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TELLUS

Evidence from the Baltic Sea for an enhanced CO_2 air–sea transfer velocity

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ABSTRACT

Surface water total CO_2 concentrations (C_T) and the CO_2 partial pressure of the surface water and in the atmosphere were measured in the eastern Gotland Sea at approximately monthly intervals during five cruises in the winter of 1999/2000. Taking into account vertical/lateral exchange processes and the decomposition of organic matter, the monthly changes in C_T were used to determine CO_2 evasion fluxes. In addition, the CO_2 fluxes were calculated on the basis of the CO_2 partial pressure differences using local wind speed (u) records and different currently applied parametrizations of the gas exchange transfer velocity (k). The latter resulted in substantially lower monthly fluxes that indicated a considerable underestimation of k from the $k(u)$ functions used. To achieve an optimal agreement between the flux calculations and the balance-derived CO_2 fluxes, the coefficients of both a simple quadratic and cubic function $k(u)$ were iterated using a least-squares fitting procedure. The resulting equations, which refer to short-term wind data and to the CO_2 exchange at 20 °C, were $k = (0.45 \pm 0.10)u^2$ and $k = (0.037 \pm 0.008)u^3$ (k, cm h^{-1}; u, m s^{-1}). These yielded higher k values than most of the previously proposed parametrizations. Unfortunately, our data did not allow us to decide whether the quadratic or cubic function is more appropriate to describe the gas exchange dynamics.

1. Introduction

On the basis of the two-layer film model a flux equation was deduced which is easy to handle and almost universally applied in marine geochemistry to estimate air–sea fluxes of trace gases (Broecker and Peng, 1974; Liss and Slater, 1974). For air–sea CO_2 exchange, the flux can be calculated by the CO_2 partial pressure difference between the atmosphere and the ocean, ($\Delta pCO_2 = pCO_2^a - pCO_2^w$), and the gas transfer velocity, k:

$$F = k\ K_0\ \Delta pCO_2 \tag{1}$$

(K_0 is the CO_2 solubility constant)

The main resistance to the CO_2 transfer is caused by molecular diffusion through a laminar layer of water adjacent to the air–sea interface. The thickness of this layer controls k and depends largely on the wind speed. Empirical equations describe k (cm h^{-1}) as a function of wind speed (m s^{-1}). A variety of different parametrizations of $k(u)$ were proposed to calculate the CO_2 transfer velocity. Simple linear relationships were suggested by Smethie et al. (1985) and Tans et al. (1990), whereas Liss and Merlivat (1986) described $k(u)$ by three separate linear functions that each refer to different states of the sea surface. Functions including a quadratic term were proposed by Jacobs et al. (1999), Nightingale et al. (2000) and Wanninkhof (1992), and recently pure cubic functions have been considered (Schneider et al. 1999; Wanninkhof and McGillis, 1999). The use of these parametrizations led to k values that may differ by more than a factor of 2. These parametrizations also account for processes not included in the film model, such as breaking waves producing bubbles and sea spray. Other processes exist that affect the transfer velocity but are not controlled by wind speed. Among these are waves travelling faster than the wind (Smedman et al. 1999), the abundance of organic surface films (Frew, 1997) and the hydrostatic increase of the CO_2 partial pressure in bubbles (Keeling, 1993). However, these processes are not taken into account by the various parametrizations of k and are considered to be of secondary importance in view of the large uncertainties that still exist in describing k as a function of wind speed.

Bakker and Watson (2001) emphasized that more open ocean CO_2 flux measurements are needed to determine more precisely the relationship between the transfer velocity and wind speed. Our approach to determining CO_2 fluxes by field measurements was based on a CO_2 balance for the surface water of the eastern Gotland Sea (Fig. 1). The Gotland Sea in winter is an ideal area for such studies since the high winter pCO_2^w and the relatively shallow (70-m) mixing depth facilitate the detection of the CO_2

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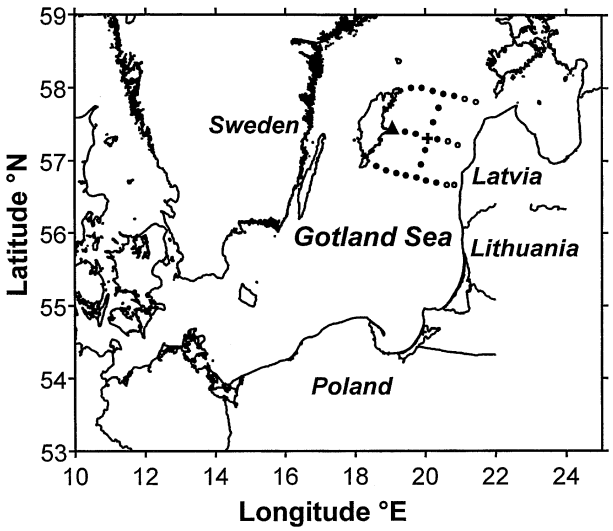

Fig. 1. The grid of stations (circles) around the "Gotland Deep" station (bold cross) in the eastern Gotland Sea (Baltic Sea), stations indicated by open circles exhibit water depths of less than 80 m, the wind measurements were performed on Östergarnsholm (triangle).

evasion flux by measuring the loss of total CO_2 (C_T) in the surface water. Moreover, low biological activity and reduced lateral water transport during winter did not bias the clearness of the gas exchange signal. In order to achieve progress concerning the parametrization of k, we then used measurements of ΔpCO_2 and wind speed to calculate the CO_2 fluxes according to eq. (1). For this purpose, existing functions $k(u)$ that refer to short-term wind data, were tested and modified for an optimal agreement with the CO_2 balance-derived fluxes.

2. Material and methods

2.1. Sampling and measurements

A grid of 26 stations covering an area of 22 000 km^2 was positioned in the eastern Gotland Sea (Baltic Sea) between the Island of Gotland (Sweden) and the Latvian coast (Fig. 1). The water depths were between 27 and 249 m. The measurements were performed during three campaigns with R/V 'A. v. Humboldt' (December 1999, January 2000, February 2000) and two campaigns with R/V 'Aranda' (Finnish Institute of Marine Research) in November 1999 and March 2000. The sampling required 2–3 d and was centred around 5 November 1999, 4 December 1999, 17 January 2000, 13 February 2000 and 16 March 2000. The temperature and salinity profiles were recorded at each station and four to six samples were taken at selected depths for chemical analyses by a conductivity–temperature–depth (CTD)-rosette system. Total inorganic carbon ($C_T = CO_2 + HCO_3^- + CO_3^{2-}$) was analysed on board using the coulometric SOMMA system (Johnson et al. 1993). Certified C_T reference material was used to calibrate the SOMMA (A. Dickson, Scripps Institution of Oceanography, USA). The analytical error of the C_T measurements was about 1–2 μmol kg^{-1} (about 0.1%).

For the analysis of particulate and dissolved organic carbon (POC, DOC), seawater was filtered immediately after sampling using cleaned Whatman GF-F filters. The filtrate was transferred into glass ampoules, which were flame sealed and filters were put into glass vials. The samples were stored deep frozen until analysis. DOC was analysed by high-temperature catalytic oxidation and subsequent infrared (IR) detection (Suzuki et al. 1992). The POC analysis was performed by an elemental analyser (type VARIO EL) after removal of inorganic carbon by acidification. The analytical uncertainty of the DOC determination was <1% c.v. and <5% c.v. for POC.

For continuous measurements of the surface water pCO_2, seawater was pumped from a depth of about 5 m. *In situ* temperature and salinity were recorded using a CTD system installed at the water inlet. A bubble-type equilibrator and a non-dispersive IR spectrometer (LI-6262) were used to determine the pCO_2^w and the atmospheric CO_2 content (Körtzinger et al. 1996). Calibration of the system was performed using ultra pure air with a certified CO_2 content (453.02 ppm; NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, CO). High-resolution (3-h) wind speed and atmospheric pressure data were obtained for the entire period of the study (November 1999–March 2000) from standard meteorological observations (Swedish Meteorological and Hydrological Institute) on the Island of Östergarnsholm, which is located close to the coast of the Island of Gotland (Fig. 1). The data did not show any systematic deviations from the ship's record during the cruises.

3. Results

3.1. Changes of total CO_2 during winter 1999/2000

Total CO_2 was determined in a dense station grid in order to account for the small-scale variability and to enhance the representativeness of mean values for the investigated area. To test the representativeness, we used the pCO_2^w measurements and compared the mean pCO_2^w that was obtained from the continuous record in the box area, with the mean calculated from pCO_2^w at the 26 stations. The difference of 5 μatm corresponds to a C_T difference of 0.7 μmol kg^{-1} and indicates that the 26 stations are a reasonable representation of the eastern Gotland Sea.

The lower box boundary for the C_T budget calculation was adjusted to 80 m since the salinity profiles recorded during the different cruises converged at this depth and thus indicated low vertical mixing. At seven stations the water depth was less than 80 m and, hence, the sediment surface represented the lower boundary. Since only about six samples were taken within the upper 80 m at each station, the C_T were interpolated between the corresponding depths in order to calculate the mean C_T. We

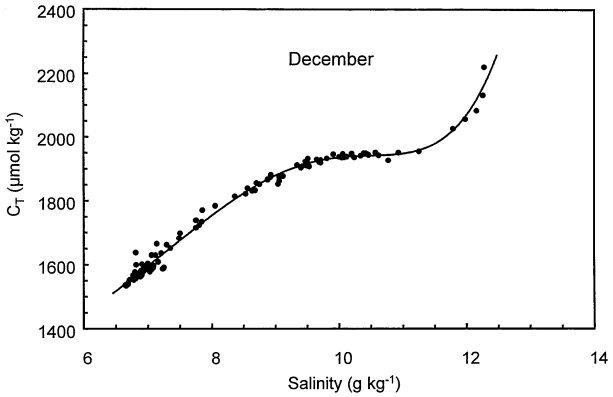

Fig. 2. Fifth-order polynomial fit (solid line) to the measured C_T/S data from December.

used the salinity as an interpolation tool because high-resolution (1-m intervals) salinity profiles were available from the CTD record and because distinct correlations existed between salinity and C_T during each cruise. A fifth-order polynomial was fitted to the pooled C_T/S data of each campaign and used to calculate quasi-continuous C_T profiles on the basis of the salinity profiles at each station. The quality of the fitting procedure is demonstrated by Fig. 2, which shows the December data and the corresponding fifth-order polynomial. In the following we also use C_T to describe the fitted vertical inorganic carbon distribution. The fitted C_T profiles for the December–March cruises at the central Gotland Sea station are presented in Fig. 3 and were used for the budget calculations. In December the mixed layer depth was about 60 m and the remnants of the summer stratification were still visible. During the following months, the erosion of the stratification continued and the mixed layer depth reached its maximum at the permanent halocline at about 75 m. During this process, CO_2-enriched water from the deeper layers of the surface box was transported into the mixed layer. However, this effect was not reflected by a corresponding increase of the mixed layer C_T because of the concurrent CO_2 loss by gas exchange.

To obtain a mean box C_T for the individual measurement campaigns, the 1-m C_T data from all 26 stations were added and divided by the sum of the box depths at the individual stations (Table 1). The C_T loss during December–January ($\Delta C_T^{bal} = -19.4$ μmol kg^{-1}) and January–February ($\Delta C_T^{bal} = -13.0$ μmol kg^{-1}) was considerable, whereas a slight increase ($\Delta C_T^{bal} = 1.2$ μmol kg^{-1}) was calculated for February–March. The data for the November–December period were not used for the budget calculations because the lateral C_T transport masked the effect of the CO_2 gas exchange (see the next paragraph). The uncertainty of the mean C_T was obtained from the standard deviation of C_T with respect to the C_T/S polynomial divided by the square root of the number of measurements.

3.2. *Vertical and Lateral C_T transport*

To derive CO_2 fluxes from the C_T changes, the effect of diapycnal mixing at the lower box boundary and of lateral water exchange must be taken into account. For the estimate of the C_T input by diapycnal mixing, we first determined the salinity flux, F_S, because the high-resolution salinity data allowed the precise determination of the gradient at the lower box boundary:

$$F_S = K_v \rho \Delta S/\Delta z. \quad (2)$$

A diapycnal mixing coefficient of $K_v = 0.46$ m^2 d^{-1} was used, which was estimated by Lass et al. (2003) for the below-halocline water in the Gotland Sea. The mean salinity gradients, $\Delta S/\Delta z$, during the measurement campaigns varied between 0.07 and 0.10 g kg^{-1} m^{-1} and were converted to a salt concentration gradient by multiplication by the density (ρ). The salt flux F_S varied between 33 and 50 g m^{-2} d^{-1} and was then used to determine the diapycnal C_T flux, which in analogy to eq. (2) is given by

$$F_{CT} = K_v \rho \Delta C_T/\Delta z. \quad (3)$$

Dividing eq. (3) by eq. (2) yields eq. (4)

$$F_{CT} = F_s \Delta C_T/\Delta S \quad (4)$$

Table 1. Inorganic carbon budget of eastern Gotland Sea surface water (0–80 m) during winter 1999/2000; using profiles of fitted inorganic carbon concentrations, mean C_T and the changes between the campaigns were calculated (ΔC_T^{bal}); these values were corrected for lateral and vertical C_T transport traced by salinity (S), and the internal supply of C_T was estimated from changes in total organic carbon (ΔC_T^{min}); the resulting changes of C_T ($\Delta C_T^{air-sea}$) were attributed to CO_2 gas exchange

Date	S	ΔS^{vert}	ΔS^{lat}	C_T	ΔC_T^{bal}	ΔC_T^{vert}	ΔC_T^{lat}	ΔC_T^{min}	$\Delta C_T^{air-sea}$
	g kg^{-1}			μmol kg^{-1}					
4 Dec 1999	7.285			1633.2 ± 1.4					
		0.016	0.015		−19.4 ± 1.8	0.9 ± 1.0	2.5 ± 2.0	3.3 ± 2.3	−26.1 ± 3.7
17 Jan 2000	7.316			1613.8 ± 1.1					
		0.012	−0.011		−13.0 ± 1.4	0.9 ± 0.9	−1.8 ± 2.0	2.0 ± 2.3	−14.1 ± 3.5
13 Feb 2000	7.317			1600.8 ± 0.9					
		0.012	0.013		1.2 ± 1.8	1.3 ± 1.5	2.1 ± 2.0	2.4 ± 2.3	−4.6 ± 3.8
16 Mar 2000	7.342			1602.0 ± 1.6					

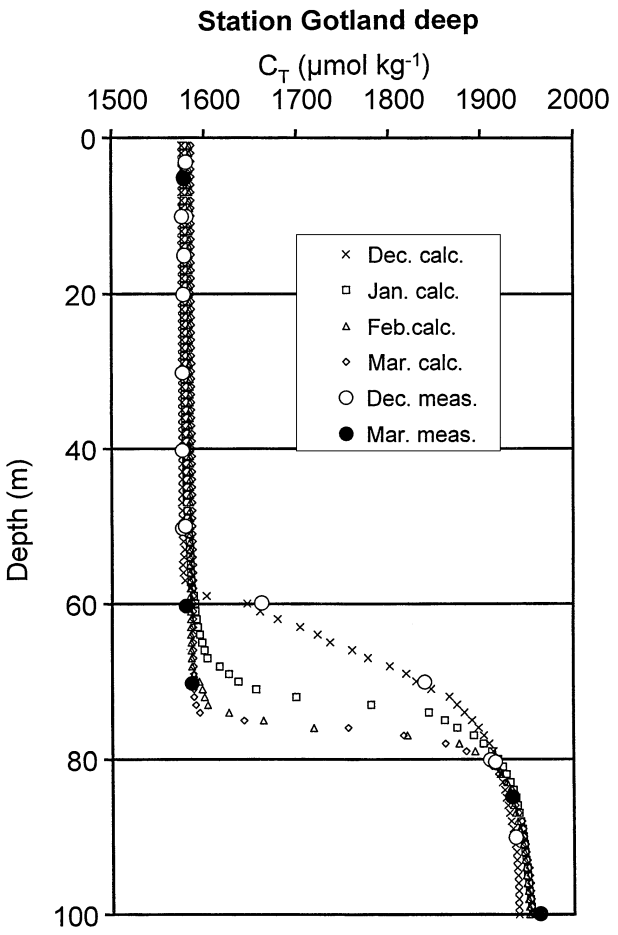

Fig. 3. Calculated C_T profiles at the Gotland deep station (bold cross in the map) for December to March based on salinity data resolved in metre steps and C_T–S relations; for clarity the measured data are given for December (circles) and March (solid circles) only.

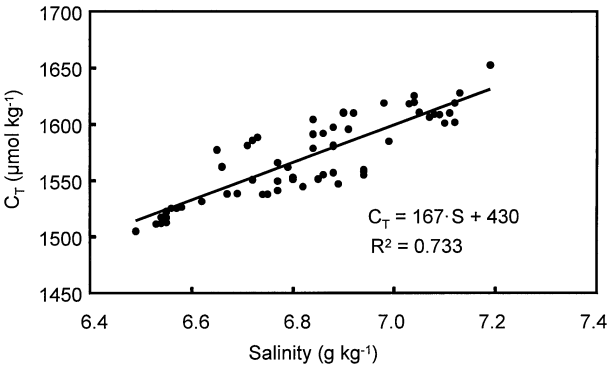

Fig. 4. Relation between total inorganic carbon (C_T) and salinity for surface water.

which allows the calculation of F_{CT} on the basis of F_S and of the corresponding $\Delta C_T/\Delta S$, which were obtained by determining the slope of the fifth-order function $C_T(S)$ at 80-m depth. The results are presented in Table 1 as concentration changes (ΔC_T^{vert}) and indicate that the contribution of the diapycnal mixing to the C_T budget was almost negligible during December–January and January–February, but was substantial for the February–March period.

To determine the lateral exchange of C_T, we first considered the salinity changes between the measurement campaigns (ΔS), which were attributed to the diapycnal mixing at the lower box boundary (ΔS^{vert}) and the lateral water exchange (ΔS^{lat}): $\Delta S = \Delta S^{lat} + \Delta S^{vert}$. The mean box salinities (Table 1) and its changes were calculated from the 1-m CTD records for each campaign, whereas the ΔS^{vert} (Table 1) were obtained from the diapycnal salt fluxes. The resulting ΔS^{lat} (Table 1) showed varying signs. This indicates that wind-driven varying currents controlled the water exchange and that the freshwater input by rivers was reduced by ice formation in the adjacent watershed area (HELCOM, 1986). To derive the lateral C_T transport, the November cruise data was used. During November a distinct thermocline still existed at 40–50 m and widely isolated the surface mixed layer from deeper water layers. Hence, the effect of lateral water transport on salinity and C_T was confined to the surface layer and not superimposed by the diapycnal mixing. Therefore, the ($\Delta C_T/\Delta S$) relationship for the November mixed layer (Fig. 4) was considered to characterize the coupling of salinity changes and C_T changes in laterally transported water masses. Hence, the slope of the regression line in Fig. 4 ($\Delta C_T/\Delta S = 167\ \mu mol\ kg^{-1}$) was used to estimate ΔC_T^{lat} by multiplication with ΔS^{lat}. The results (Table 1) show that the effect of the lateral C_T transport exceeded that of the diapycnal mixing, but was still in the range of uncertainty of the ΔC_T^{bal}. The error given in Table 1 for ΔC_T^{vert} and ΔC_T^{lat} was derived from the uncertainty of the mixing coefficient which was estimated to be about a factor of 2. For November–December ΔS^{lat} was 0.1, yielding a ΔC_T^{lat} that was about seven times higher than during the following periods and which was the largest contribution to the C_T budget. Consequently, an unacceptable uncertainty was introduced to the C_T budget and data from this period were excluded from the calculations of the CO_2 gas exchange.

3.3. *Mineralization of organic matter*

Mean DOC and POC profiles were determined for each campaign and used to calculate the mean box total organic carbon concentrations (TOC). The TOC which on average was composed of 98% DOC and 2% POC, showed a high variability within the box area with mean values (±1 standard deviation) for December–March of 332.0 (±13.5), 321.7 (±10.4), 328.7 (±17.6) and 322.1 (±13.9) $\mu mol\ kg^{-1}$. The standard error which entered the error calculation was about one order of magnitude less due to relatively large number of samples (n was between about 60 and 100 for each POC and DOC data set). Since DOC

production is linked to primary production and the POC values were nearly constant on a low level (9.9, 5.5, 6.7, 7.4 μmol kg^{-1}), significant DOC production, i.e. 321.7–328.7 μmol kg^{-1} during December–January was unlikely. Hence, a linear trend function was fitted to the TOC averages yielding a TOC decrease of about 2–3 μmol kg^{-1} between the individual campaigns. The decreasing trend of DOC from December to March is confirmed by a 7-yr monitoring data set for the Gotland Sea (Leinweber, 2002). This TOC loss was considered to be equivalent to the C_T production by mineralization (ΔC_T^{min}, Table 1) of organic matter. Mineralization at the sediment surface at the shallow stations was neglected because the sediments consisted mainly of sands which do not accumulate organic matter (Emelyanov, 2001). The effect of sinking particles on the TOC inventory was ignored since sediment trap data from the central grid station showed that the POC export was negligible. The POC export accounted for a mean carbon loss in the upper 80 m of the water column of less than 0.6 μmol kg^{-1} during the period of our study (Wasmund et al. 2001, 2002).

3.4. *Calculation of the CO_2 air–sea flux*

The balanced changes in C_T must be caused by lateral/vertical transport, the mineralization of organic matter and the air–sea exchange:

$$\Delta C_T^{bal} = \Delta C_T^{lat} + \Delta C_T^{vert} + \Delta C_T^{min} + \Delta C_T^{air\text{–}sea}. \quad (5)$$

Eq. (5) allows the calculation of the air–sea exchange term, $\Delta C_T^{air-sea}$, since all other terms were determined on the basis of our measurements (Table 1). The C_T balance yielded a C_T decrease by air–sea exchange of 26.1 μmol kg^{-1} for December–January, 14.1 μmol kg^{-1} for January–February, and 4.6 μmol kg^{-1} for February–March. Relating these values to the mean box depth (70.3 m), the air–sea fluxes are obtained for the three time intervals: −41.5, −37.1 and −10.1 mmol m^{-2} d^{-1} (Fig. 5). The relative uncertainty of the air–sea exchange estimates was acceptable for the December–January and the January–February periods (14% and 25%, respectively), but was markedly higher with regard to the February–March interval (83%).

3.5. *Estimating the CO_2 fluxes using the ΔpCO_2 and the transfer velocity*

An attempt was made to reproduce the budget derived CO_2 fluxes on the basis of eq. (1) using the measured ΔpCO_2 (Fig. 6a) and existing parametrizations of the transfer velocity, k. In addition to the traditional Liss and Merlivat (1986) equations, we applied the quadratic (eq. 6) and the cubic (eq. 7) formulations for the dependence of k on short-term wind speed (u) proposed by Wanninkhof (1992) and Wanninkhof and McGillis (1999),

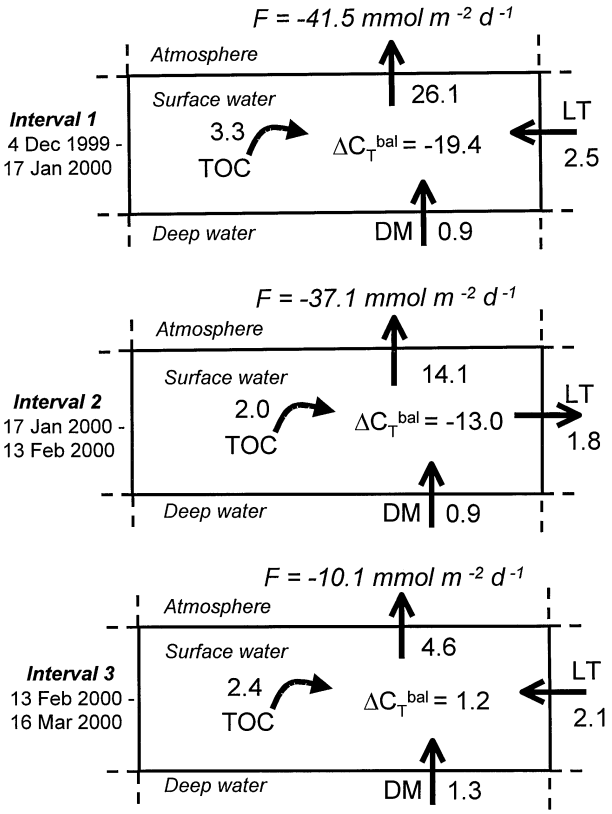

Fig. 5. Changes in total inorganic carbon (ΔC_T^{bal}) in the surface water box during three intervals between 4 December 1999 and 16 March 2000, which were caused by lateral transport (LT), diapycnal mixing (DM), remineralization and, most important by the CO_2 gas exchange across the sea surface (in μmol kg^{-1}); the average air–sea flux (F) for each interval is given in italics.

respectively.

$$k = 0.31u^2(Sc/660)^{-1/2} \quad (6)$$

$$k = 0.028u^3(Sc/660)^{-1/2}. \quad (7)$$

The calculation of k was performed for 3-h time steps using the wind speed data from the coastal station on the Island of Gotland (Fig. 6b). The Schmidt numbers, Sc, were determined according to an algorithm proposed by Wanninkhof, (1992) using 3-h sea surface temperatures, SST, and salinities, S, that were obtained by linear interpolation of the corresponding mean during each cruise (Table 2).

For the flux estimates (eq. 1) we calculated 3-h pCO_2^w values by linear interpolation of the mean pCO_2^w that were determined for each cruise (Table 2). The pCO_2^a was obtained from the mean of the CO_2 mole fraction in dry air for all cruises (377.2 ± 3.2 ppm) and multiplication by the 3-h atmospheric pressure that was reduced by the water vapour saturation pressure. Linear interpolation was also applied to calculate the solubility constants

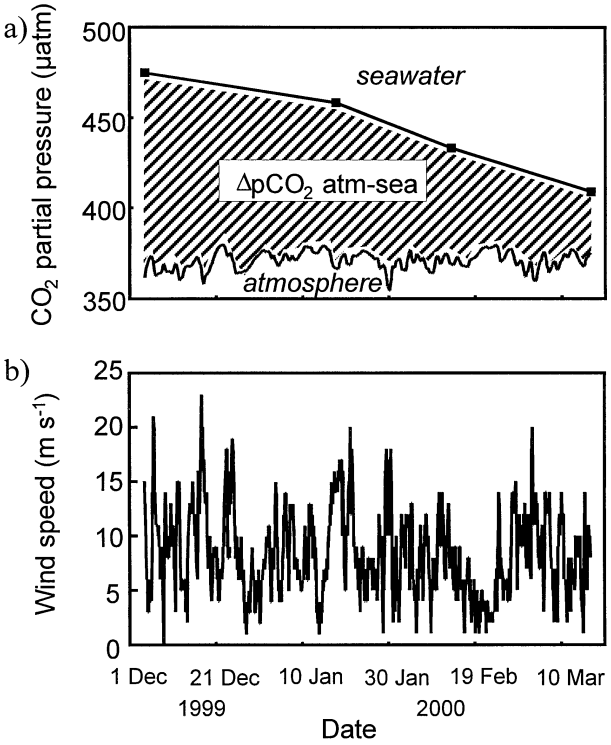

Fig. 6. (a) Average measured partial pressure of CO_2 in the surface water (about 5% c.v.) for four campaigns, which have been interpolated (top solid line); pCO_2-atmosphere was calculated from the mean molar ratio of CO_2 in the atmosphere (377.2 ± 3.2 μmol mol^{-1}) at atmospheric pressure; ΔpCO_2 is shown by hatching. (b) Wind speed at 3 h intervals from Östergarnsholm (SMHI).

Table 2. Mean grid surface water salinity, temperature, and CO_2 partial pressure measured in water of 5 m depth

Date	S g kg^{-1}	T °C	pCO_2^w μatm
4 Dec 1999	6.59	6.43	474.7
17 Jan 2000	7.08	4.01	458.2
13 Feb 2000	7.17	3.18	433.1
16 Mar 2000	7.26	2.69	408.9

K_0 (Weiss, 1974) from the SST and S for each time step. The resulting 3-h CO_2 fluxes were added up for the periods between the measurements and compared with the budget derived fluxes. Figure 7 shows that the application of the Liss–Merlivat equations yielded calculated CO_2 fluxes that were by a factor of 2–3 below the balanced flux. The discrepancies were less drastic and confined to December/January and January/February intervals when using the Wanninkhof (1992) quadratic (eq. 6) and the cubic function $k(u)$ (eq. 7 of Wanninkhof and McGillis, 1999). Nevertheless, the differences (30%–50%) indicated that these parametrizations also considerably underestimate the air–sea gas exchange rates derived in this study. This conclusion was not

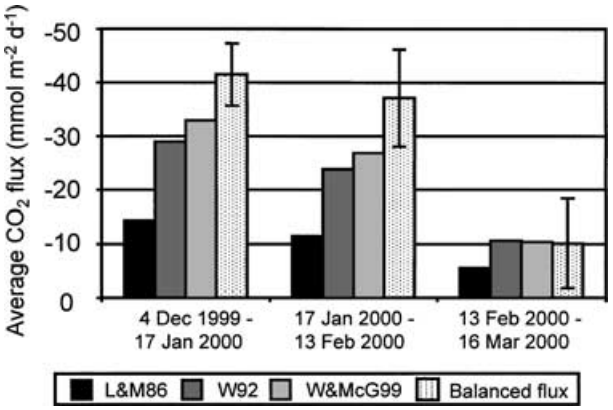

Fig. 7. Comparison of balanced fluxes with predicted fluxes; the balanced loss of inorganic carbon from Gotland Sea surface water (±standard error) and the calculated fluxes using selected parametrizations from the literature are compared: Liss and Merlivat (L&M86), Wanninkhof (W92), and Wanninkhof and McGillis (W&McG99).

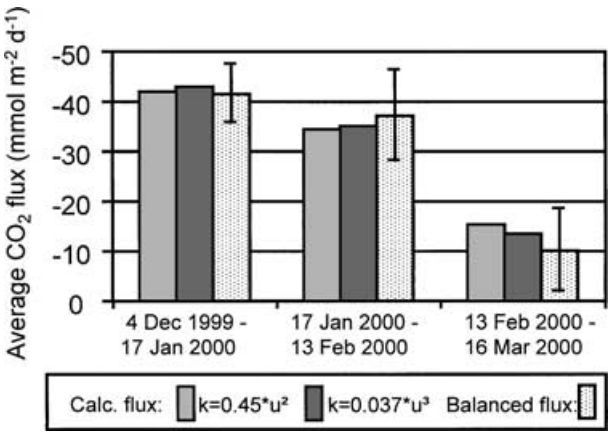

Fig. 8. Comparison of the balanced fluxes with predicted fluxes; significantly improved reproduction of the balanced flux (± standard error) with the new quadratic and cubic parametrizations of this study for the first and the second interval.

supported by the February–March data. However, during this period the decreasing ΔpCO_2 and lower wind speed (an average of 7.3 m s^{-1} in comparison to 8.8 m s^{-1} for December–January and 9.0 m s^{-1} for January–February) reduced the air–sea exchange and consequently increased the relative uncertainty (82%) of the budget-derived flux.

We then examined how the coefficients in the quadratic and cubic functions (eqs. 6 and 7) must be modified in order to achieve an optimal agreement between the calculated and the experimentally derived CO_2 fluxes. A least-squares fit was applied and yielded 0.45 ± 0.10 and 0.037 ± 0.008 for the quadratic and cubic function, respectively. Figure 8 indicates the improved reproduction of the balanced fluxes, but also shows that the quality of the quadratic and the cubic fit did not differ significantly.

4. Discussion and conclusions

The presently favoured parametrizations of the transfer velocity are based on a quadratic dependence of k on wind speed. However, it was shown that neither Wanninkhof's quadratic function for short-term wind speeds (Wanninkhof, 1992) nor the Liss and Merlivat (1986) equations, which may be approximated by a quadratic function, yielded CO_2 fluxes consistent with our CO_2 balance (Fig. 7). The discrepancy between these parametrizations and the quadratic function that was obtained from our data is demonstrated by a plot of the corresponding functions $k(u)$. Figure 9 shows that our quadratic function deviates from Liss and Merlivat (1986) and Wanninkhof's (1992) curves. Differences were also found when applying recent quadratic approaches proposed by Jacobs et al. (1999) and Nightingale et al. (2000). One may speculate that regional differences in wind/wave interaction may have led to higher transfer velocities in the eastern Gotland Sea. However, these effects are difficult to quantify and it appears that the main reason for the conflicting parametrizations are the different methodologies that were applied to derive functions $k(u)$ for short-term wind speeds. Recently, a carbon budget approach of a traced water parcel was performed during Gas Ex-98 (Feely et al. 2001). Changes of inorganic carbon concentration in surface water due to CO_2 gas exchange were consistent with current gas exchange parametrizations within the range of uncertainty. The error involved in this estimate was higher in comparison with our study due to a larger impact of biology and mixing on the inorganic carbon concentration.

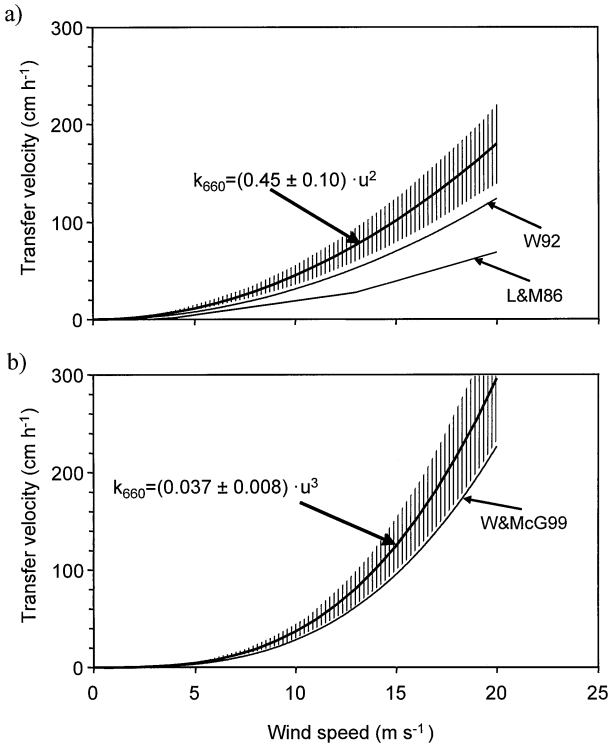

Fig. 9. Parameterizations of the transfer velocity (k) as a function of wind speed (u) of this study are compared with parametrizations from the literature, hatches showing the standard error; (a) $k(u^2)$, Liss and Merlivat (1986, L&M86) and Wanninkhof (1992, W92); (b) $k(u^3)$ and Wanninkhof and McGillis (1999, W&McG99).

Direct information concerning the relationship between short-term wind speed and k may be obtained from eddy covariance measurements. This method has been applied by Jacobs et al. (1999) and McGillis et al. (2001) and yielded a quadratic and a cubic function, respectively. However, CO_2 covariance measurements at sea are a methodological challenge and the data published so far still contain considerable uncertainty (Jacobs et al. 1999; McGillis et al. 2001). Our data did not indicate whether the quadratic or the cubic approach is more appropriate to describing the gas exchange dynamics at the sea surface. However, previous preliminary investigations of the annual carbon budget in the Baltic proper indicated a cubic dependence with a coefficient (0.045) that was about 20% higher than that obtained from our study (Schneider et al. 1999). Moreover, a summer carbon budget aimed at estimating biological production rates and including the CO_2 air–sea exchange, required a cubic relationship in order to approximately obtain consistency with the availability of nutrients (Schneider et al. 2003). The use of our quadratic parametrization yielded CO_2 fluxes into the sea during the low-wind summer period that were clearly too high to be balanced by primary production rates. Regarding our studies, we therefore prefer a cubic function with a clearly steeper dependence on wind speed than that proposed by (Wanninkhof and McGillis, 1999; Fig. 9b).

We applied both our quadratic and cubic $k(u)$ to establish a global ocean/atmosphere CO_2 balance using the ΔpCO_2 data base compiled by Takahashi et al. (2002) and presented with a monthly resolution on a 4°(latitude) × 5°(longitude) grid for the year 1995. Weibull parameters of monthly wind speed distributions based on actual measurements were used, given for the global ocean in 5° latitudinal bands for each the Atlantic Ocean, the Indian Ocean, the west and the east Pacific Ocean for the year 1983 (Pavia and O'Brien, 1986). Since these data were confined to 60°N–50°S, data for the remaining ocean areas (16%) were taken from the adjacent latitudinal bands. By the use of regionally and monthly differentiated wind speed distributions we accounted for the effect of potential covariation of wind speed and ΔpCO_2 and thus reduced the risk of introducing a bias into the flux calculations in this respect. The resulting global CO_2 balance revealed an excess (anthropogenic) CO_2 uptake by the ocean of 1.8 ± 0.4 Pg-C yr^{-1} for the quadratic and 2.0 $\pm$ 0.4 Pg-C yr^{-1} for the cubic approach which are both within the range of model-based estimates.

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