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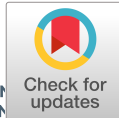
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A Simple Model of Chemistry Effects on the Air-Sea CO₂ Exchange Coefficient

Key Points:

- Modification of CO₂ air-sea exchange by the ocean CO₂ carbonate buffer is found to be negligible
- The flux gradient method for estimation the flux is valid for CO₂ if the measurements in water is more than 2 m

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Abstract The transfer of CO₂ between air and water can be quantified by the use of a transfer or exchange coefficient. Here we have studied the effect on the exchange coefficient of CO₂ from inclusion of the carbonate buffer system in water. The methodology has been to solve the flux budget for the chemical reaction equations in the water column, combining the vertical flux in the air and the flux across the interface by the introduction of a so called resistance model for the whole system where the system has been simplified with respect to variation of certain parameters. The thermal effects on the flow and chemistry modeling have in the present study not been included, although this also plays a significant role on the air-sea exchange. The model shows the effects on the air-sea exchange coefficient from the carbonate chemistry in the water column are negligible if the measurements are taken at sufficient depth in the water. Hence, it is found that the skin layer or interface layer contains the largest resistance and therefore controls the flux. It is also shown that measurement of the near-surface CO₂ gradients in ocean water is very difficult, as the gradients of CO₂ occur within the first meter from the water surface. In reality, the equilibrium is reached within the first meter from the water surface. The results justify the use of standard methods to estimate the flux of CO₂ by measuring a concentration at typical larger than 3 m depth and 10 m above the surface.

1. Introduction

The ocean is an important sink to the atmospheric carbon dioxide (CO₂) serving to keep the atmospheric concentration level of this important climate gas down. Thus, air-sea exchange of CO₂ plays an important role in the climate gas budget and a detailed understanding of the mechanisms controlling the exchange is important to estimate future CO₂ concentrations in the atmosphere with a sufficiently high accuracy to predict future temperature changes and climate effects. The air-sea flux of a weakly soluble gas such as CO₂ is water-phase controlled (Wanninkhof et al., 2009) and is commonly estimated from the difference in CO₂ concentrations across the air-sea interface. The exchange is often expressed in terms of the partial pressure of the gas in air and in water by equations of the form

$$Flux = kK_0\Delta pCO_2, \quad (1)$$

where ΔpCO_2 is the difference in the partial pressure of CO₂ across the interface, K_0 is the aqueous-phase solubility of CO₂, and k is a gas transfer velocity, being a function of several parameters, but usually only parameterized by the wind speed or the surface stress (Garbe et al., 2014; Wanninkhof et al., 2009). In reality, k depends of many chemical, physical, and biological processes in between the layers where the CO₂ gradient is measured. For example, Wanninkhof and Knox (1996) studied the chemical enhancement on the CO₂ fluxes focusing on the chemical rates in the marine microlayer (molecular boundary layer) and found that the chemical rates should be added to the physical exchange rates; however, they also showed that the chemical enhancement is only of little importance on a global scale. Air-water exchange of gases can be enhanced by wave breaking and specifically the bubble-mediated transfer. Thus, Woolf et al. (2007) introduced a bubble-mediated flux term as a part of the exchange coefficient. Andreas et al. (2016) suggested that sea spray can also affect the gas exchange. The estimation of CO₂-fluxes across the air-sea interface is therefore associated with many sources of uncertainties, and several parameterizations of k have been suggested in the literature (Liss & Merlivat, 1986; Ho et al., 2006; Nightingale et al., 2000; Prytherch et al., 2010; Rutgersson & Smedman, 2010; Wanninkhof & Knox, 1996; Wanninkhof et al., 2002; Woolf, 2005).

However, the water column part of the CO₂ gradient driving the exchange has only received little attention. CO₂ is often sampled meters above and below the sea surface to establish ΔpCO₂. Ward et al. (2004) and Woolf et al. (2016) addressed the effect on ΔpCO₂ from temperature gradients in the microlayer, showing that the bulk CO₂ collected at a certain depth has to be adjusted according to the temperature gradient in order to reflect the ΔpCO₂ driving the flux. Ward et al. (2004) describes how the temperature can change across the very shallow molecular boundary layer, and Woolf et al. (2016) investigated the solubility change of CO₂ due to temperature gradients and salinity. It could be anticipated that chemical reactions within the bulk water between the measurement point and the molecular boundary layer can alter the carbonate chemistry in the water to such an extent that this also needs to be considered when parameterizing the exchange coefficient for flux calculations. This was also pointed out and studied by Bolin (1960) several years ago. He concluded that the chemical time scale was much smaller than the turbulent transport time scale. However, this was based on very large exchange rates (0.01 to 1 cm s⁻¹) and an assumption of an equilibrium between CO₂ in air and CO₂ in the sea. In the present study, we do not take salinity and temperature into account. However, we will evaluate the importance of chemical processes affecting the CO₂ gradient measured at distances of meters on each side of the marine surface using today's parameterization of exchange velocities. We apply a mathematical model developed for a first-order decaying chemical process combined with an atmospheric boundary layer model, where the chemical as well as the turbulent time scale is taken into account in the equations (see Kristensen et al., 1997).

2. Model Description

In order to describe and evaluate the effect on chemistry on the vertical flux of CO₂, we formulate a model where we split the vertical transport in three compartments:

1. the flux of CO₂ above the sea surface,
2. the flux across a stagnant interfacial layer, and
3. the flux below the ocean surface.

In the model the atmospheric concentration of CO₂ in a given height z ($C_a(z)$) is related to the corresponding concentration of CO₂ in a given water depth defined as $C_w(z)$. At a given depth the water concentration $C_w(z)$ will approach the equilibrium concentration within seconds to minutes. Here the equilibrium concentration in water is independent of the immediate exchange with the atmosphere but reflects the carbonate buffer system, which changes on a slower time scale, in the order of hours to days (only significant fluxes over a longer time period will alter the balance of the buffer system).

A schematic presentation of the model developed within the following paragraphs is shown in Figure 1. We have chosen not to focus on the skin layer, since the purpose is to illustrate the effect from the buffer system in the water column on parameterization of the flux.

The general assumptions made in the modeling of the fluxes across the surface shown in Figure 1 are as follows:

- We assume a stationary situation within the time scales considered (typically defined as the period of the typical measurements, that is, half an hour).
- The fields of concentrations are homogeneous in the horizontal directions in the water as well as in the air.
- The field of turbulence is homogeneous in the horizontal direction in the water and in the air.
- To simplify, we neglect the role of stability in the air, and of vertical variation in temperature as well as variation of the composition of the water.
- Chemistry and physics in the skin layer are not included in the present discussion.

In the following, we will explain the assumptions and theory of the three compartments that is, the air, the interface, and the water in details.

2.1. Concentrations and Fluxes in the Layer Above the Sea

In the air CO₂ is considered a passive gas, because there are no significant chemical reactions that alter the concentrations; hence, the vertical flux is considered constant. Thus, we obtain the well-known logarithmic concentration profile where the concentration of CO₂ in air is represented by $C_a(z)$:

$$C_a(z) = C_a(0) - \frac{\overline{wC_0}}{\kappa U_*} \ln\left(\frac{z}{z_{0a}}\right). \quad (2)$$

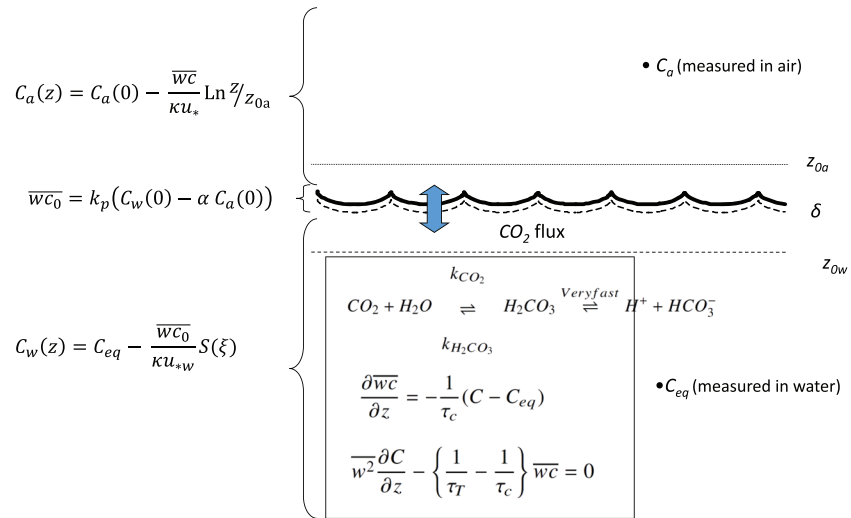


Figure 1. A schematic view of the model setup with the equations for the different processes in water, the skin layer, and air.

Additionally, we state the similar wind profile for illustration

$$U_a(z) = \frac{u_*}{\kappa} \ln\left(\frac{z}{z_{0a}}\right). \quad (3)$$

Here, $U_a(z)$ is the wind speed, and u_* is the friction velocity, describing the vertical momentum transport, with κ being the von Karman constant. C_a is the concentration at the height z_{0a} , and we have here taken z_{0a} for the gas concentration to be equal to the roughness length for the velocity profile. This assumption is fairly good for the smooth to medium rough conditions over water according to Brutsaert (1975). The flux of CO_2 in the air is here described as $\overline{w_c}$.

2.2. The Fluxes Across a Stagnant Interfacial Layer

The stagnant interfacial layer consists of the roughness scales in air and the water as shown in Figure 1. The chemical and physical processes in this layer are not considered in this paper. This layer includes three thin layers: a roughness sublayer in the water, a roughness sublayer in the the air, and a very thin molecular boundary layer with a thickness (δ) of 0.1–200 μm (Coantic, 1986) all layers depending on the wind speed. We assume that the fluxes through these layers are given by equation (1), which can also be described in terms of concentrations instead of partial pressure, and the flux $\overline{w_c}$ across this interfacial stagnant layer can thus be described as

$$\overline{w_c} = k_p (C_w(0) - \alpha C_a(0)), \quad (4)$$

where α is the dimensionless solubility of CO_2 in water and where $C_w(0)$ is the concentration in the water at z_{0w} , $C_a(0)$ is the concentration in the air at z_{0a} , and k_p is the exchange velocity across the stagnant interfacial layer. The concept of using a water roughness z_{0w} originates from the model of the upper oceanic boundary layer, which is assumed to behave as the atmospheric boundary layer (Zilintikevich & Kreimann, 1991). Here we assume that CO_2 acts as a passive tracer in this very thin layer; that is, all carbonate chemistry occurs below the molecular boundary layer. However, we do know that temperature gradients in the water column affect the CO_2 concentration, but to evaluate the effect of chemical reactions over the measured concentration gradient, we will neglect temperature gradients. The exchange coefficient has, as cited in the introduction, been parameterized by several authors, and in wind/water tunnels the exchange coefficient k is often found to depend linearly on u_* for unbroken surfaces and can be written as

$$k = b u_{*a} Sc(T)^n. \quad (5)$$

Here $Sc(T)$ is the Schmidt number for the tracer as a function of the temperature. T and u_{*a} are the atmospheric friction velocity, b is a nondimensional coefficient, and n is an exponent discussed in

Goddijn-Murphy et al. (2016). The form used here is taken from tunnel data (Ocampo-Torres & Donelan, 1994) where $n = 1$ for unbroken surfaces. This linear relationship between u_* and the exchange coefficient is also supported by McGillis et al. (2007). However, the value of n in the present study is not important, as we are investigating the effects of chemistry in the water column.

For any given neutral wind, we can now determine the transfer across the interface, using equations (4) and (5). The relationship between the wind speed at a given height z above the water surface is expressed by equation (3), with the roughness given by equation (6) (Charnock, 1955). The exchange velocity u_{*a} , to be used in (5), can now be found by iteration. The empirical coefficient c over open waters can be taken as 0.014 from Charnock (1955).

$$z_{0a} = c \frac{u_{*a}^2}{g}, \quad (6)$$

$$u_{*w} = \frac{u_{*a}}{30}. \quad (7)$$

Equation (7) specifies the relation between u_* in air and in water, which is here due to the density differences between air and water. The logarithmic wind profile can then be turned upside down so the profile specification of the velocity of the water from the surface and downward also follows a logarithmic profile with the corresponding water momentum flux and roughness (Zilintikevich & Kreimann, 1991) where the water roughness is

$$z_{0w} = c_w \frac{u_{*w}^2}{g}. \quad (8)$$

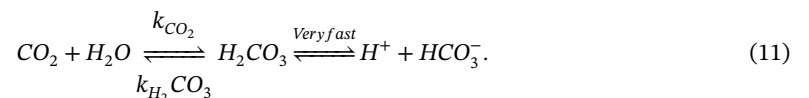
The coefficient c_w is estimated to about 5,000 as a value in the middle of the interval: 10^3 – 10^4 suggested by Figure 4.2 in Zilintikevich and Kreimann (1991). By iteration of the equations (6), (7), and (3) the friction velocity in water can be expressed as a function of the wind speed.

2.3. Concentration and Fluxes in the Water

First, we shall focus on the chemistry alone; second we will introduce the fluid motion as well. In the following, we simplify the carbonate buffer system and describe it as a simple first order decaying process, thereby obtaining an analytical solution for the fluxes in the water phase. In the water column the concentration of CO_2 changes due to the reactions with water (Stumm & Morgan, 1981):



The latter chemical reaction is only important for pH higher than 10, and the first reaction dominates when pH is around 8 or less, which corresponds more or less to the mean value of the pH values in the ocean (Stumm & Morgan, 1981). CO_2 is hydrated and forming carbonic acid H_2CO_3 , which again is protolyzed to HCO_3^- and CO_3^{2-} . The total reactions can therefore be written as



Here we assume an equilibrium in the carbonate system between HCO_3^- and H_2CO_3 with the reaction rates $k_{\text{H}_2\text{CO}_3}$ and k_{CO_2} in order of 10 to 20 and 0.025 s^{-1} (Stumm & Morgan, 1981).

Given the assumption that the total alkalinity, pH, and the temperature do not change from the skin layer to the depth of the observation point, the chemistry in the water is reduced to a first-order process arguing that the time scale of transforming CO_2 to H_2CO_3 is slower than the rest of the reaction velocities in the carbonate system. Furthermore, there is a huge buffer in the sea implying that the equilibrium concentration does not change over the time scale considered as we described in the assumptions of the model.

In the water we therefore obtain the following conservation equations.

$$\frac{\partial C}{\partial t} = -k_{CO_2}C + k_{H_2CO_3}C_{H_2CO_3} \approx (-1/\tau_c)(C - C_{eq}), \quad (12)$$

where C is the CO_2 concentration, $C_{H_2CO_3}$ is the H_2CO_3 concentration, and C_{eq} is the equilibrium concentration of CO_2 in the water due to the buffer system, which is given by the alkalinity, pH, and sea water temperature.

We have here parameterized the buffer mechanism of CO_2 in order to close equation (12). Hence, we assume that the midterm of equation (12) can be written as $(-1/\tau_c)(C - C_{eq})$. When the concentration of C is higher than C_{eq} , that is, a downward flux of CO_2 , the rate of change constant is $1/\tau_c = k_{CO_2}$. In the following, $\tau_c = 40$ s is chosen to be the reference for the chemical time scale.

Assuming stationary conditions and horizontal homogeneity a conservation equation for C can now be obtained as a balance between flux divergence and the local source, that is,

$$\frac{DC}{dt} = \frac{\partial \overline{wc}}{\partial z} + \frac{\partial C}{\partial t} = 0, \quad (13)$$

which combined with equation (12) gives

$$\frac{\partial \overline{wc}}{\partial z} = \frac{1}{\tau_c}(C - C_{eq}). \quad (14)$$

As stated, we have assumed stationarity and horizontal homogeneity. Following the methods applied within atmospheric chemistry for similar situations, Kristensen et al. (1997) derived an analytic solution for the flux of a decaying tracer. This solution is based on a second-order closure model for the flux and mean concentration of a decaying tracer in a stationary and horizontally homogeneous field of turbulence combined with a stationary concentration field. From Kristensen et al. (1997), the equation for the flux of a decaying species in a turbulent field based on the assumptions above is

$$\overline{w^2} \frac{\partial C}{\partial z} - \left\{ \frac{1}{\tau_T} - \frac{1}{\tau_c} \right\} \overline{wc} = 0, \quad (15)$$

where τ_T is the turbulent time scale defined as z/u_* , while τ_c is determined as discussed above. The flux budget equation (15) has here been reduced by the following:

- The chemical conversion can be described by a first-order process, as given by equation (12).
- The equation for correlation between pressure and concentration fluctuations has been closed with the flux and a turbulent time scale.
- Third-order correlations have been neglected.

As τ_c is going to infinity, we obtain the equations of a passive tracer, and the equation for the flux is reduced to the ordinary K closure for a passive scalar.

Inserting the derivative of the conservation equation (14) with respect to z into the flux budget equation (15), we obtain a closed form of the flux budget equation, that is,

$$\tau_c \frac{\partial^2 \overline{wc}}{\partial z^2} - \left\{ \frac{1}{\overline{w^2} \tau_T} - \frac{1}{\overline{w^2} \tau_c} \right\} \overline{wc} = 0. \quad (16)$$

In this equation we introduce the following variables from Kristensen et al. (1997):

$$\frac{\kappa u_{*w}}{\sqrt{\overline{w^2}}} = a \approx \frac{1}{3}, \quad (17)$$

$$K_w = \overline{w^2} \tau_T \approx \kappa u_{*w} (z + z_{0w}). \quad (18)$$

It is assumed that the turbulent time scale or the diffusivity K_w beneath the water surface has a finite value determined by z_{0w} . This assumption of a time scale different from zero, where z equals to zero, is different

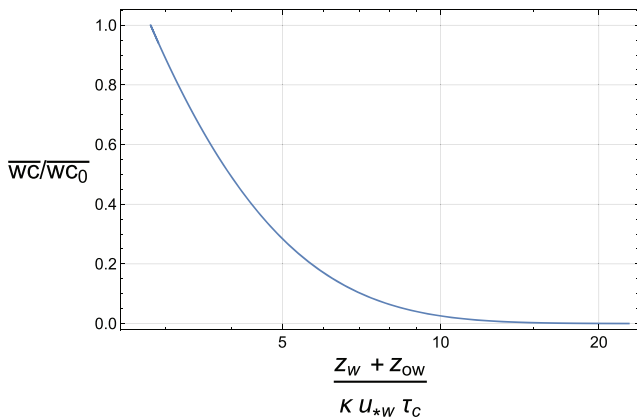


Figure 2. The normalized flux versus the normalized depth (from equation (22)). The equation is evaluated for $U(10 \text{ m}) = 10 \text{ m/s}$. The normalized depth corresponds to the Damköhler number, that is, the ratio between the chemical and the turbulence time scales. It is seen that the normalized flux vanishes for a normalized depth of about 10.

where

$$\xi_0 = \frac{Z_{0w}}{\kappa U_{*w} \tau_c}, \quad (23)$$

and $U(a, b, z)$ is the confluent hypergeometric function, and F is a factor used to ensure the flux upper boundary conditions, that is, $f(\xi_0) = F = \overline{wc}_0 / (\kappa u_{*w})$. The corresponding normalized concentration profile $S(\xi)$ above the equilibrium concentrations in water can be found by inserting equation (22) in equation (14), which yields

$$S(\xi) = \frac{F e^{-a\xi}}{e^{-a\xi_0} U\left(\frac{1}{2a}, 0, 2a\xi_0\right)} \times \left\{ U\left(1 + \frac{1}{2a}, 0, 2a\xi\right) + aU\left(\frac{1}{2a}, 0, 2a\xi\right) \right\}. \quad (24)$$

Figure 2 shows the flux profile obtained from equation (22). The normalized flux is seen to decrease with increasing normalized depth. At the normalized depth of 10 to 15, it is seen that the flux has reduced to 3–4% of the surface flux, which is small compared to overall uncertainties on surface flux estimates (Fairall et al., 2000; Norman et al., 2012; Sørensen & Larsen, 2010). The figure is shown for a wind speed U of 10 m/s. However, the ratio of 10–15 applies to all wind speeds, as also documented by Kristensen et al. (1997) for a similar process. Both the chemical removal and the turbulent flux are driven by the difference between C and C_{eq} . This difference vanishes at a certain depth dependent on the time scales of the two processes (the turbulence and chemistry) as described above.

The flux profile in Figure 2 shows that the flux of CO_2 is not constant but changes with the depth due to the chemical removal. The changes are largest near the surface and approach zero at depths where the normalized depth is about 10–15. It is now possible to investigate in which depths the flux becomes negligible and thereby also in which depth the concentration will be close to the equilibrium concentration. Since the time scale of the turbulence depends on the wind, this depth will be wind speed dependent.

Figure 3 shows the depth where the Damköhler number is 10 as function of the wind speed and thereby also the depth where the concentration

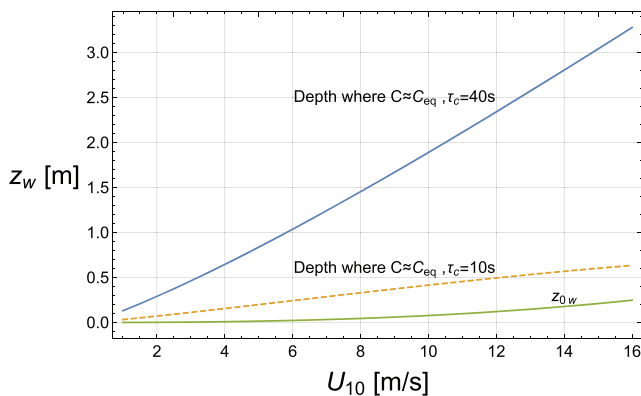


Figure 3. The depth where the flux becomes negligible and the concentration approaches the equilibrium concentration as function of wind speed. For comparison, also, the roughness length, Z_{0w} , is indicated.

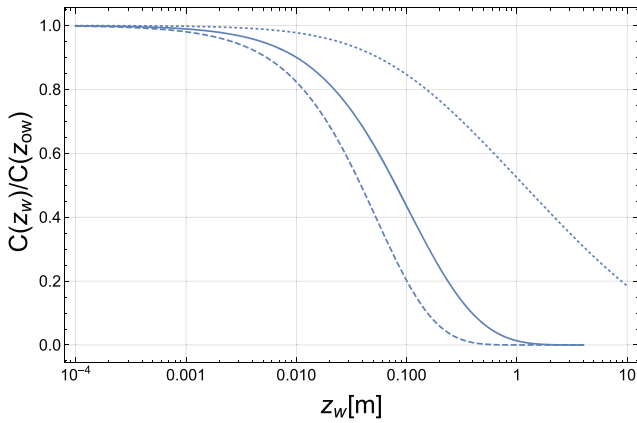


Figure 4. The concentration profile of the difference between the equilibrium concentration and CO₂, shown for three different chemical time scales 10, 40, and 10,000 s (dashed, full, and dotted lines) as function of depth. All the profiles are calculated for the wind speed equal 10 m/s at 10 m.

approaches the equilibrium concentration. As seen from the figure, the gradient of the concentration occurs at shallow depths. This implies that the task of measuring a concentration profile different from the equilibrium concentration can be challenging due to the wind induced waves.

Besides the effect on the solubility, the effect of temperature will also alter the chemical timescale. In Figure 4 we have tried to show the effects of temperature on the water concentration profile by choosing two different time scale for the chemistry. Short time scale results in faster transformation of CO₂ to the equilibrium concentration C_{eq} . In comparison a time scale of 10,000 s⁻¹ is also shown to illustrate a nearly passive tracer.

3. The Exchange Coefficient With Chemistry Included

Based on the model described in the previous sections, we will now explore the modification of the exchange coefficient induced by the concentration gradients in water and air. We use the following equations:

$$\overline{wc}_o = k_p(C_w(0) - \alpha C_a(0)), \quad (25)$$

$$C_w(z_w) = C_{eq} - \frac{\overline{wc}_o}{\kappa u_{*w}} S(\xi), \quad (26)$$

$$C_a(z) = +C_a(0) - \frac{\overline{wc}_o}{\kappa u_*} \ln(z/z_o), \quad (27)$$

where equation (25) describes the flux over the interface, equation (26) the concentration profile in water, and equation (27) the concentration profile in air. Combining these equations, we obtain the following equation:

$$\overline{wc}_o = \left[\frac{1}{k_p} + \frac{S(\xi_0)}{\kappa u_{*w}} + \frac{\alpha}{\kappa u_*} \ln(z/z_o) \right]^{-1} \times (C_{eq} - \alpha C_a(z)) \quad (28)$$

The CO₂ concentration in the water at a depth below approximately 30 m will in general not be a function of depth, and the concentration will be equal to the equilibrium concentration as discussed in section 2.3. Hence, we can conclude that for the depths normally used for the pCO_2 measurements, which are larger than 3 m, the exchange coefficient can be expressed as

$$\overline{wc}_o = k(C_{eq} - \alpha C_a(z)), \quad (29)$$

$$k = \left(\frac{1}{k_p} + \frac{S(\xi_0)}{\kappa u_{*w}} + \frac{\alpha}{\kappa u_*} \ln(z/z_o) \right)^{-1}. \quad (30)$$

It is seen that the flux can be written as a new exchange coefficient k , which includes the skin-layer coefficient k_p , the concentration modification in the water, and the logarithmic profile in air. This is equivalent to a traditional resistance model (Joffe, 1988) and (Geernaert et al., 1998) including the turbulent water mass, the skin layer, and the air. Equation (29) describes the flux derived from measurements at a depth where the equilibrium has been achieved, and a typical measuring height

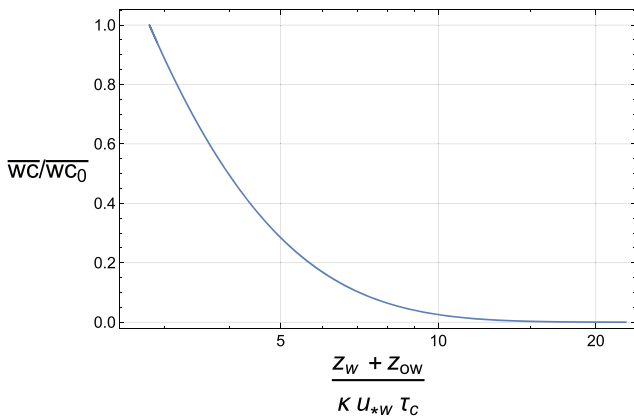


Figure 5. The exchange coefficient normalized with the exchange coefficient for an approximately passive tracer gas k_{inert} (where $\tau_c = 10,000$ s) as function of the wind speed at 10 m. The dashed line represents a chemical time scale of 10 s, and the full line shows the case of 40 s

z above the water surface. The ratio k/k_{inert} , that is, the exchange coefficient for value of τ_c where chemistry is influencing the gradients divided by process where chemistry is neglectable, for example, τ_c large (e.g., 10,000 s) is shown in Figure 5 as a function of wind speed. From this we can conclude that chemistry in the bulk water only has a minor effect on the exchange coefficient k in the order 5% to 8% with an diminishing effect as function of wind speed. The figure also shows the smallest time scale has a larger effect compared to reference time scale of 40 s.

4. Summary of the Effects of Chemistry

The basis assumption behind the use of flux gradient relation in equation (1) is that the concentrations in the air and the water are horizontally homogeneous and stationary in the two fluids with the only concentration gradient to be right at the interface. However, there is a concentration gradient both in the air and the water. In this paper we have studied the effects of the vertical concentration gradient in the water induced by the flux across the interface, including both the chemistry and the diffusion processes. The methodology has been to combine the turbulent flux budget with the chemical reactions in water, including a constant flux in the air.

We have shown that the effects of water chemistry on the air-sea exchange coefficient are negligible. The skin layer still contains the largest resistance and therefore controls the flux. The reason why the effect is small is mainly because of the size of the carbonate buffer and the speed of the chemical reactions involved.

Note that the theoretical calculations show that the gradients of CO_2 occur in the near surface. In real life, it is very difficult to verify these CO_2 gradients in water, since the depth of the equilibrium is reached within the first 3 m. For low wind speeds, the layer where the gradients exist will be very shallow, whereas for higher wind speeds, the layer will be deeper, but the presence of waves will make near surface measurements difficult.

Notation

$U + u$	the Reynold's convention with capital letters being mean value.
α	the dimensionless solubility
τ_T	is the turbulent time scale
τ_c	is the chemistry time scale
a	pertains to the atmosphere, used when clarifying
a	is $u_* w / (\langle w^2 \rangle)^{1/2}$
b	const. in equation (5) relating k to u_* and $Sc(T)$
C_{eq}	the equilibrium concentration of CO_2 in water given by the buffer of the carbonate system
$C + c$	concentration of CO_2
c	in subscript: pertaining to xchemistry
c	Charnock's constant in Charnock's roughness formulation
F	normalized flux at the surface, that is, $\overline{w c_0} / \kappa u_*$
g	acceleration due to gravity
k	exchange velocity
k_p	exchange velocity across the interfacial layer, z_{0a} and z_{0w}
K	diffusivity
K_0	solubility of CO_2 in the water
Sc	the Schmidt number
T	temperature (Kelvin)
T	in subscript due to turbulent mixing" (equation (14))
$(U + u, v, w)$	wind or current vector
u_*	friction velocity
z	height scale z_w positive downward in the water, z_a positive upward in the air
z_0	roughness length of the water surface, z_{0a} seen from the air flow above, z_{0w} as seen by the water current below

w index pertains to water, used when clarifying
 \overline{wC} vertical flux of concentrations

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