

Oceanic convective mixing and the impact on air-sea gas transfer velocity

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[1] Combination of surface water cooling and a deep ocean mixed layer generates convective eddies scaling with the depth of a mixed layer that enhances the efficiency of the air-sea transfer of CO₂ (and possibly other gases). This enhancement is explained by the convective eddies disturbing the molecular diffusion layer and inducing increased turbulent mixing in the water. The enhancement can be introduced into existing formulations for calculating the air-sea exchange of gases by using an additional resistance, due to large-scale convection acting in parallel with other processes. The additional resistance is expressed here as $\frac{1}{r_{wc}} = \gamma \sqrt{\frac{w_*}{u_{*w}}}$, where $\frac{w_*}{u_{*w}}$ characterizes the relative role of surface shear and buoyancy forces. **Citation:** Rutgersson, A., A. Smedman, and E. Sahlée (2011), Oceanic convective mixing and the impact on air-sea gas transfer velocity, *Geophys. Res. Lett.*, 38, L02602, doi:10.1029/2010GL045581.

1. Introduction

[2] Oceans are of great critical concern for the global carbon cycle, and the air-sea exchange of CO₂ plays an important role. The exchange of CO₂ between ocean and atmosphere is controlled by the air-sea difference in CO₂ partial pressure ($\Delta p\text{CO}_2$) at the surface and by the efficiency of the transfer processes. Partial pressure at the water surface is controlled by biological, chemical, and physical processes in the water. The efficiency of the transfer processes is determined by the resistance to the transfer in the atmosphere and the ocean. CO₂ diffusivity is much greater in the atmosphere than in the water and the largest impact on CO₂ transfer is by molecular diffusion and turbulent mixing in the aqueous boundary layer. It is generally agreed that the molecular diffusion layer is dominating and that processes disturbing this layer control the transfer. Most investigations describe transfer efficiency in terms of transfer velocity. Traditional estimates of air-sea exchange use relatively simple empirical wind speed-dependent expressions of transfer velocity [Wanninkhof, 1992; Liss and Merlivat, 1986; Wanninkhof et al., 2009]. There are, however, several other physical processes contributing to air-sea transfer, including microwave breaking [Zappa et al., 2001], spray and bubbles [Woolf, 1993, 1997], and buoyancy in air and water [Rutgersson and Smedman, 2010]. In the low to intermediate wind-speed regime (below 10 ms⁻¹) the primary driving mechanism that regulates transfer velocity across the air-water interface is presumed to be near-surface turbulence [Fairall et al., 2000].

At higher winds, exchange by bubbles and breaking waves play a significant role. Studies have also shown that transfer velocity is well described by the turbulence dissipation rate [e.g., Zappa et al., 2004], but do not identify the generation or scale of the turbulence. Turbulence in the upper ocean is generated by thermal convection at the surface, Langmuir turbulence, as well as traditional shear-generated turbulence.

[3] Water-side convection is generated by cooling at the surface caused by heat loss due to heat transport and evaporation. When wind is in the low to intermediate speed regime, convection is important for mixing. For intermediate to higher winds, stress-induced mixing is typically dominant. The cooling at the surface leads to denser surface water and circulation due to buoyancy; it may generate a large enough disturbance of the molecular diffusion layer to significantly enhance the transfer [Eugster et al., 2003; Rutgersson and Smedman, 2010]. Using data from the GasEx-2001 experiment, McGillis et al. [2004] demonstrated that CO₂ flux had a strong diurnal cycle and relatively high transfer velocity values; this was mainly explained by convection in the aquatic boundary layer. MacIntyre et al. [2001] suggested that traditional parameterization based on wind speed would underestimate gas flux by a factor of two in tropical regions due to ocean convection. In the work of Rutgersson and Smedman [2010] the depth of the mixed layer during convective conditions was shown to be a controlling parameter, and the characteristic velocity scale was determined by the depth of the mixed layer and the strength of the buoyancy. In this study we demonstrate the importance of water-side convection to transfer velocity, we show limitation in a previously suggested method to introduce water-side convection [Jeffery et al., 2007] and suggest a new alternative method for introducing water-side convection to calculations of transfer velocities using the concept of resistance.

2. Measurements

[4] The measurements used in this study are taken at the Östergarnsholm site in the Baltic Sea, it is located at 57°27'N, 18°59'E. The site has been running semi-continuously since 1995; a 30 meter land-based tower is situated on the southern tip of a very small, flat island in the Baltic Sea, and a buoy for CO₂ partial pressure in the water. Data from the Östergarnsholm site have been used in many air-sea interaction studies and the impact of surrounding areas has been well investigated. The relative role of upwind areas (flux footprint) can be estimated by applying expressions originally developed for atmospheric dispersion. For wind directions 80° < WD < 210°, the data are known to represent open sea conditions, in the sense that the wave field is mainly undisturbed and the atmospheric turbulence and fluxes of momentum, sensible heat, and latent heat are not influenced

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by either the limited water depth or the coast [Högström *et al.*, 2008]. Rutgersson *et al.* [2008] investigated CO₂ measurements, showing that for wind from the 80° < WD < 160° sector, the buoy represents the footprint of the tower.

[5] The measurement and instrumentation protocols are further described by Rutgersson *et al.* [2008, 2009] and Sahlée *et al.* [2008]. Mixed layer depth was determined from a three-dimensional ocean model for the Baltic Sea [Funkquist and Kleine, 2007], as described by Rutgersson and Smedman [2010].

3. Theory

3.1. Calculated Fluxes

[6] The surface flux is determined by properties of the gas, processes at the surface, in the water, and in the atmosphere. A two-layer film model is almost universally applied in estimating air-sea fluxes of trace gases. The air-sea exchange of CO₂ can be calculated from the air-sea difference in partial pressure of CO₂ at the surface and in gas transfer velocity (k) using the following equation [Wanninkhof, 1992; Donelan and Wanninkhof, 2002]:

$$F = kK_0\Delta pCO_2 \quad (1)$$

where K_0 is the salinity- and temperature-dependent CO₂ solubility constant. The transfer velocity is usually considered to be dependent on wind speed, and also on the Schmidt number (Sc) [Jähne and Haussecker, 1998]. Rutgersson and Smedman [2010] suggested

$$k = \sqrt{\frac{660}{Sc}} 0.24U_{10}^2 \quad (2)$$

for measurements from the Baltic Sea, excluding cases with water-side convection. This is relatively close to several previously derived expressions [Nightingale *et al.*, 2000; Sweeney *et al.*, 2007; Wanninkhof *et al.*, 2009].

3.2. Buoyancy at the Surface

[7] The buoyancy at the surface (B) is important for convection in the water, where water-side buoyancy is a function of surface cooling (i.e., net heat flux) and evaporation, which increases the salinity and density of the surface water, thereby enhancing buoyancy. The water-side buoyancy flux is defined according to Jeffery *et al.* [2007]:

$$B = \frac{gaQ_{net}}{c_{pw}\rho_w} + \frac{g\beta_{sal}Q_{lat}}{\lambda\rho_w} \quad (3)$$

where a is the thermal expansion coefficient, g acceleration of gravity, Q_{net} is the net surface heat flux (i.e., sensible and latent heat flux plus net long-wave radiation), c_{pw} is the specific heat of water, ρ_w is the density of water, β_{sal} is the saline expansion coefficient, Q_{lat} is the latent heat flux, and λ is the latent heat of vaporization. Following convective scaling in the atmosphere [Deardorff, 1970], the water-side convective velocity scale is defined as follows [MacIntyre *et al.*, 2001; Jeffery *et al.*, 2007]:

$$w_* = (Bz_{ml})^{1/3} \quad (4)$$

where w_* is the characteristic velocity scale of the oceanic turbulence generated by convection (corresponding velocity scale in the atmosphere is here denoted w_{*atm}) and z_{ml} , the depth of the mixed layer, is the characteristic length scale. According to equation (4) stronger buoyancy flux (a larger value of B) and a deeper mixed layer (a larger value of z_{ml}) then produce enhanced convective mixing in the water. For an atmospheric flow with combined convective and shear-generated turbulence, u_{*a}/w_{*atm} characterizes the comparative energetics role of surface shear and buoyancy forces [Zilitinkevich, 1994], where u_{*a} is the atmospheric friction velocity. We here suggest to use the corresponding parameter for the ocean, u_{*w}/w_* , where u_{*w} is the friction velocity for the ocean. Convection in the ocean has been previously expressed in terms of surface renewal theory, focusing on the interfacial molecular sub-layers. One example is from Clayson *et al.* [1996], who used shear and convective surface renewal timescales for the diffusion in the molecular sub layers, determining the convective timescale only by surface heat flux.

3.3. Modified NOAA-COARE Gas Transfer Parameterization Using the Concept of Gustiness

[8] The NOAA-COARE (National Oceanic and Atmospheric Administration-Coupled Ocean-Atmosphere Response Experiment) gas transfer algorithm is frequently used to calculate the air-sea exchange of momentum, heat and humidity as well as other gases [Fairall *et al.*, 1996a, 2003].

[9] It is physically-based, derived from surface renewal theory, and is well suited for detailed estimates of air-sea CO₂ exchange, as well as for other gases [Fairall *et al.*, 2000]. The gas transfer parameterization considers resistance to transfer in air and water, and includes both molecular and turbulent components in air and water:

$$k = \frac{u_{*a}}{\left(\sqrt{\frac{\rho_w}{\rho_a}} r_w\right) + r_a\alpha} \quad (5)$$

where r_a is resistance in the atmosphere, r_w is resistance in the water, α is the dimensionless solubility, and ρ_a is air density. The concept of resistance in air-sea gas transfer is known for a long time [e.g., Liss, 1973]. The parameterization requires the specification of a number of empirical coefficients, which can be fitted using field measurements. It has been modified to include enhanced gas transfer due to bubbles [Woolf, 1997], which in practice acts as a parallel resistor to the transfer by molecular diffusion and turbulence in the water:

$$\frac{1}{r_w} = \frac{1}{r_{wt} + r_{wm}} + \frac{1}{r_B} \quad (6)$$

where r_{wt} and r_{wm} are the turbulent and molecular resistors in the water, respectively, and r_B is the resistance due to bubbles. In the work of Jeffery *et al.* [2007], the NOAA-COARE algorithm was modified and the sub-layer effects of both buoyancy and convective mixing were introduced. Convection in the ocean was introduced in a similar way as convection in the atmosphere, where a gustiness parameter is included, this prevents the transfer coefficients from approaching zero at low mean winds. In the atmosphere the average wind speed is expressed as a function of the vector wind and the convective velocity scale (originally from Godfrey and Beljaars

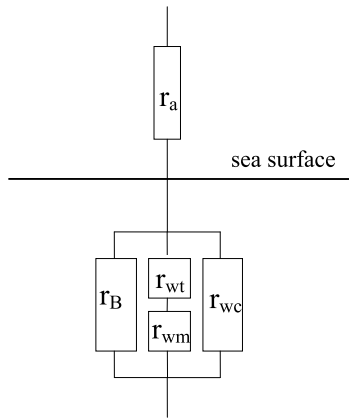


Figure 1. Schematic representation of processes acting as resistors at the air-sea interface. Where r_a is the total air-side resistance and the water-side resistance includes r_{wt} and r_{wm} (the turbulent and molecular resistors in the water), and r_B (the resistance due to bubbles).

et al. [1991]). For the ocean, the water-side convective addition (w_{gw}) to the water velocity is calculated using the convective velocity scale:

$$w_{gw} = \beta w_* \quad (7)$$

where the empirical coefficient β was set equal to 1.

[10] Buoyancy was introduced in the NOAA-COARE algorithm by rewriting equation (5) as

$$k = \left(\frac{r_w}{u_{*w}} + \frac{r_a \alpha}{u_{*a}} \right)^{-1} \quad (8)$$

Here the water-side friction velocity is calculated as a function of water-side drag (C_{dw}) and water velocity (S_w):

$$S_w^2 = u_{ref}^2 + w_{gw}^2 \quad (9)$$

where u_{ref} is the velocity of the water at some reference depth (analogous to wind speed at some reference height, see *Jeffery et al.* [2007] for details). Using the velocity of the water and the water-side roughness length (used to calculate u_{ref}) can cause problems since these parameters are not concepts commonly used in ocean research [*Fairall et al.*, 2000]. The enhancement of air-sea transfer due to water-side convection is treated analogous to atmospheric gustiness. There are, however, significant differences between these two processes. In the air, the additional gustiness velocity is added to represent velocity of the air during conditions where there is zero mean vector wind. In the water, the enhanced turbulence due to convection and the impact of this large-scale turbulence on the molecular diffusion layer enhances the transfer.

3.4. Introducing the Concept of Resistance With Water-Side Convection

[11] The effect of buoyancy on the turbulence and molecular layers in the water is introduced using other methods employed in previous studies, such as using the buoyancy effect of the rate of dissipation of turbulent kinetic energy or

a buoyancy-driven surface renewal timescale [e.g., *Soloviev and Schuessel*, 1994; *Fairall et al.*, 1996b; *Clayson et al.*, 1996]. We here introduce an additional process that disturbs the molecular diffusion layer and enhances turbulence in the water-side turbulent layer, thus adding, in practice, resistance to the transfer in the molecular diffusion layer in parallel with other processes disturbing the molecular diffusion layer.

[12] Figure 1 shows a sketch of the different processes most likely to disturb the molecular diffusion layer by using the concept of resistors, analogous to resistors in an electric circuit. Here, total resistance is expressed as

$$\frac{1}{r_w} = \frac{1}{r_{wm} + r_{wt}} + \frac{1}{r_B} + \frac{1}{r_{wc}} \quad (10)$$

where r_{wc} is resistance due to water-side convection. Other possible processes can be added in equation (10). Increased water-side convection has the effect of increasing transfer velocity.

[13] Following the reasoning by *Zilitinkevich* [1994] for an atmospheric flow with shear and buoyancy forces the addition due to water-side convection is expressed here as

$$\frac{1}{r_{wc}} = \gamma \sqrt{\frac{w_*}{u_{*w}}} \quad (11)$$

where γ is an empirical coefficient. The addition due to convection is more dominant when the turbulence generated by shear (u_{*w}) is small.

4. Results

[14] The thick (solid and dashed) lines in Figure 2 show the transfer velocity calculated from measurements and

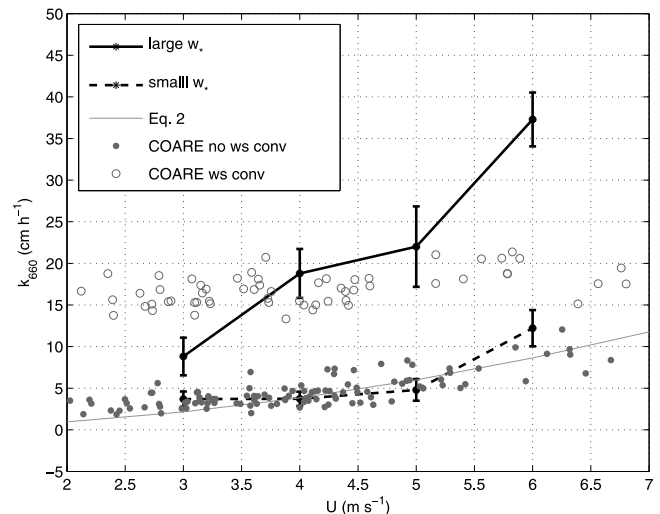


Figure 2. Transfer velocity as a function of wind speed derived from measurements and parameterizations. Lines with error bars represent bin averages of transfer velocities from measurements separated into large (thick solid line) and small (thick dashed line) values of w_* . Error bars represent \pm one standard error. Thin solid line shows transfer velocity from equation (2). Filled circles are transfer velocities calculated using the modified COARE algorithm (Section 3.3) for data with small w_* ; open circles are for data with large w_* (water-side convection present).

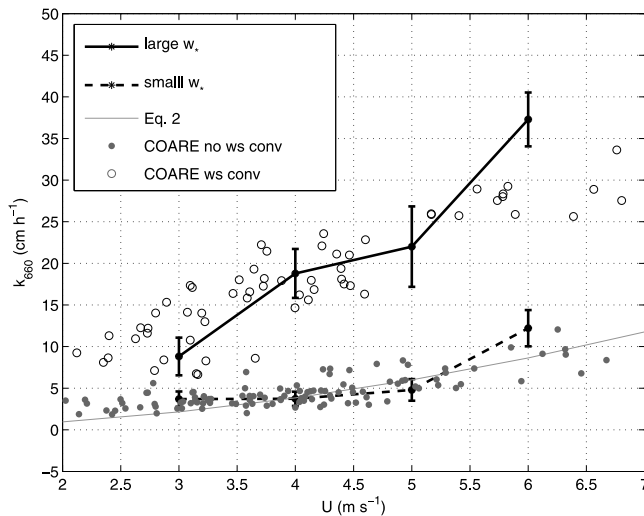


Figure 3. As Figure 2, but here the COARE transfer velocities has been calculated using concept of resistors (Section 3.4).

averaged over wind speed intervals. Data is divided into large ($w_* > 0.010$) and small ($w_* < 0.008$) water-side convective velocity scales (where a large w_* correspond to a deep mixed layer $z_{ml} > 20$ m and convection at the surface). The thin line represents equation (2). In the work of Rutgersson and Smedman [2010] $w_* > 0.006$ was determined as a limit where water-side convection is active.

4.1. Water-Side Convection in the NOAA-COARE Algorithm Using the Concept of Gustiness

[15] When introducing the water-side convection in the modified NOAA-COARE algorithm (Section 3.3) there are empirical coefficients to be determined. In the work of Jeffery *et al.* [2007] the coefficient β in equation (9) was selected as $\beta = 1.0$, which slightly enhances the calculated transfer velocity due to convection and the enhancement was calculated as between 0 and 1.4 cm h^{-1} in an idealized model. Using the data from the Östergarnsholm site (measured u_{*s} , sensible and latent heat flux and estimated long wave radiation) to evaluate the modified NOAA-COARE algorithm with $\beta = 1$, the enhancement is of the order of 0.2 cm h^{-1} (between 0 and 0.7). This is too small to explain the enhancement in measurements due to water-side convection shown in Figure 2. Using the modified NOAA-COARE algorithm and $\beta = 20$, the water-side convection data are of the same order of magnitude as the transfer velocity data from the direct measurements (open circles in Figure 2 represent $w_* > 0.010$). The variation in wind speed is, however, smaller than seen in the measurements. Transfer coefficient calculated with the NOAA-COARE algorithm agrees well with the measurements for data with no water-side convection (filled circles in Figure 2).

4.2. Introducing Water-Side Convection in the NOAA-COARE Algorithm Using the Concept of Resistance

[16] In Figure 3 the circles show transfer velocity calculated using the NOAA-COARE algorithm, but with water-side convection instead introduced as an additional resistance (equations (10) and (11)). The agreement between calculated transfer velocity and transfer velocity from measurements is

significantly improved. For the data in Figure 3 the empirical coefficient in equation (11) is $\gamma = 2 \cdot 10^{-4}$.

5. Summary and Conclusions

[17] In the presence of cooling of the water surface in combination with a deep ocean mixed layer the generation of convective eddies scaling with the depth of a mixed layer enhances the efficiency of the air-sea transfer of CO_2 (and possibly other gases). This enhancement can be explained by the convective eddies disturbing the molecular diffusion layer and inducing increased turbulent mixing in the water. This induces a significant increase in the efficiency of the air-sea exchange, seen in several previous studies [MacIntyre *et al.*, 2001; Eugster *et al.*, 2003; McGillis *et al.*, 2004; Rutgersson and Smedman, 2010]. In these studies, the variation of mixed layer depth was caused either by a diurnal or seasonal difference in heating. The enhancement can be introduced in existing formulations for calculations of air-sea exchange of gases. One suggestion from Jeffery *et al.* [2007] was to introduce water-side convection as an additional ocean gustiness velocity, since this is often done in atmospheric research. This method do not agree with our data, and has limitations when interpreting the mechanism. The alternative suggestion from this study is that buoyancy throughout the depth of the mixed layer acts to disturb the molecular diffusion layer, in addition to enhancing turbulence; it thus acts to increase the efficiency of the transfer significantly. The additional resistance is expressed here as $\frac{1}{r_{wc}} = \gamma \sqrt{\frac{w_*}{u_{*s}}}$, where $\frac{w_*}{u_{*s}}$ characterizes the relative role of surface shear and buoyancy forces. For the data used in this study the empirical coefficient was determined to be $\gamma = 2 \cdot 10^{-4}$. Using the concept of resistors acting in parallel is appealing since it also allows for introducing other mechanisms that are not presently fully known. One such possible process is the Langmuir circulation [e.g., Sullivan and McWilliams, 2010] interacting with shear-induced turbulence, as well as convective buoyancy in the water.

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