24, .18, .27 and .19 Pg C yr\(^{-1}\) for different parameterizations shown in auxiliary material Figure S1: Wanninkhof’s wind-speed square and cubic models with or without a simple non-zero adjustment of 10 cm/hr), while the mean wind speed from SSM/I wind is 0.5 m/s stronger than the CDC model wind. The stronger global averaged wind may not necessarily force a larger ocean CO\(_2\) uptake. As shown in Figure 3 (middle), the SSM/I wind is stronger than CDC model wind both at high and low latitudes. Since the high latitudes have a less weight in the total global CO\(_2\) air-sea flux budget, the stronger SSM/I winds in the equatorial regions force a larger out-gassing (Figure 3, left), thus a smaller global ocean uptake. Bentamy et al. [2001] compared satellite winds with buoy observations from September 1996 to June 1997. Their results indicate that for most wind ranges, the bias between SSM/I and buoy wind speed is low except for comparison with low wind data of TOA buoys which located in the tropical Pacific Ocean.

[18] Solubility is weakly dependant on sea surface temperature and salinity, therefore there is little change in global ocean CO\(_2\) uptake (less than 0.01 Pg C yr\(^{-1}\)) calculated with equation 1 at different SST values [Takahashi et al., 2002] (CDC model, and Satellite derived SST) as the approximate bias is described in equation 6. However, the solubility difference across the surface diffusive layer introduces an additional term (equation 5) in the gas flux calculation. This variation of solubility is due to the temperature and salinity gradient of the cool and saline skin layer. Using the temperature difference across the thermal diffusive layer, the additional oceanic CO\(_2\) uptake is estimated to be 0.6 [Robertson and Watson, 1992] and 0.4 [Van Scoy et al., 1995] Pg C yr\(^{-1}\). We obtain the same quantitative estimations from the data sets used here with different parameterizations for the piston velocity (auxiliary material Table S1).

However, since the mass boundary layer is much thinner than the thermal boundary layer, the temperature change within the mass diffusive layer is only a small fraction of cool skin temperature. A more reasonable estimation of temperature differences across the mass diffusive layer is equation 2, scaling cool skin temperature by the ratio of Schmidt numbers. Using estimated temperature change across the CO\(_2\) diffusive layer, our calculations show an increase in global CO\(_2\) oceanic uptake a little over 0.05 Pg C yr\(^{-1}\), which is much less than the earlier estimation with thermal layer approximation. Furthermore, the contributions from salinity and temperature changes are almost equal but have different sign, or the combined skin layer effect is insignificant to global CO\(_2\) flux. Solubility is a weaker function of salinity than that of temperature. However, the skin salinity have to be counted in full for the skin effect as the salty skin layer is within the mass diffusive layer and is different from that of the thermal layer.

4. Concluding Remarks

[19] By introducing a non-zero flux perturbation into the gas exchange parameterization, we show a large increase in
estimation of out gassing from the vast equatorial regions. In low wind speed regimes, forced and free convective forcing may be a significant factor in causing the variability of gas transfer velocities. To account for a high variability of gas transfer velocities at a given wind speed, the parameterization coefficients have to vary with space, time, and sea states in accordance with the changes of dominant forcing mechanisms. Oceanic and laboratory observations of air-sea gas exchange is exceedingly needed considering the existing small database especially at both low and high wind. Satellites can measure ocean surface variables over the whole ocean at an increasingly higher spatial and temporal resolution. Several of these variables form the basis for estimations of the air-sea fluxes of momentum, freshwater, and heat, while only wind speed is used for gas exchange parameterization so far. It is known that the variability of satellite wind is higher at the extremes of wind speeds both high and low wind speeds. This work demonstrates that reducing the uncertainty of ocean wind from satellite data at low wind speed in equatorial region is of significance to the estimation of the CO₂ global budget. In the case of poorly soluble gases, such as CO₂, the concentration gradient in surface water is the main thermodynamic control of the flux through air-sea interface. The temperature and, to a lesser extent, salinity dependence of solubility α is of concern in calculating interfacial gas fluxes. Our analysis and calculation confirm that the cool skin effect has indeed been much underestimated. We also, for the first time, estimate the salty skin effect on CO₂ flux estimation. The salty skin effect almost cancels the revised cool skin effect.

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Supplement II for derivation of Eq. 3 and some calculation results

Equations and boundary conditions for cool skin layer are:

\[ T_t - \kappa_T T_{zz} = 0 \]
\[ -k_T T_z|_{z=0} = Q(t) \]
\[ T|_{t=0} = T_B, \]

where vertical z-axis points upward with free surface at \( z = 0 \). \( Q(t) \) is heat flux, positive for heat flux into air. \( T_B \) and \( T_{sk} \) are sea bulk water and surface temperature respectively. \( \kappa_T = k_T/\rho c_p \) is thermal diffusivity (\( \approx 1.4 \times 10^3 \text{cm}^2/\text{s} \)), where \( k_T \) is heat conductivity.

Assuming a constant heat flux, it can be shown that:

\[ T - T_B = -\frac{Q}{k_T} \sqrt{4\kappa_T t} \left( \frac{1}{\sqrt{\pi}} e^{-\frac{z^2}{4\kappa_T t}} + \frac{z}{2\sqrt{4\kappa_T t}} \cdot \text{erf} \left( -\frac{z}{\sqrt{4\kappa_T t}} \right) \right). \]

Therefore:

\[ T_{sk} - T_B = \frac{\sqrt{k_T \pi}}{\sqrt{\kappa_T}} Q. \] (A)

where \( T_{sk} = T|_{z=0} \).

Equations and boundary conditions for salty skin layer are:

\[ S_t - \kappa_S S_{zz} = 0 \]
\[ \kappa_S S|_{z=0} = \frac{Q(t)}{\rho L} S|_{z=0} \]
\[ S|_{t=0} = S_B. \]

The surface boundary condition is derived from evaporation constrain, \( w \frac{\partial S}{\partial z} = E \). \( w \) is an equivalent upwelling velocity. \( E \) is evaporation rate which relates to water latent heat lost due to evaporation:

\[ LE = Q. \]

\( L \) is vaporization latent heat (540 cal g\(^{-1}\) or 2258 KJ kg\(^{-1}\) for boiling water). A solution for salinity profile under constant heating is:

\[ S - S_B = -S_B \left( 1 + \text{erf} \left( \frac{z}{2\sqrt{\kappa_S t}} \right) \right) + S_B e^{Hz+H^2\kappa_S t} \left( 1 + \text{erf} \left( H\sqrt{\kappa_S t} + \frac{z}{2\sqrt{\kappa_S t}} \right) \right), \]

where \( H = \frac{Q(t)}{\rho L \kappa_S} \). Hence,

\[ \frac{S_{sk} - S_B}{S_B} = e^{H^2\kappa_S t} \left( 1 + \text{erf} \left( H\sqrt{\kappa_S t} \right) \right) - 1. \] (B)

where \( S_{sk} = S|_{z=0} \). Substituting \( Q \) by \( (T_{sk} - T_B) \) (Eq. A), we have:

\[ H\sqrt{\kappa_S t} = \frac{k_T \sqrt{\pi}}{2L \sqrt{\kappa_T \rho}} (T_{sk} - T_B) = G(T_{sk} - T_B). \]
Expressing Eq. B in power series of \((T_{sk} - T_B)\):

\[
\frac{S_{sk} - S_B}{S_B} = \sum_{n=1} \frac{G^{2n}}{n!} (T_B - T_{sk})^{2n} + \frac{2}{\sqrt{\pi}} \sum_{n=0} \frac{2^n G^{2n+1}}{(2n+1)!!} (T_B - T_{sk})^{2n+1}.
\]

For \(G (T_B - T_{sk}) \ll 1\),

\[
\frac{S_{sk} - S_B}{S_B} = \frac{2}{\sqrt{\pi}} G (T_B - T_{sk}) + O \left( G^2 (T_B - T_{sk})^2 \right).
\]

If we take \(L = 580\) and \(c_p = 1\), then \(G\) is about \(\frac{1}{58}\),

\[
S_{sk} - S_B \approx 0.02 S_B (T_B - T_{sk}).
\]

Using the temperature difference across the thermal diffusive layer and across the mass diffusive layer, and using the salinity difference across the skin layer, our quantitative estimations of the increased \(CO_2\) flux from different parameterizations for the piston velocity are listed in Table S1.