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The annual cycle of carbon dioxide and parameters influencing the air–sea carbon exchange in the Baltic Proper

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ABSTRACT

A land-based field station, two moored buoys and data from the Finnpartner ship were used to investigate the variability of the air–sea CO_2-flux and parameters controlling the flux during one year in the Baltic Sea region. The agreement between the sea surface partial pressure of CO_2 measured near the tower and from the ship in the central parts of the Baltic Proper was relatively good during most of the period. But, during periods with intense biological activity or strong upwelling there were significant differences. The flux of CO_2 was measured with the eddy-correlation method. The transfer velocity was calculated from the flux measurements and the instrumental uncertainty in calculations of the hourly values of transfer velocity was of the order of 20%. The calculated value of the transfer velocity increased with increasing the wind speed. The relation showed, however, great scatter and no clear wind-dependent relation could be determined. It was shown that for the measured flux and for transfer velocities estimated from measurements it is important to know the variability of pCO_2^w in the footprint area. This is of particular importance when investigating the processes influencing the flux. When calculating the air–sea flux of CO_2 the greatest uncertainty is in the determination of the transfer velocity, but it was shown that also the partial pressure of CO_2 in the surface water is crucial to determine with good accuracy.

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1. Introduction

Carbon dioxide (CO_2) plays a key role in climate and climate change. To understand the effects of anthropogenic emissions of CO_2 it is crucial to understand all parts of the carbon cycle. The oceans absorb a large portion of the anthropogenic CO_2 from the atmosphere. There has been a large number of measurements of oceanic CO_2 during the last decades but the quantification of the total oceanic uptake as well as the regional distribution is still uncertain (Siegenthaler and Sarmiento, 1993; Takahashi et al., 2002; IPCC, 2007). To estimate the uptake of coastal and marginal waters, like the Baltic Sea, is more difficult due to the impact of coastal processes. According to Gattuso et al. (1998) coastal oceans (defined as shallow areas where land, ocean and atmosphere interact) occupy only 7% of the global ocean surface, but account for 14–30% of the global marine primary production. Muller-Karger et al. (2005) estimate that the continental margins contribute more than 40% to the organic carbon burial in sediments. In the global carbon cycle the total exchange at the sea surface is important and presently not very accurately described. This is explained by lack of detailed understanding of the processes controlling air–sea exchange. For near coastal regions this lack of understanding of the processes has a greater impact due to larger variability of the parameters controlling the transfer.

The Baltic Sea is a semi-enclosed sea on relatively high latitudes (Smedman et al., 2005). Previous investigations from the Baltic Proper showed large variability of partial pressure of CO_2 at the sea surface (pCO_2^w) in time and in space. The amplitude of the annual cycle of pCO_2^w varies significantly

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depending on the region (Schneider et al., 2006) where the largest seasonal amplitude (400 µatm) occurs in the North-eastern Baltic Proper and the smallest amplitude (120 µatm) is found in the transition areas to the North Sea. The average CO_2 uptake of the Baltic Proper was estimated to 0.9 mol m^{-2} a^{-1} (Thomas and Schneider, 1999). In Algesten et al. (2004) the annual cycle of pCO_2^w was investigated for the Bothnian Sea, where an even larger annual cycle was seen. Winter values were above 500 µatm and summer values of about 100 µatm.

The exchange of CO_2 between the ocean and the atmosphere is controlled by the air–sea difference in partial pressure of CO_2 (ΔpCO_2) at the surface and of the efficiency of the transfer processes. The partial pressure at the water surface is controlled by biological, chemical and physical processes in the ocean. The efficiency of the transfer processes is determined by the resistance to the transfer in the atmosphere as well as in the ocean. The largest resistance to the CO_2 transfer is found in the molecular diffusion through the laminar layer in the water. Thus the thickness of this layer controls the transfer. It can be expected that processes such as state of the waves, bubbles, sea spray, and turbulence in the atmosphere and ocean and surface films are of great importance (Bock et al., 1999). In most investigations the efficiency of the transfer is described by a transfer velocity. The transfer velocity is most commonly described by a quadratic or cubical wind speed dependence (Wanninkhof, 1992; Wanninkhof and McGillis, 1999; Weiss et al., 2007). Most investigations of the relation between the transfer velocity and wind speed show a significant scatter, in part due to uncertainties in measurements, but also because there are other processes of importance (Fairall et al., 2000). When we want to model the air–sea exchange of CO_2 we thus need to be able to describe the biological, chemical, and physical properties of the ocean as well as the meteorological conditions in the atmosphere.

The purpose of this study is to investigate the limitations as well as advantages of a stationary field station measuring CO_2 and CO_2 flux with a high resolution in time. We also want to describe the annual cycle and the variability of parameters of importance when calculating the air–sea exchange. In this investigation we use eddy-correlation measurements to examine the flux of CO_2 across the air–sea interface. This approach has also been used in previous investigations of the exchange of CO_2 in the open ocean (McGillis et al., 2004; Iwata et al., 2005) as well as in the Baltic Sea (Weiss et al., 2007). The use of the eddy-correlation technique for direct measurements of the flux is analysed and the effect of horizontal variation in the water value of pCO_2 on measured flux investigated. A significant number of previous investigations of the air–sea exchange of CO_2 include assumptions with respect to atmospheric variability and representativity in the ocean. These assumptions include the use of a monthly mean wind speed (Algesten et al., 2004) and constant values of atmospheric partial pressure of CO_2 (DeGrandpre et al., 2002; Jabaud-Jan et al., 2004). We will highlight the effects of some of these assumptions using data from the Östergarnsholm field station. The consequences of the uncertainties of the formulations for transfer velocities have previously been illustrated in several studies, in Takahashi et al. (2002) global estimates of the total CO_2 uptake by the oceans are increased by 70% using the formulation by Wanninkhof and McGillis (1999) compared to using the one by Wanninkhof (1992).

2. Measurements

2.1. The Östergarnsholm site

Most of the measurements used in this study are taken at the Östergarnsholm island in the Baltic Sea. The location of this station is (57° 27′N, 18° 59′E) (see Fig. 1). The measuring site at Östergarnsholm has been running since 1995. It is a land-based 30 m tower situated on the southern tip of a very small, flat island in the Baltic Sea. The flux of some quantity measured at a certain height is influenced by the surface conditions at a certain distance upwind; this area of influence is called the flux footprint. The relative role of upwind areas can be estimated by applying expressions originally developed for atmospheric dispersion. The flux footprint is highly dependent on atmospheric stability. In Högström et al. (2008) it was estimated that for very stable conditions 60% of the fluxes measured at 10 m origin at an area between 1.7 and 22 km from the tower and for very unstable conditions 60% of the fluxes measured at 10 m origin at an area between 75 and 300 m from the tower. It is the sea surface partial pressure of CO_2 (pCO_2^w) in this area that is of importance for the flux measured in the tower. Shoaling waves in the footprint area can affect the fluxes measured at the tower. Shallow water effects were analysed in Smedman et al. (1999) and they found that during the investigated case fluxes were not significantly altered with wave periods up to 8 s. Less than 1% of the investigated data includes wave periods larger than 8 s.

For the wind directions (80°<WD<210°), the data has been shown to represent open sea conditions in the sense that the wave field is mainly undisturbed and the atmospheric turbulence as well as the fluxes of momentum, sensible and latent heat are not influenced by the limited water depth or the coast (Högström et al., 2008).

In this analysis we divide the data into three sectors, 50°<WD<80°, 80°<WD<160° and 160°<WD<220°. The sector 50°<WD<80° represents a footprint area with a disturbed wave field due to the limited water depth. This sector is included in the analysis to investigate if the pCO_2^w measured by the SAMI sensor (further described in Section 2.1.2) could be representative for this footprint area in spite of the disturbed wave field. The SAMI sensor is approximately in the footprint of the tower for the sector 80°<WD<160° and the tower data should here give the best representation of the surface measurements. For the sector 160°<WD<220° the wave field is mainly undisturbed, but this sector is investigated separately since the footprint covers a more near coastal region with possibly altered pCO_2^w compared to the value measured by the SAMI sensor.

2.1.1. Atmospheric data

The tower is instrumented with high-frequency instrumentation for the turbulence data as well as slow response sensors for profile measurements. The wind speed, wind direction and temperature are measured at five levels (7, 11.5, 14, 20 and 28 m above the tower base). Relative humidity is measured at 8 m. Half-hourly values of CO_2 in the atmosphere are measured at 9 m above the tower base using an infrared gas analyser (IRGA, PP-systems). The accuracy of the IRGA is 2–3 ppm and it is calibrated each half hour with a zero gas (N_2) and each fourth hour with a reference gas (CO_2=500 ppm). Due to measurement problems during 2005 part of the data was adjusted using the atmospheric

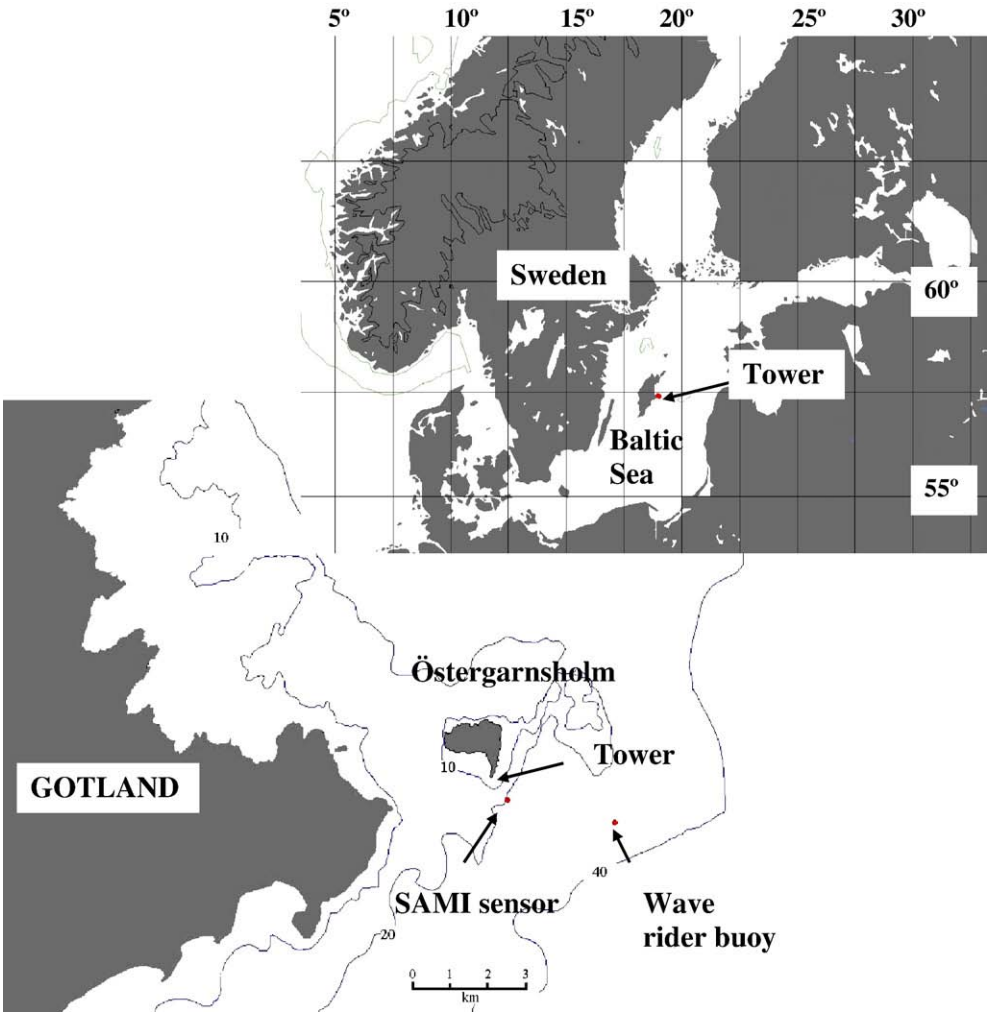

Fig. 1. The Baltic Sea and the Östergarnsholm field station. The positions of the tower, the SAMI sensor and the DWR (Waverider buoy) are shown by arrows in the lower figure.

measurements from the Polish Baltic Sea station (55°25′N, 17°04′E) run by Morski Instytut Rybacki. Air samples are collected weekly in glass flasks at 28 m above the sea level from ferry boats running between Gdynia, Poland and Karlskrona, Sweden and are a product of the NOAA, Global Monitoring Division (http://www.cmdl.noaa.gov). Measurements of three orthogonal high-frequency wind components are taken with SOLENT 1012R2 sonic anemometers at three levels (9, 16.5 and 25 m above the tower base). The coordinate system of the wind components is rotated so that the u-component is in the mean wind direction and v perpendicular to the mean wind for each half hour. The mean vertical wind, w, is assumed to be zero for about one month of data for each separate 20° sector in order to correct for any tilting of the boom. The humidity and CO_2 fluctuations are measured with a LICOR-7500 open-path analyser at 9 m above the tower base. Sea levels varies slightly, but the tower base is in general 1 ± 0.5 m above mean sea level.

2.1.2. Surface water pCO_2 and SST

In May 2005 we deployed a so called SAMI sensor (submersible autonomous moored instrument) at about 4 m depth, 1 km SE of the tower (see Fig. 1). The instrument is designed for continuous measurements of CO_2-partial pressure in the water. The SAMI gives measurements of pCO_2 and SST at an hourly temporal resolution. It has been used in several regions and is described in detail in (DeGrandpre et al., 1995, 1999, 2000).

The principle of operation of the SAMI sensor is based on the optical detection of pH changes in a buffer solution at equilibrium with seawater. CO_2 equilibrates with a buffer solution by diffusion through a gas permeable membrane. The buffer solution contains a fluorescing dye that is sensitive to changes in pH and thus reacts upon changes in the pCO_2. An optical device measures the fluorescence signal that is calibrated against the pCO_2. The SAMI sensor is calibrated prior to deployment and the measurement is checked for stability each 3.5 day. According to the manufacturer the accuracy is ±1 μatm and no drift at all for several months of measurements. The SAMI sensor also measures temperature at the depth of 4 m and with an accuracy of ±0.1 to 0.2 K.

Additional water temperature measurements are made from a Directional Waverider buoy (DWR) about 4.0 km SE of

Östergarnsholm. The DWR measures the water temperature at a depth of 0.5 m with an accuracy of ±0.2 K.

2.2. Ship data

The ship data used to compare with the field station and the SAMI sensor were collected on the cargo ship Finnpartner, which commutes regularly between the Mecklenburg Bight and the Gulf of Finland (Schneider et al., 2006). For the determination of the pCO_2, seawater was continuously supplied to a bubble-type equilibrator and air was pumped in a closed loop through the water in order to generate a CO_2 equilibrium that was achieved within 34 min. The CO_2 content in the air equilibrated with the surface water was determined by IR detection (LICOR CO_2 Analyzer 6262) and used to calculate the pCO_2. Additionally, the atmospheric CO_2 concentrations were determined once during each transect. The Finnpartner passes Gotland every second day either east or west of Gotland. Here we used the data from the eastern Gotland Sea when the ship was closest (23 km) to the Östergarnsholm field station.

3. Theory

3.1. Calculated fluxes

A two layer film model can be used for a flux equation, which is almost universally applied in estimates of air–sea fluxes of trace gases. The exchange of CO_2 between the sea and the atmosphere can be calculated from the air–sea difference in partial pressure of CO_2 at the surface and of the gas transfer velocity (k) using the equation (Wanninkhof, 1992; Donelan and Wanninkhof, 2002):

$$F = kK_0\Delta pCO_2 \tag{1}$$

where K_0 is the salinity and temperature dependent CO_2 solubility constant. K_0 is calculated using the empirical formulation from Weiss (1974). k is the transfer velocity of the exchange, $\Delta pCO_2 = pCO_2^a - pCO_2^w$ is the air–sea difference in partial pressure, where pCO_2^a and pCO_2^w are the values in the atmosphere and sea respectively.

The transfer velocity is considered to depend mainly on wind speed and on the Schmidt number. The Schmidt number (Sc) is the ratio of the kinematic viscosity of seawater to the diffusion coefficient of the considered gas. For wind speeds larger than 5 ms^{-1} Liss and Merlivat (1986) suggested that k is proportional to $Sc^{-1/2}$. Different functions which refer to Sc = 660 (CO_2 at 20 °C) have been proposed to describe k_{660} as a function of wind speed at a reference height of 10 m (U_{10}). Wanninkhof (1992) suggested a quadratic equation:

$$k_{660} = 0.31U_{10}^2 \tag{2}$$

which gives k for any other Sc by

$$k = 0.31U_{10}^2\sqrt{\frac{660}{Sc}} \tag{3}$$

A cubic dependence is given from Wanninkhof and McGillis (1999):

$$k = 0.0283U_{10}^3\sqrt{\frac{660}{Sc}} \tag{4}$$

a recent investigation from the Baltic Sea (Weiss et al., 2007) suggest a combination of quadratic and linear wind speed dependence.

$$k = \left(0.365U_{10}^2 + 0.46U_{10}\right)\sqrt{\frac{660}{Sc}} \tag{5}$$

3.2. Eddy-correlation fluxes

The CO_2 air–sea flux at the tower is directly measured with the eddy-correlation technique, a widely used technique for

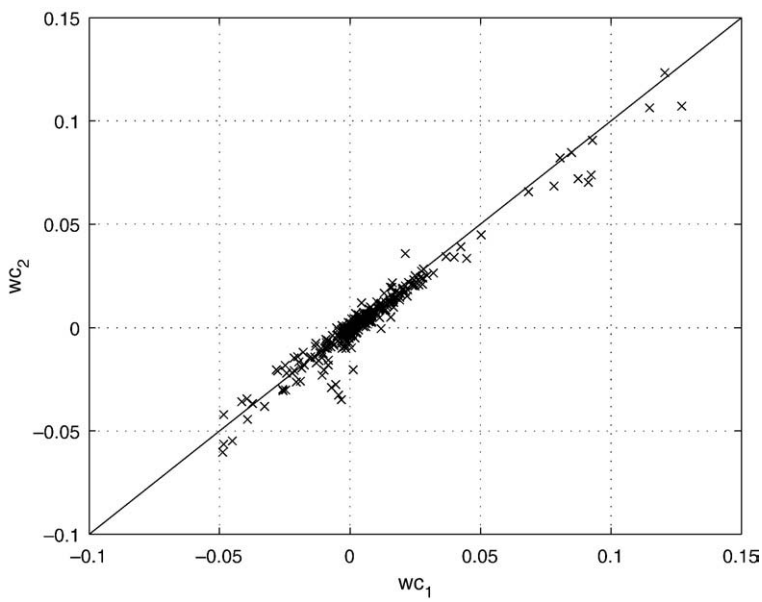

Fig. 2. Hourly values of the fluxes of CO_2 (in ppm ms^{-1}) using the two different instrument (crosses), solid line shows the 1:1 relation.

the exchange of momentum, heat and humidity. This is a method to directly measure the amount and direction of the flux of CO_2 between the sea and the atmosphere. The idea behind this technique is that high-frequency fluctuations (of the order of 10 to 20 Hz) of vertical wind and the measured parameter (in this case CO_2) are taken simultaneous and are correlated. Applying Reynolds decomposition on the product between the measurements of vertical velocity, w, and CO_2 concentration, c, the mass flux of CO_2 is:

$$F = \overline{w'c'} + \overline{w}\ \overline{c} \tag{6}$$

where overbars represent time averages and primes are deviations from the mean. The last term is usually neglected in eddy-correlation measurements since the mean vertical velocity is negligible. However, when measuring the flux of CO_2 this term need to be included since the difference in density between upward and downward moving air result in a non-negligible vertical velocity. This can be done for the calculated fluxes (Webb et al., 1980) or on the high-frequency fluctuations (Sahlée et al., 2008a). For the present data this term is included using the equation from Webb et al. (1980).

4. Results

4.1. Instrumental uncertainty in measurements

From Eq. (1) an estimate of the mean percentage uncertainty of k can be obtained:

$$\frac{\Delta k}{k} = \sqrt{\left(\frac{\Delta\,\overline{w'c'}}{\overline{w'c'}}\right)^2 + \left(\frac{-\Delta K_0}{K_0}\right)^2 + \left(\frac{-\Delta\left(p\mathrm{CO}_2^{\mathrm{a}} - p\mathrm{CO}_2^{\mathrm{w}}\right)}{\left(p\mathrm{CO}_2^{\mathrm{a}} - p\mathrm{CO}_2^{\mathrm{w}}\right)}\right)^2} \tag{7}$$

where Δ represents the mean relative instrumental uncertainty in the measurement. During April to June 2006, an additional LI-7500 was mounted on the 9 m level in the tower for comparative flux measurements. The two instruments were mounted with a spatial separation of 0.3 m, and the fluctuations correlated with vertical wind using the same sonic anemometer.

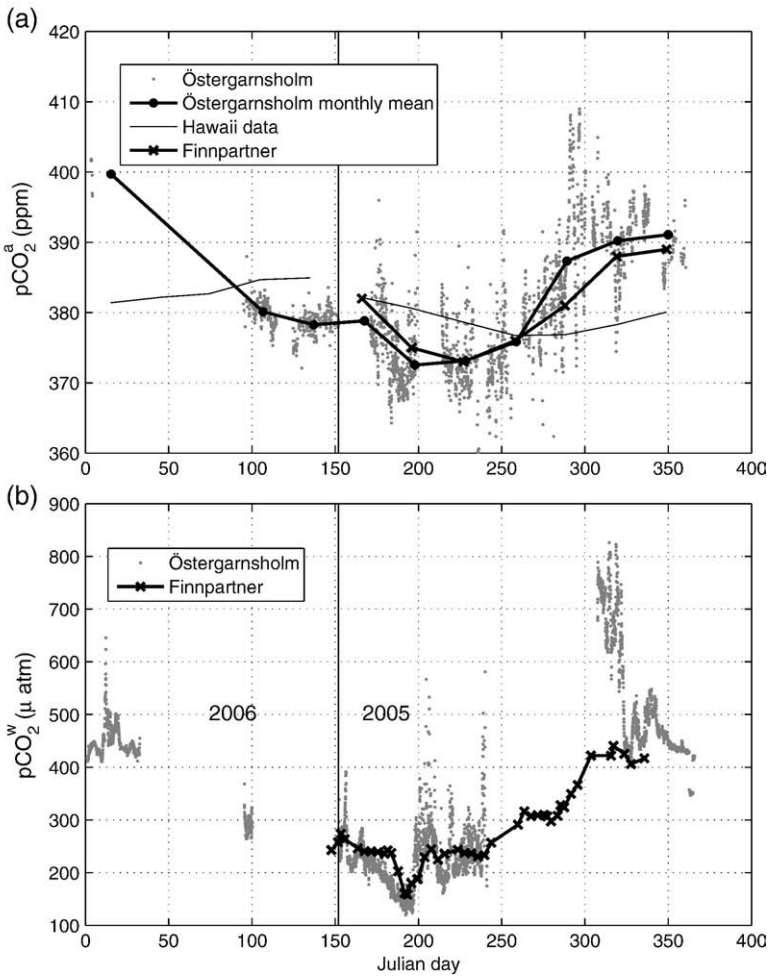

Fig. 3. In (a) the annual cycle of concentration of CO_2 in the atmosphere is shown, dots are measurements from Östergarnsholm, and solid line with dots the monthly mean values. Solid thin line represents the monthly mean values from the Hawaii data, dashed line is monthly mean value from the Finnpartner ship. In (b) the pCO_2 in the sea is shown where the dots are measurements from the Östergarnsholm site and solid line data from the Finnpartner ship. It should here be noted that the Julian day on the x-axis shows the annual cycle from January 1st to December 31st. The dates are thus not continuous since it covers the period June 2005 to May 2006.

The flux calculated from the two instruments is shown in Fig. 2. Based on the difference between the two instruments the uncertainty in the flux measurement (the first term on the right-hand side of Eq. (7)) was estimated to 17%. This is larger than the corresponding uncertainty of humidity flux from the same instrument (Sahlée et al., 2008b). The solubility is calculated from SST and salinity. Assuming that the SST is estimated with an accuracy of 0.2 K and the salinity within 0.5 Psu the second term on the right side is estimated to 1%. The absolute value of the difference (pCO_2^a–pCO_2^w) is of the order of 100 µatm. The SAMI sensor gives an accuracy of 1 µatm, the accuracy of the measured pCO_2 in the atmosphere is 3 µatm, the last term on the right-hand side is then estimated to 4% (neglecting situations when ΔpCO_2 approaches zero). By substituting these values into Eq. (7) the mean percentage uncertainty in the transfer velocity calculated from measurements is estimated to be slightly below 20%. The largest uncertainty is thus in the high-frequency CO_2 flux measurement. This estimated uncertainty reflects the instrumental errors and not potential methodological biases. It is also possible that errors in measured sensible heat fluxes influences through the Webb correction (Liu et al., 2006).

4.2. Annual cycle

Fig. 3a and b shows the annual cycle of the mean atmospheric CO_2 mixing ratio and pCO_2^w for the period June 1st 2005 to May 31st 2006. There is a large variability both in the sea and in the atmosphere. A strong seasonal cycle can be seen in both parameters, but superimposed is a large short-term variability. The atmospheric concentration is largest during winter (up to 410 ppm in the data shown here) and lowest in autumn (on occasions below 365 ppm). The seasonal amplitude is significantly greater than in the data from the station Mauna Loa, Hawaii. These data are often used when investigating the global trend in atmospheric CO_2-concentrations (Keeling and Whorf, 2005). The seasonal cycle is also shifted compared to the Hawaii data. The difference to the Hawaii data is not surprising since those data is from a significantly higher altitude and at different latitude. The Östergarnsholm data are more influenced by the regional seasonal cycle of the growth season on the northern hemisphere. There is also a certain disagreement between the monthly mean values from Östergarnsholm and the Finnpartner; this is due to the

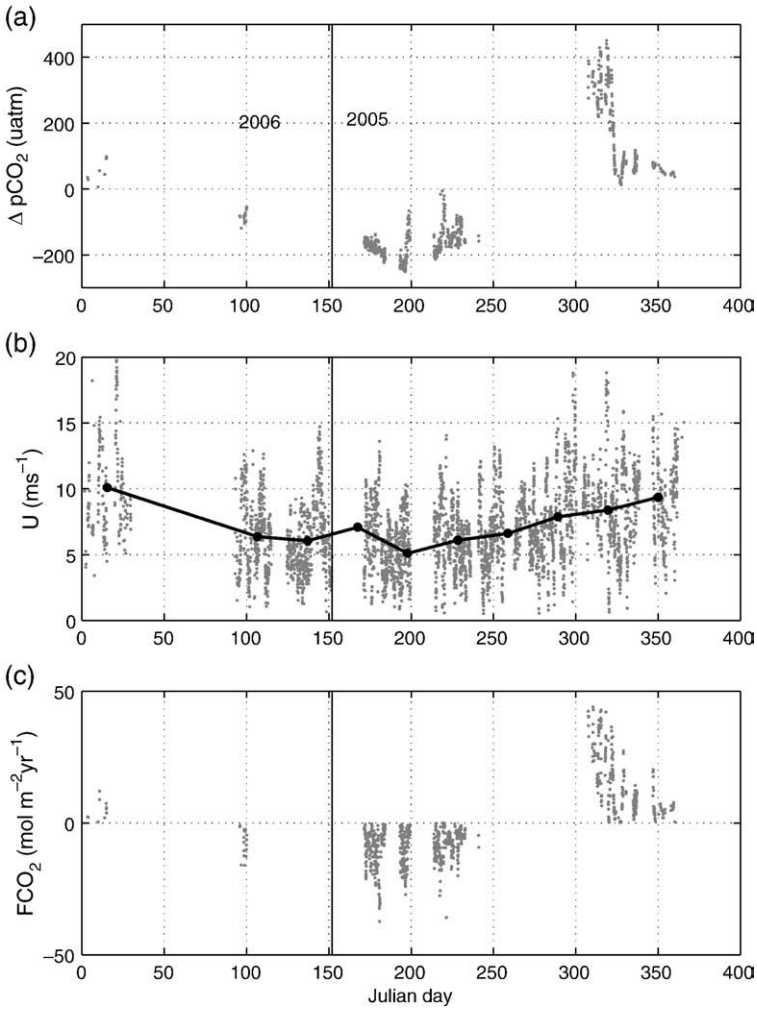

Fig. 4. The annual cycle of (a) ΔpCO_2, (b) wind speed measured at the Östergarnsholm site, dots show hourly values and line the monthly averages. (c) Show the flux calculated from Eqs. (1) and (3). All data represents the Östergarnsholm site, period is the same as Fig. 3.

extended periods missing in the data from Östergarnsholm making the monthly averages not representative of the monthly values.

The surface water pCO_2 shows a much greater seasonal variation, the SAMI sensor gives slightly over 100 µatm in June and over 800 µatm in November. The short-term variability measured by the SAMI sensor is surprisingly large. The agreement with the ship data from Finnpartner (solid line) is as good as can be expected considering the distance between the measurements. There is large difference in summer (Julian day about 180 to 190) where higher biological activity closer to the shore can be expected to give lower pCO_2^w in the Östergarnsholm data. In November (Julian day 300 to 325) the pCO_2^w measured at Östergarnsholm are very high (almost twice that measured at Finnpartner). This period is identified as part of an extended upwelling situation where colder water with high values of pCO_2^w reach the surface. Such upwelling events usually reach to some km horizontal distance from the coast and thus not to the position of the ship.

The annual cycle of the parameters used in calculation of the CO_2-flux are shown in Fig. 4a (air–sea difference in partial pressure) and Fig. 4b (wind speed). The flux of CO_2 across the interface calculated using Eq. (1) with Eq. (3) for the transfer velocity is shown in Fig. 4c. The difference in partial pressure is negative in April to August and positive in October to January resulting in a downward and an upward transport respectively. This result differs from Weiss et al. (2007) where the difference in partial pressure was dominantly negative and the flux of CO_2 were downward during the entire investigated year (with a few exceptions). The difference between these regions, Baltic Proper (this study) and the Arkona Basin (Weiss et al., 2007) is in agreement with Thomas and Schneider (1999) who found a large difference in the magnitude of the seasonal cycle between different regions of the Baltic Sea. Regions further to the North-east had larger seasonal amplitude than southern parts of the Baltic Proper. The wind speed in Fig. 4b is higher during fall and winter giving a higher transfer velocity and a more efficient exchange during these seasons.

4.3. Agreement with directly measured fluxes

Two separate periods of four weeks each were selected to investigate the accuracy of the flux calculations using directly measured fluxes. Period I (June 20 to July 17 2005) is shown in Figs. 5–8. This is a period with relatively low wind speeds (Fig. 5) and an air temperature increasing from 15 to 24° (Fig. 6). The atmospheric stratification is dominantly stable with occasional unstable situations. The flux of CO_2 calculated using Eq. (3) for the transfer velocity and directly measured is shown in Fig. 7. The calculated flux agree relatively well with the measured during a part of the period, but the agreement is very low during other parts. There are also significant periods where the measured and calculated fluxes have opposite directions. In Fig. 8, fluxes calculated using Eq. (3) for the transfer velocity are shown together with the measured fluxes for different wind directions (intervals defined in Section 2.1). A period with a larger horizontal temperature gradient (with SST difference, ΔSST, between DWR and SAMI sensor of more than 2°) has been separated from the other data (dots). The calculated fluxes do not agree very well with the measured during this situation.

For the data in the sector with wind directions between 80° and 160° and small ΔSST (stars), where the SAMI sensor is in the direction of the footprint area for the flux measurements, the agreement between measured and modelled data is good. For the wind directions from the sector 50° to 80° the measured flux tends to be larger (downward) than the calculated and for wind directions from the sector 160° to 220° the scatter is very large and includes periods where the measured and calculated

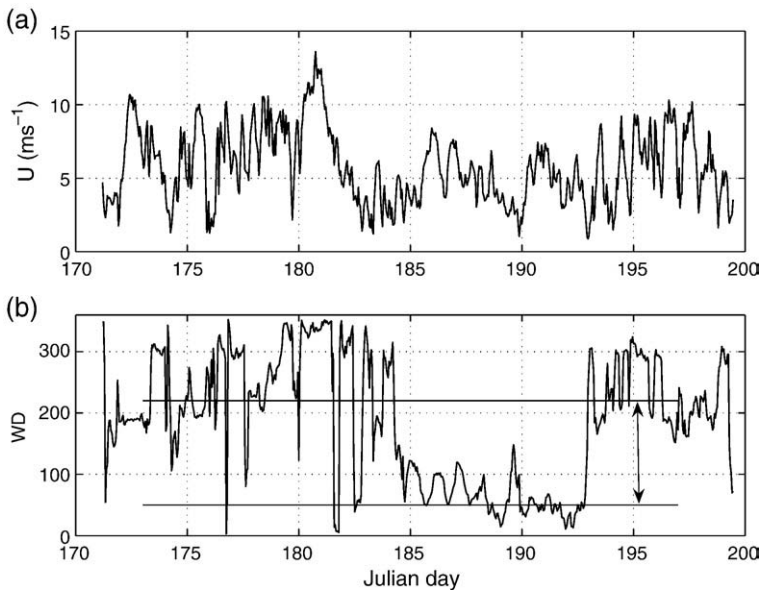

Fig. 5. Data from June 20 to July 17 2005 of (a) wind speed and (b) wind direction. Thin straight lines in (b) show the limitation wind directions in which the tower measurements represent sea conditions.

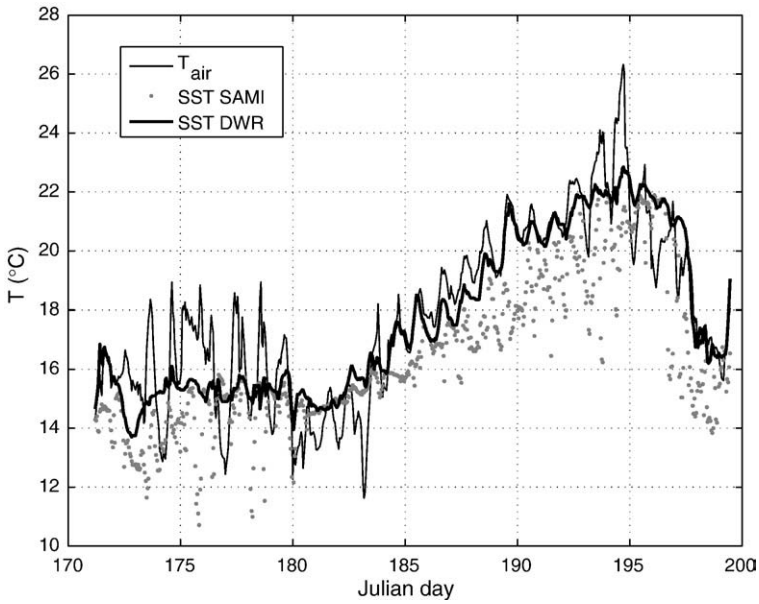

Fig. 6. Air temperature (thick solid line), water temperature at 4 m depth taken by the SAMI sensor (dots) and water temperature at 0.5 m depth taken by the DWR (thin solid line). Period as in Fig. 5.

flux has opposite directions. Assuming that Eq. (3) for the transfer velocity can be used to calculate the flux of CO_2 with relatively good accuracy the conclusion can only be that the pCO_2^w in the surface water do not represent the footprint area of the flux measurements in sectors 50° to 80° and 160° to 220°. It is most likely a significant horizontal variability of pCO_2^w in the surface layers of the sea during this time of the year, which could be explained by a large biological activity. This is also a period with mainly low wind speeds, which results in less efficient horizontal mixing in the sea and increasing the heterogeneity of the biological activity.

Period II (November 6 to December 4, 2005) is shown in Figs. 9–11. It is a period with much higher wind speed, up to almost 20 ms^{-1} (Fig. 9). Air temperature and SST can be seen in Fig. 10 and a relatively unusual situation (during late autumn) with a long period of stable stratification early in Period II. The measured and calculated flux of CO_2 for period II are shown in Fig. 11. There is fewer data during this period, but the agreement between measured and calculated fluxes is relatively good, regardless of wind direction (within the sector 50 to 220°).

For the calculated flux in Figs. 4, 7, 8 and 11, Eq. (3) is used to calculate the transfer coefficient (Wanninkhof, 1992). There

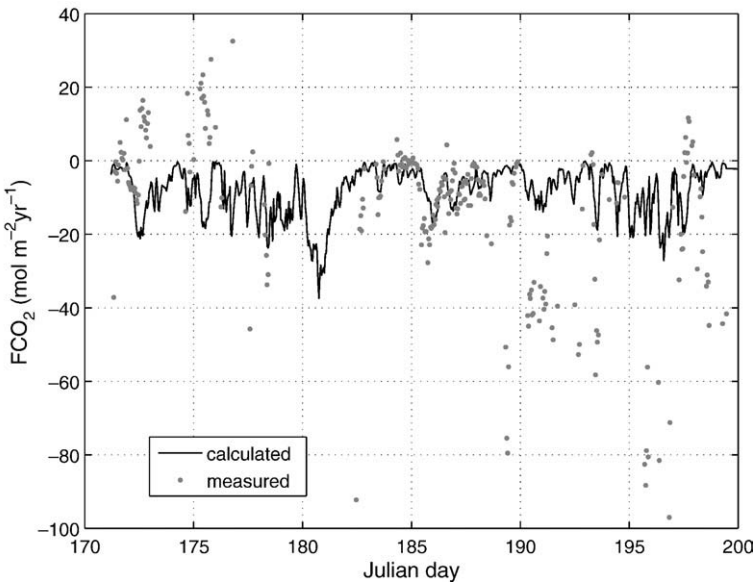

Fig. 7. Flux of CO_2 from eddy-correlation measurements (dots) and calculated by Eq. (3) (solid line). Period as in Fig. 5.

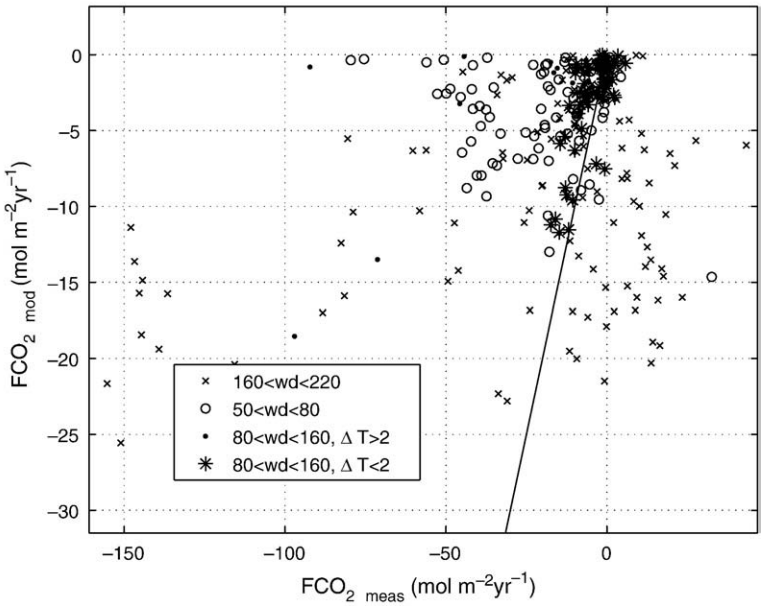

Fig. 8. Comparison by directly measured and calculated flux of CO_2 (using Eqs. (1) and (3)) for period I. Solid line shows the 1:1 relation. Different symbols represent different wind direction intervals, dots and stars show 80<WD<160 with ΔT>2 and <2 respectively. Period as in Fig. 5.

is presently no agreement within the scientific community on the relation between flux and wind speed, since most investigations show a significant scatter. Fig. 12 shows the transfer velocity estimated using measurement and calculated with Eqs. (3), (4) and (5) for different wind speeds. Table 1 shows the correlation coefficient and the mean difference (bias) between the transfer velocity calculated from measurements and calculated using Eqs. (3)–(5).

Table 1 and Fig. 12 show that the transfer velocity from measured data for these two periods agree the best with Eq. (5) (from Weiss et al. (2007)), mainly due to a better representation of the fluxes during higher wind speeds in Period II (November). Looking only at Period I, Eq. (4) (with a cubic wind speed dependence) agrees the best. The different agreement for the different seasons is an indication that also other processes acting differently on different seasons are of importance for the flux.

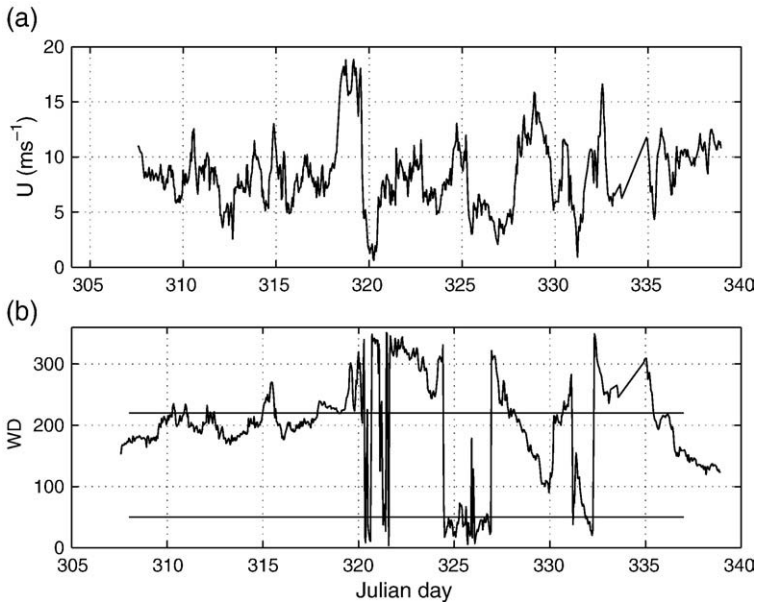

Fig. 9. Data from November 6 to December 4 2005 of (a) wind speed and (b) wind direction. Thin straight lines in (b) show the limitation wind directions in which the tower measurements represent sea conditions.

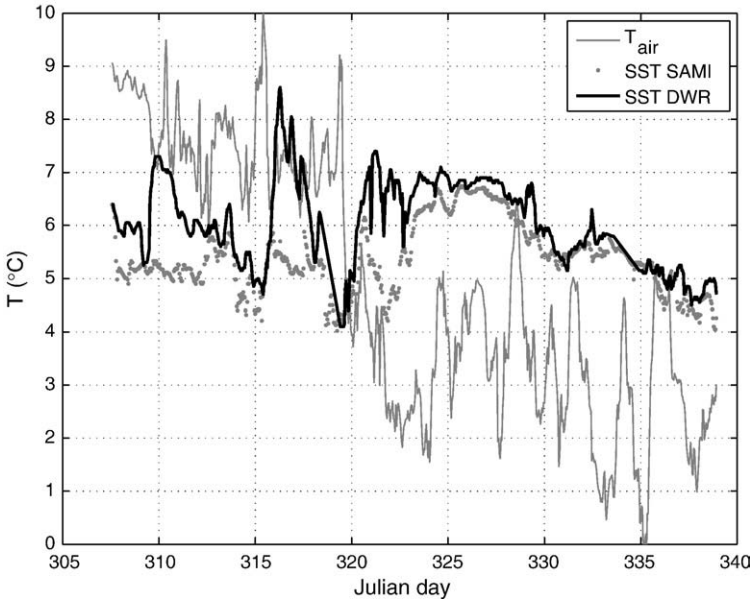

Fig. 10. Air temperature (thick solid line), water temperature at 4 m depth taken by the SAMI sensor (dots) and water temperature at 0.5 m depth taken by the DWR (thin solid line). Period as in Fig. 9.

4.4. Sensitivity of calculated fluxes to variability in the parameters

4.4.1. Partial pressure of CO_2 in the atmosphere and in the sea

Mean weekly fluxes are calculated for the two periods (Period I and Period II) using Eq. (1). Hourly mean values for partial pressure in the water, air and for the wind speed are used if nothing else is mentioned. In Fig. 13 calculated weekly fluxes are shown using Eq. (5), black bars represent calculated fluxes using hourly values of the partial pressures from the tower. For the grey bars a constant value of pCO_2^a of 380 µatm is used. Using a constant value of 380 µatm has a relatively small effect on the calculated fluxes, it gives an average overestimation of the absolute value of the calculated flux of 4% for the investigated data. Maximum weekly difference was 2.5 mol m^{-2} yr^{-1} in week 4 of period II, a period where the measured value of pCO_2 was 395 µatm. The calculated flux is

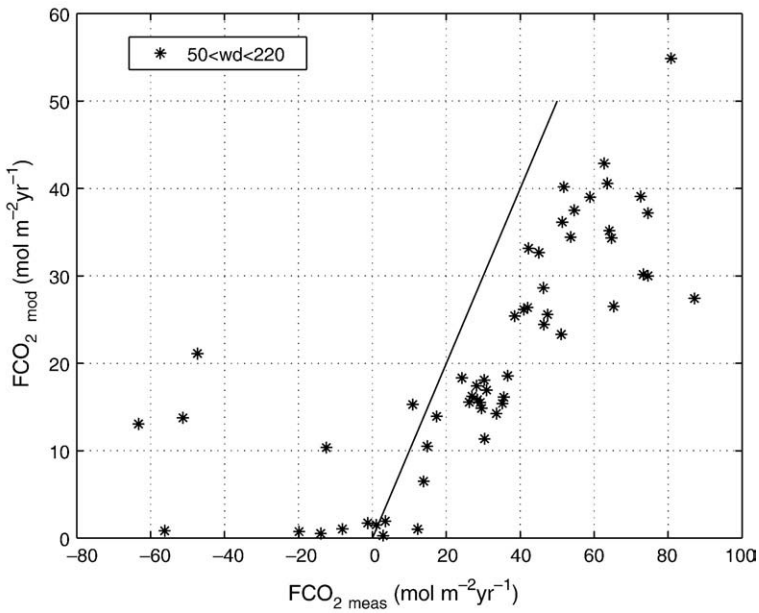

Fig. 11. Comparison by directly measured and calculated flux of CO_2 (using Eqs. (1) and (3)) for Period II. Solid line shows the 1:1 relation. Period as in Fig. 9.

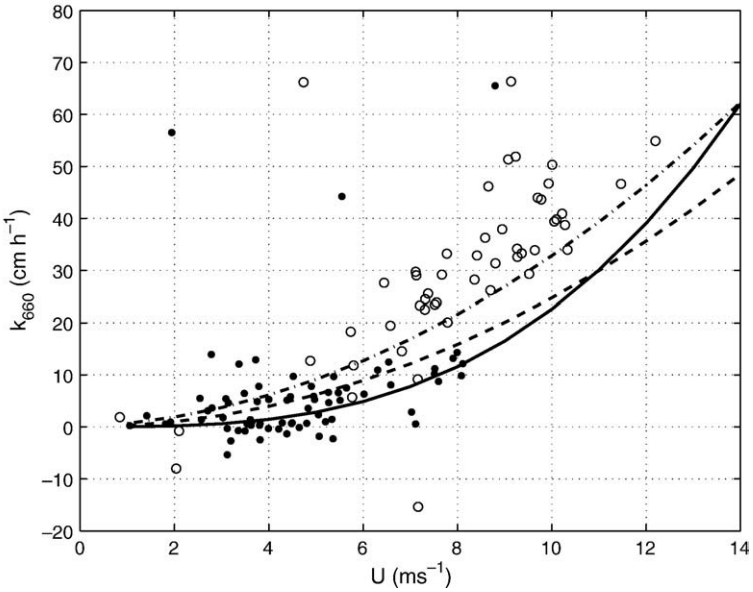

Fig. 12. Transfer velocity estimated from measurements (circles), where filled circles are from Period I and open circles from Period II. For Period I only data with wind directions between 80° and 160° are included. Calculated transfer velocities using Eq. (3) (dashed), Eq. (4) (solid) and Eq. (5) (dashed-dotted) respectively.

thus relatively insensitive to uncertainties in the atmospheric value of pCO_2^a, but a constant pCO_2^a would give a slightly too large seasonal cycle of the flux.

For the white bars in Fig. 13 the flux is calculated using pCO_2^w measured by the Finnpartner ships in the central part of the Baltic Proper. The results here shows slightly smaller downward flux in the summer when the coastal biology gives lower pCO_2^w and significantly smaller upward flux in winter when the near coastal values were significantly larger. It is clear that for period I, the pCO_2^w are relatively similar near the tower and in the central parts and thus the calculated flux agrees relatively well. For period II, where there was a strong upwelling, and the pCO_2^w measured in the central parts are significantly lower than the partial pressure near the coast the difference in the calculated fluxes are significant. One can thus conclude that it is of very large importance to use pCO_2^w representative for the investigated area — otherwise the calculated fluxes can be very misleading. Calculated fluxes for the central parts of the Baltic Proper are not necessarily representative for the near coastal region. For the periods investigated here, the magnitude of the fluxes is significantly larger in the coastal region than the central Baltic Proper.

4.4.2. Consequences of measuring at 4 m depth

The measurements of pCO_2^w from the SAMI sensor are taken at a depth of 4 m (in the case of the ship data at 3–4 m). However, the pCO_2^w controlling the exchange is the value at the surface. One generally assumes that the sea surface layer is well mixed and that the measured value from about 4 m represents the near surface value. To investigate the error introduced by using the measured value at 4 m as the surface value we would need vertical profiles of pCO_2^w, which we have no access to for the present period. We can study the variation in temperature between 0.5 m and 4 m. Fig. 6 shows the temperature from Period I measured by the SAMI sensor (at 4 m) and at the DWR. At the DWR the temperature is measured at 0.5 m depth, but at horizontal distance of 3 km from the SAMI sensor. From Fig. 6 it is interesting to note that the temperature at 0.5 m depth is several degrees higher during some periods and shows a pronounced diurnal cycle (following the air temperature). This feature is not seen at 4 m depth. This strong diurnal cycle is not typical for the data from this site, but the investigated period is in the middle of the summer, with strong insulation and low wind speed. The effect of a temperature increase at the surface on the gas exchange can be substantial. Since the pCO_2^w is increasing by about 4%K^{-1}, the ΔpCO_2 may strongly be affected and even change its sign. Additionally, the temperature dependency of the solubility constant has to be taken into account whereas the temperature effect on the transfer velocity (Schmidt number) is of minor importance.

Calculating the flux for the June period using temperatures from the DWR at 0.5 m depth decreases the flux with about 5% for period I. During a shorter period when the temperature difference is almost 5 °C the magnitude of the fluxes are decreased by over 20%. For the period II the two temperatures follows much more closely, with only short periods of differences up to 2 °C.

It can thus be concluded that the direct effects of vertical differences of the temperature in the sea surface layer on the air–sea fluxes are in general relatively minor compared to other uncertainties. This strong vertical variability of temperature could nevertheless be an significant factor. If this

Table 1
Statistics of the comparison between calculated transfer velocity and estimated from measurements

	r_0 (tot)	Bias (tot)	r_0 (Per I)	Bias (Per I)	r_0 (Per II)	Bias (Per II)
Eq. (3)	0.96	8.64	0.73	1.41	0.87	17.7
Eq. (4)	0.94	8.93	0.72	−1.28	0.84	21.8
Eq. (5)	0.96	6.45	0.73	4.04	0.87	9.5

The correlation coefficient (r_0) and mean difference (bias) are shown. Results are shown for all data (tot) and for Period I and II separately.

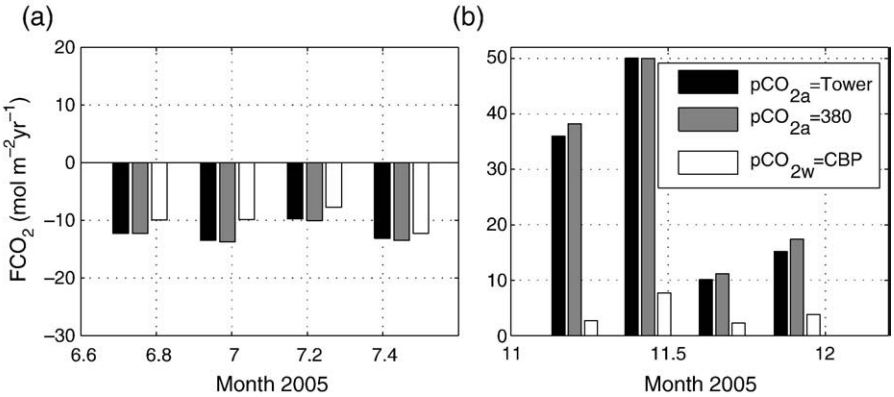

Fig. 13. Weekly mean fluxes for (a) Period I and (b) Period II. Eq. (5) is used to calculate the fluxes with constant values of pCO_2^a equal to 380 μatm (grey) and pCO_2^w measured by the Finnpartner ship (white). The Finnpartner ship data represents central Baltic Proper (CBP).

difference is an indication of inefficient vertical mixing, it could be an indication also of vertical variability of the biological activity. Since the biological activity influences the pCO_2^w an additional pCO_2^w gradient may be generated, which can have significantly larger importance for the exchange. Thermal skin layer effects may also be of importance for the air–sea exchange of CO_2 (Zülicke, 2005; Robertson and Watson, 1992).

4.4.3. Wind speed and transfer velocity

Three different formulations of transfer velocity (Eqs. (3)–(5)) are used to calculate weekly mean flux using hourly values of wind speed, Table 2. The calculated flux is very sensitive to the method of calculating the transfer velocity. In general Eq. (5) gives the highest absolute value of the calculated flux (which can also be seen from Fig. 12). On the average Eq. (5) gives 34% higher absolute value of the calculated flux than Eq. (3) and 40% higher than Eq. (4). For the week with the largest difference Eq. (5) gives 13.5 mol m^{-2} yr^{-1} larger flux than Eq. (4) and 11.5 mol m^{-2} yr^{-1} larger than using Eq. (3).

Weekly mean fluxes are also calculated using average weekly wind speeds. Using the weekly average winds gives 15 to 35% lower absolute value of the total calculated flux depending on the equation used. The difference is clearly largest for Eq. (4) where we have a cubic dependence on the wind speed and is also largest for the week with the highest wind speed (or rather the largest variability in the wind).

Table 2
Weekly mean fluxes (in mol $m^{-2}yr^{-1}$) for period I and II using three different equations for the transfer velocity (June week 1 to 4 and November week 1 to 4)

	June 1	June 2	June 3	June 4	Nov 1	Nov 2	Nov 3	Nov 4
Eq. (3)	−8.5	−10.0	−6.5	−9.0	27.0	38.5	7.5	11.5
Eq. (4)	−6.0	−8.0	−3.5	−6.5	22.5	48.0	6.5	13.0
Eq. (5)	−12.0	−13.5	−9.5	−13.0	36.0	50.0	10.0	15.0
Eq. (3)$\overline{u_{week}}$	−7.0	−8.3	−6.0	−7.0	26.0	27.5	5.0	10.5
Eq. (4)$\overline{u_{week}}$	−3.5	−5.0	−3.0	−3.5	20.5	22.0	3.5	10.5
Eq. (5)$\overline{u_{week}}$	−10.0	−12.0	−9.0	−10.0	35	37.5	7.5	13.5

For the first three rows hourly values of the wind speed is used and for the last three rows weekly mean wind speed is used.

5. Discussion

The greatest uncertainties when calculating the flux of CO_2 between the sea and the atmosphere originate from the uncertain description of the transfer velocity. In spite of a number of studies this is an uncertain parameter and should most likely be parameterized also by other factors than the wind speed. The second parameter of great importance is pCO_2^w. In a near coastal region, like the Östergarnsholm site, the representativity of the pCO_2^w is crucial when calculating the fluxes. The horizontal variability in the water can be significant and this is of great importance for the measured as well as calculated flux. For the measured flux it is important to know the pCO_2^w in the footprint area, when investigating the processes controlling the flux. The length of the footprint area depends on the atmospheric stratification, and the very large footprint area for stable stratification makes these situations more uncertain. The importance of horizontal variability is larger for CO_2 than when investigating other parameters. In Högström et al. (2008) it was concluded that the wave field represents open sea conditions in the sector 80<WD<210 and for the transfer coefficients of heat and humidity the sector 80<WD<220 have previously been used with good accuracy (Rutgersson et al., 2001; Sahlée et al., 2008b). When calculating CO_2 from the Östergarnsholm site the sector 80<WD<160 is to be used (at least during the biologically active season). It is likely that this great variability is mainly present during summer since it is probably caused by the different biological activity in the near coast and at further distances from the coast.

When calculating the flux of CO_2 one should remember that the calculated flux represents the area of the measured pCO_2^w. This has the implication that flux calculated in the central parts of the Baltic Sea, can be very different from the flux in the near coastal regions.

The vertical difference of temperature was here estimated to be up to 5°, this is an uncertain value since the difference can also be explained by horizontal variations. The vertical differences in temperature do, however, have a relatively small impact on the exchange of CO_2. A similar result was found in Ward et al. (2004), where the vertical difference in SST changed the flux with of the order of 4%. If the gradient in the

water temperature is an indication of a vertical gradient also in biological activity this could have a great impact on the exchange. Such a gradient could be due to different biological activity at 4 m depth and at the surface and low vertical mixing.

6. Summary and conclusions

The purpose of this study is mainly to investigate how we can use, and what we can learn from a land-based field station about the air–sea exchange of CO_2. A land-based field station, two oceanic buoys and data from the Finnpartner ship is used to investigate the variability of the air–sea CO_2-flux and parameters controlling the flux during one year. In addition the sensitivity to uncertainties in the parameters used when calculating the flux was investigated. The agreement between pCO_2^w measured near the tower and from the ships in the central parts of the Baltic Sea was relatively good during most of the period.

- It is shown that for the measured flux it is important to know the variability of pCO_2^w in the footprint area when investigating the processes influencing the flux. Horizontal variations can be large during the biologically active season.
- The instrumental uncertainty in calculations of the hourly values of transfer velocity was for the present data estimated to be of the order of 20%.
- For the present measurements the transfer velocity suggested by Weiss et al. (2007) gives the best agreement. This is mainly true for the autumn data. The data from summer shows better agreement with the cubic wind speed dependence of Wanninkhof and McGillis (1999).
- When calculating the air–sea flux of CO_2 the greatest uncertainty is in the determination of the transfer velocity.

A land-based system like the one described in this study can thus be used to investigate air–sea exchange of CO_2, with the advantage of giving parameters with a high temporal resolution. This is crucial when investigating the processes influencing the exchange. Features of particular importance in coastal regions (i.e. enhanced biological activity, upwelling, sea-breeze circulation) can accurately be described, even if this implies that the calculated flux is not representative for the flux outside the coastal region.

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