Using eddy covariance to estimate air–sea gas transfer velocity for oxygen

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ABSTRACT

Air–sea gas transfer velocity for O_2 is calculated using directly measured fluxes with the eddy covariance technique. It is a direct method and is frequently used to determine fluxes of heat, humidity, and CO_2, but has not previously been used to estimate transfer velocities for O_2, using atmospheric eddy covariance data. The measured O_2 fluxes are upward directed, in agreement with the measured air–sea gradient of the O_2 concentration, and opposite to the direction of the simultaneously measured CO_2 fluxes. The transfer velocities estimated from measurements are compared with prominent wind speed parameterizations of the transfer velocity for CO_2 and O_2, previously established from various measurement techniques. Our result indicates stronger wind speed dependence for the transfer velocity of O_2 compared to CO_2 starting at intermediate wind speeds. This stronger wind speed dependence appears to coincide with the onset of whitecap formation in the flux footprint and the strong curvature of a cubic wind-dependent function for the transfer velocity provides the best fit to the data. Additional data using the measured O_2 flux and an indirect method (based on the Photosynthetic Quotient) to estimate oxygen concentration in water, support the stronger wind dependence for the transfer velocity of O_2 compared to CO_2.

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1. Introduction

Air–sea exchange of oxygen is a research area of increasing scientific interest. Oxygen in the ocean is of crucial importance, as it is strongly linked to both the carbon and nitrogen cycles (Arrigo, 2005; Keeling et al., 2010) and is a key component in eutrophication (Karlsson et al., 2002). Gas transfer velocity describes the efficiency of the gas transfer process across the air–sea interface. Over the years numerous laboratory and field studies have been made to study gas transfer velocity. Several expressions have been proposed, relating the gas transfer velocity to different physical variables such as sea spray and bubbles (Monahan and Spillane, 1984; Wallace and Wirick, 1992; Woolf, 1997; Asher and Wanninkhof, 1998; McNeil and d'Asaro, 2007), surface films (Broecker et al., 1978; Frew, 1997; Salter et al., 2011), water-side convection (MacIntyre et al., 2002; Rutgersson and Smedman, 2010; Rutgersson et al., 2011) and rain (Ho et al., 1997, 2004; Zappa et al., 2009; Takagaki and Komori, 2007); still, wind speed holds as the most robust single parameter to describe the transfer velocity (Liss and Merlivat, 1986). The relative importance of these different processes

for air–sea gas exchange is likely to vary for gases of different solubility and is still not fully understood (Garbe et al., 2014). It is well known that transfer velocities for water vapor and heat (corresponding to very high solubility) have a weaker wind speed dependence than CO_2 (e.g. Rutgersson et al., 2001). Studies on the transfer velocities for acetone (Yang et al., 2014) and DMS (Huebert et al., 2010; Marandino et al., 2007) gases with relatively high solubility, has shown less wind speed dependence than the transfer velocity for CO_2. By introducing eddy covariance measurements of oxygen (having a solubility 60 times lower than CO_2), knowledge about the effect of a variety of processes on the transfer velocity could fundamentally increase.

The onset of breaking waves is expected to enhance the water-side turbulence (Kitaigorodskii, 1984; Woolf, 2005); in addition, it has been suggested that bubbles injection occurring in the near surface waters enhance the transfer process (Keeling, 1993; Woolf, 1993). Monahan and Spillane (1984) suggested a relation whereby the whitecap coverage scales to the cube of the wind speed. A cubic wind speed dependence for the transfer velocity, however, has only been verified for a few field studies (e.g. Wanninkhof and McGillis, 1999; Kihm and Körtzinger, 2010). Woolf (1997) proposed a relation of the transfer velocity to wind speed, using a theoretical model including injection of air bubbles in the bulk of the water. The importance of bubbles injection from wave breaking to the gas transfer velocity has been suggested to be inversely proportional to the gas solubility (Keeling, 1993; Asher

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et al., 1996; Woolf, 1997; Asher and Wanninkhof, 1998). However, the transfer velocities for different gases have also shown to be highly sensitive to void fraction and bubble distribution (Woolf, 1993; Woolf et al., 2007) within the water column.

Here we use the eddy covariance (EC) method to directly measure the air–sea gas flux of O_2 and estimate a gas transfer velocity for oxygen. Only few previous studies exists using atmospheric EC data for oxygen (Andersson et al., 2014). Previous estimates of the gas transfer velocities of oxygen have instead been made using a budget method (Kihm and Körtzinger, 2010) or eddy covariance fluxes in water (McNiel and d'Asaro, 2007). Kihm and Körtzinger (2010) found a stronger wind speed dependence for the transfer velocity of O_2 compared to prominent parametrizations for CO_2. However, for most cases the gas transfer velocity of O_2 is assumed to follow the same wind speed dependence as other nonreactive gases with low solubility. We will here use three different types of data to estimate the transfer velocity for oxygen. In all data sets the transfer velocities are determined from the measured EC O_2 flux. For data set 1 (cf. 4.1) and 2 (cf. 4.2) measured air–sea gradient of oxygen are used in the computation of the transfer velocities, while for period 3 the concept of PQ (Photosynthetic Quotient cf. 3.3) was applied to determine the oxygen concentration in water within the flux footprint.

2. Theory

The air–sea flux, F, of a non-reactive gas such as O_2 can be described by

$$F = k(C_w - \alpha C_a) \tag{1}$$

where k is the transfer velocity, C_w denotes the gas concentration in the bulk water, α the Ostwald solubility constant, and C_a the gas concentration in the air near the water surface. This transfer efficiency is also commonly described in terms of the resistance R, which is inversely proportional to k. The two-layer film model (Liss and Slater, 1974) describes the total resistance as the sum of the air resistance R_a and water resistance R_w:

$$k^{-1} = R_a + R_w = (k_a/\alpha)^{-1} + (\varepsilon k_w)^{-1} \tag{2}$$

where ε denotes a chemical enhancement factor. For slightly soluble gases such as O_2 the transfer resistance is found in the aqueous sublayer, and hence $k \approx k_w$. The water-side resistance can then be divided into individual resistances describing each process.

Using Eq. (1) and solving for k gives a relation where the transfer velocity is expressed by the measured oxygen flux F_{O_2} and the air–sea gradient of the oxygen concentration:

$$k_{O_2} = F_{O_2}(C_w - \alpha C_a)^{-1} \tag{3}$$

The air–sea gradient can also be expressed in terms of air–sea difference in partial pressure ΔpO_2, giving the following expression for k_{O_2}:

$$k_{O_2} = F_{O_2}(K_0 \Delta pO_2)^{-1} \tag{4}$$

where K_0 is the gas specific solubility constant. To compare k_{O_2} values measured at different locations with different temperature T and salinity S, the measured k_{O_2} is normalized with respect to Schmidt number Sc.

$$k_{660} = k_{O_2}(Sc/660)^{-1/2} \tag{5}$$

where k_{660} is the transfer velocity scaled to the Schmidt number of 660 (for CO_2 at 20 °C in seawater). The Schmidt number describes the rate of diffusion across the air–sea interface and is defined as the ratio of viscous diffusion to the rate of mass diffusion (Wilke and Chang, 1955). The in situ Schmidt number can be obtained from the measured temperature and salinity using the empirical relation from Wanninkhof (1992). For a liquid interface with waves, most models predict k to be proportional to $Sc^{-1/2}$. For gases of relatively low solubility, such as O_2, wave breaking and bubble-mediated transfer is suggested to play a role also for Schmidt number coefficient.

3. Site and data analysis

3.1. Östergarnsholm

The measurements used in this study are taken at the Östergarnsholm site in the Baltic Sea. This station is located at 57°27′N, 18°59′E (Fig. 1). The site has been running semi-continuously since 1995. The site includes a land-based 30-m tower with the base 1 ± 0.5 m above mean sea level, situated on the southern tip of a flat island in the Baltic Sea and mooring instruments mounted on a buoy 1 km SE of the tower.

The tower is equipped with both slow response instrument for profiles and high frequency instruments for turbulent fluxes. The mooring instruments consists of an SBE 37 SMP-IDO (Seabird Electronics Inc., Bellevue, Washington, USA) measuring dissolved oxygen concentration, oxygen saturation, temperature, salinity and a SAMI-2 CO_2 (Sunburst Sensors, Missoula, MO, USA) measuring the partial pressure of CO_2 and water temperature, both mounted at 4 m depth. The temperature recordings from the SBE 37 are used in the analysis. Since 2013 the mooring station is also equipped with a temperature and conductivity profile system (Onset Computer Corp., Bourne, Massachusetts, USA) measuring at a depth of 0.5 m, 5 m, 10 m, 15 m and 20 m depths. The bottom structure in the area is flat with a typical depth of 20–25 m, depending on sea surface level. Data from the site have been used for numerous studies on varies aspects on air–sea interaction and gas exchange (e.g. Rutgersson and Smedman, 2010; Smedman et al., 1999). The fluxes of momentum, sensible heat and latent heat are shown to represent open sea conditions for wind directions (WD) 80° < WD < 190° and coastal marine conditions for 200° < WD < 220° (Högström et al., 2008). The fluxes of CO_2 are shown to represent open sea conditions for wind direction 80° < WD < 160° (Rutgersson et al., 2008).

3.2. Atmospheric data

The high frequency oxygen data were measured at the height of 27 m with the commercially available optode system Microx TX3 in combination with the sensor without optical isolation (PreSens, Precision Sensing GmbH, Regensburg, Germany). The eddy covariance system also included a sonic anemometer CSAT3 (Campbell Scientific, North Logan, Utah, USA). The Microx TX3 together with the non-optical isolated sensor probe attains a response time of about 0.5 s with a precision of 0.1% air saturation. The measured oxygen concentration are sensitive to temperature fluctuations. With the thermistor connected the Microx TX3 compensate for temperature fluctuations on a temporal scale down to 20 s. The humidity and CO_2 fluctuations are measured with a LICOR-7500 (LICOR-Inc., Lincoln, NE, USA) open-path analyzer. A seasonal cycle is observed for CO_2 in the