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Variability of the Gas Transfer Velocity of CO_2 in a Macrotidal Estuary (the Scheldt)

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ABSTRACT: We report a large set of 295 interfacial carbon dioxide (CO_2) flux measurements obtained in the Scheldt estuary in November 2002 and April 2003, using the floating chamber method. From concomitant measurements of the air-water CO_2 gradient, we computed the gas transfer velocity of CO_2. The gas transfer velocity is well correlated to wind speed and a simple linear regression function gives the most consistent fit to the data. Based on water current measurements, we estimated the contribution of water current induced turbulence to the gas transfer velocity, using the conceptual relationship of O'Connor and Dobbins (1958). This allowed us to construct an empirical relationship to compute the gas transfer velocity of CO_2 that accounts for the contribution of wind and water current. Based on this relationship, the spatial and temporal variability of the gas transfer velocity in the Scheldt estuary was investigated. Water currents contribute significantly to the gas transfer velocity, but the spatial and temporal variability (from daily to seasonal scales) is mainly related to wind speed variability.

Introduction

A rigorous estimation of the exchange of carbon dioxide (CO_2) across the air-water interface is critical to determine ecosystem metabolism (Smith and Key 1975) and to budget the annual sink or source for atmospheric CO_2 at local (Borges and Frankignoulle 2002), regional (Lefevre et al. 1999), and global scales (Takahashi et al. 2002). The flux of CO_2 across the air-water interface (F) can be computed according to:

$$F = k\alpha\Delta pCO_2 \quad (1)$$

where α is the solubility coefficient of CO_2, ΔpCO_2 is the air-water gradient of the partial pressure of CO_2 (pCO_2), and k is the gas transfer velocity of CO_2 (also referred to as piston velocity). A positive F indicates a transfer of CO_2 from the water to the atmosphere.

Because highly precise and accurate methods to measure ΔpCO_2 are now available, the largest uncertainty in the computation of F comes from the k term in both open oceanic and coastal environments. Based on numerous theoretical, laboratory, and field studies, it is well established that the most important process controlling k is turbulence at the air-water interface (in the case of sparingly soluble gases such as CO_2 the critical process is turbulence in the liquid phase). In open oceanic waters, the gas transfer velocity of CO_2 is usually parameterized as a function of wind speed, because wind stress is the main generator of turbulence in these systems. At low wind speeds, the air-water gas transfer is further modulated by the presence of surfactants, convective cooling, chemical enhancement, and rain. At high wind speeds, capillary and gravity waves, bubbles, and spray also strongly contribute to air-water gas transfer.

Gas transfer velocities in estuaries have been estimated from the mass balance of naturally occurring or opportunistic tracers such as Chlorofluorocarbons (Clark et al. 1992) and ^{222}Rn (Elsinger and Moore 1983; Hartman and Hammond 1984, 1985), from the mass balance of purposeful tracers, ^{3}He and SF_6 (Clark et al. 1994, 1996; Carini et al. 1996), from the mass balance of O_2 (Devol et al. 1987), and from floating chamber measurements of ^{222}Rn (Hartman and Hammond 1984; De-

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vol et al. 1987; Richey et al. 2002), O_2 (Marino and Howarth 1993; Richey et al. 2002; Kremer et al. 2003a), and CO_2 (Borges et al. 2004). The floating chamber technique provides gas transfer velocity estimates at short time scales (minute), compared to the tracer mass balance approaches (hour to day), but it has been dismissed by several workers (e.g., Liss and Merlivat 1986; Raymond and Cole 2001). One of the critiques is that the chamber covers the water surface and eliminates wind stress. For sparingly soluble gases such as CO_2, gas transfer is controlled by turbulence in the liquid phase. If the floating chamber does not disrupt the underlying water turbulence, then the corresponding gas transfer measurements should be reasonable estimates of those from the undisturbed surface. The disturbance of the floating chamber on the surface wind boundary layer was tested experimentally by Kremer et al. (2003b). They measured O_2 fluxes using a floating chamber with an adjustable speed fan to generate air turbulence and a control floating chamber. Under moderate wind conditions, the additional air turbulence from the fan only increased the fluxes by 2–12% compared to the control chamber. Kremer et al. (2003b) also report a series of experiments comparing the floating chamber technique with mass balance approaches of O_2, ^{222}Rn, and ^{3}He in various experimental settings (laboratory tanks, outdoor tanks, mesocosms, and lakes). Fluxes based on the floating chamber technique agreed with the other direct methods within 10–30%. Two publications report large discrepancies between the floating chamber technique and other approaches (Belanger and Korzum 1991; Matthews et al. 2003) that, in our opinion, highlight the limits of the method rather than dismiss it altogether. Belanger and Korzum (1991) compared O_2 evasion rates from pools by a mass balance approach and floating chamber measurements. They concluded that the floating chamber measurements were biased by temperature and pressure changes during the experiments. The duration of these measurements was several hours, and temperature and pressure changes are not expected to interfere during very short deployments of the floating chamber (such as in our case). Matthews et al. (2003) compared k estimates in a small sheltered boreal reservoir, based on floating chamber and SF_6 evasion techniques. During their experiment, wind speeds were extremely low, on average 0.2 m s^{-1} and never exceeding 0.5 m s^{-1}. As noted by Kremer et al. (2003b), the fluxes measured in nearly motionless waters with a floating chamber should be taken with caution. Also, estuarine environments (such as in our case) are expected to be much more turbulent due to tidal currents than the reservoir studied by Matthews et al. (2003).

Another critique of the floating chamber technique is that the interference from the chamber itself would result in artificially high k estimates. This issue will remain unresolved until a field intercomparison of methods is carried out; the next best approach is the comparison of k-wind relationships in similar systems. Figure 1 shows that k estimates from floating chamber CO_2 measurements in two coral reef systems reported by Frankignoulle et al. (1996a) follow the McGillis et al. (2001) relationship for wind speed below 6 m s^{-1}. At wind speeds above 6 m s^{-1}, the k estimates given by Frankignoulle et al. (1996a) are in fact below the values computed from the Liss and Merlivat (1986) parameterization. The generic relationship of Marino and Howarth (1993) that includes k estimates from floating dome O_2 measurements in lakes, estuaries, and open oceanic waters falls between the parameterizations from Jacobs et al. (1999) and McGillis et al. (2001). In estuaries, the relationship of Kremer et al. (2003a) based on floating chamber O_2 measurements in Sage Lot Pond and Childs River estuaries is well below the parameterization from Clark et al. (1995) based on tracer measurements in the Hudson River and San Francisco Bay (Fig. 1). The relationship from Marino and Howarth (1993) refitted taking into account exclusively the floating chamber O_2 measurements in the Hudson River are above the Clark et al. (1995) parameterization. As noted by Raymond and Cole (2001) gas tracer experiments measure average gas transfer velocities over long time scales (days to weeks) compared to floating dome measurements that give virtually immediate estimates. The higher k values reported by Marino and Howarth (1993) compared to those by Clark et al. (1995) could be due to short-term enhancement related to the contribution of water currents to interfacial turbulence. Peak-flow water currents of 40 and 200 cm s^{-1} were reported by Clark et al. (1995) and Marino and Howarth (1993), respectively. Zappa et al. (2003) report k values based on the vertical gradient technique in Plum Sound estuary that are up to 8 cm h^{-1} higher at the same wind speed than the estimates from Carini et al. (1996) based on SF_6 release experiment in the same estuarine system. This value corresponds roughly to the difference between the estimates based on the Marino and Howarth (1993) and the Clark et al. (1995) parameterizations at a wind speed of 6 m s^{-1}.

Based on a large data set of floating chamber CO_2 flux measurements in three European estuaries (Randers Fjord, Scheldt and Thames), we recently showed that a simple parameterization of k

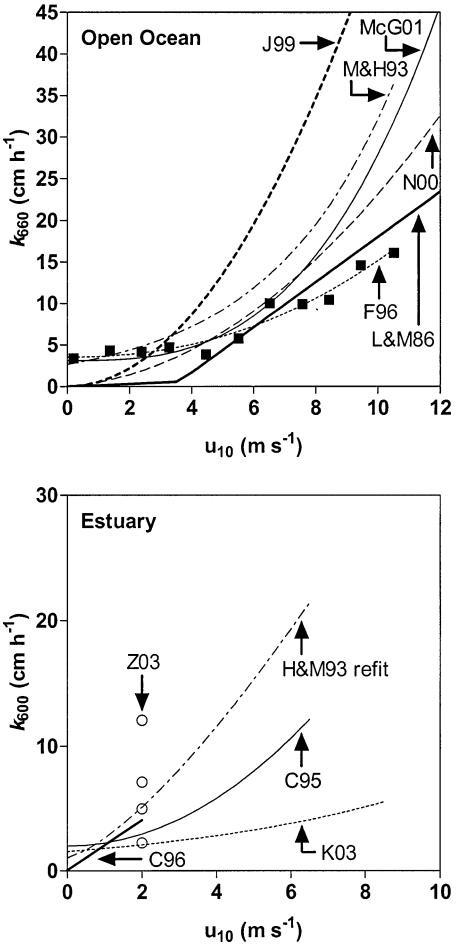

FIG. 1. Comparison of gas transfer velocity parameterizations as a function of wind speed in open oceanic waters and estuaries. The Liss and Merlivat (1986) relationship is based on a SF_6 release experiment in a lake by Wanninkhof et al. (1985) and wind tunnel experiments by Broecker and Siems (1984) (L&M86; solid bold line). The Jacobs et al. (1999) relationship is based on gradient flux technique measurements (wind speed range 3–14 m s^{-1}) in the North Sea (J99; bold short dashed line). The Nightingale et al. (2000) relationship is based on two SF_6 and ^3He release experiments (wind speed range 3–14 m s^{-1}) in the North Sea (N00; long dashed line). The McGillis et al. (2001) relationship is based on direct covariance technique measurements (wind speed range 1–16 m s^{-1}) in the North Atlantic Ocean (McG01; solid line). The Marino and Howarth (1993) relationship is based on floating dome O_2 measurements (wind speed range 0–10 m s^{-1}) in various estuaries, lakes, and open oceanic waters (M&H93; dashed-dotted line). The F96 relationship is based on the original data from Frankignoulle et al. (1996a) of floating dome CO_2 measurements (wind speed range 0–11 m s^{-1}) in Yonge Reef and Moorea coral reefs. The k_{660} data were averaged over wind speed bins of 1 m s^{-1} (squares). The best fit to the data is given by $k_{660} = 3.6(\pm 0.7) + 0.07(\pm 0.07)u_{10}^{(2.2\pm 0.4)}$ ($r^2 = 0.952$, n = 11) (F96; short dashed line). The Kremer et al. (2003a) relationship is based on floating dome O_2 measurements (wind speed range 0–8.5 m s^{-1}) in Childs River and Sage Lot Pond estuaries (K03; dashed line). The Clark et al. (1995) relationship is based on SF_6 release experiments (wind speed range 1–6.5 m s^{-1}) in the Hudson River estuary and ^{222}Rn mass balance in San Francisco Bay (C95; solid line). The Carini et al. (1996) is based on a SF_6 release experiment (wind speed range 0–2 m s^{-1}) in Park River estuary (C96; bold solid line). The Zappa et al. (2003) data are based on gradient flux technique measurements in Plum Island Sound (Parker River) estuary during a half tidal cycle at constant low wind speed (1.9 m s^{-1}) (Z03; open circles). The H&M93 relationship is based on the original data from Marino and Howarth (1993) of floating dome O_2 measurements (wind speed range 0–6.5 m s^{-1}) in the Hudson River estuary. The best fit to the unbinned data is given by $k_{600} = 1.1(\pm 4.0) + 1.7(\pm 2.2)u_{10}^{(1.4\pm 0.7)}$ ($r^2 = 0.864$, n = 9) (H&M93 refit; dashed-dotted line). Note different x and y scales in plots A and B; k is normalized to a Schmidt number of 660 and 600 in plots A and B, respectively.

as a function of wind speed is estuary specific (Borges et al. 2004). This is related to the fact that the contribution to the gas transfer velocity of CO_2 from turbulence generated by tidal currents is negligible in microtidal estuaries such as the Randers Fjord, but is substantial in macrotidal estuaries such as the Scheldt and Thames. The aim of the present work is to study the temporal and spatial variability of k in the Scheldt estuary based on a recently obtained data set of interfacial CO_2 flux measurements using the floating chamber technique.

Materials and Methods

During two cruises in the Scheldt estuary (November 2002 and April 2003), 9 stations were occupied for 24 h and flux measurements were carried out approximately every 10 min during daytime (Table 1).

pCO_2 was measured (1-min recording interval) with a nondispersive Infra-Red Gas Analyser (IRGA) in air equilibrated with subsurface water (pumped from a depth of 2.5 m). For a detailed description of the equilibration technique and calibration procedures of the IRGA refer to Frankignoulle et al. (2001) and Frankignoulle and Borges (2001).

The air-water CO_2 fluxes were measured with the floating chamber method from a drifting rubber boat in order to avoid the interference of water turbulence within the chamber created by the passing water current observed in earlier measurements carried out from a fixed point (Frankignoulle unpublished data). Care was taken to maintain the floating chamber about 2 to 3 m away from the rubber boat to avoid interference on the air and water boundary layers. The chamber is a plastic right circular cone (top radius = 49 cm; bottom radius = 57 cm; height = 28 cm) mounted on a float, and connected to a closed air loop with an air pump (3 l min^{-1}) and an IRGA, both powered with a 12 V battery. The IRGA was calibrated daily using pure nitrogen and a gas mixture with a CO_2 molar fraction of 351 ppm. The readings of

TABLE 1. Average (± standard deviation) of depth, wind speed (u_{10}), water current (w), salinity, pCO_2 in subsurface water (pCO_{2water}), atmospheric pCO_2 (pCO_{2air}), atmospheric CO_2 flux (F), and the gas transfer velocity of CO_2 (k_{600}) at 9 stations in the Scheldt estuary, sampled in November 2002 and April 2003 (n indicates the number of measurements).

Date	Longitude (°E)	Latitude (°N)	Depth (m)	u_{10} (m s^{-1})	w (cm s^{-1})	Salinity	pCO_{2water} (ppm)	pCO_{2air} (ppm)	F (mmol m^{-2} d^{-1})	k_{600} (cm h^{-1})	n
November 6, 2002	4.314	51.127	13	4.0 (0.2)	86.1 (3.5)	0.41 (0.01)	7,358 (22)	381 (1)	980 (375)	15 (1)	28
November 8, 2002	4.399	51.226	11	6.8 (0.2)	18.8 (5.6)	0.49 (0.02)	6,959 (11)	393 (1)	1,377 (438)	22 (1)	32
November 10, 2002	4.040	51.410	14	7.5 (0.3)	48.4 (4.8)	13.31 (0.38)	1,403 (48)	396 (1)	259 (141)	27 (2)	38
November 12, 2002	4.215	51.395	17	8.4 (0.5)	9.6 (2.6)	7.69 (0.16)	2,229 (28)	387 (1)	516 (95)	30 (2)	14
April 2, 2003	4.303	51.124	12	8.2 (0.3)	82.2 (4.3)	0.57 (0.01)	6,451 (35)	374 (1)	1,244 (448)	21 (1)	38
April 4, 2003	4.250	51.348	14	3.3 (0.1)	43.1 (6.2)	6.29 (0.14)	2,917 (56)	386 (1)	251 (66)	11 (1)	40
April 6, 2003	4.399	51.226	9	5.1 (0.2)	73.0 (6.9)	1.22 (0.13)	5,756 (107)	373 (1)	925 (247)	18 (1)	36
April 8, 2003	3.931	51.381	15	4.7 (0.2)	61.5 (5.8)	19.29 (0.13)	789 (6)	381 (1)	65 (26)	19 (1)	42
April 9, 2003	4.164	51.381	19	7.1 (0.2)	27.2 (3.7)	9.38 (0.25)	1,840 (55)	379 (1)	311 (114)	23 (1)	27

FIG. 2. The gas transfer velocity of CO_2 (k_{600} in cm h^{-1}) as a function of wind speed at 10 m height (u_{10} in m s^{-1}) in the Scheldt estuary and two published relationships. The open squares correspond to k_{600} from which the contribution of water currents was removed ($k_{600wind}$). The contribution of water currents to k_{600} was estimated from the conceptual relationship of O'Connor and Dobbins (1958), using water current measurements concomitant to the CO_2 flux measurements and it was removed from individual k_{600} estimates before the data were bin averaged. The data were averaged over wind speed bins of 1 m s^{-1} (error bars correspond to the standard deviations on the bin averages). The error bar on top left corner of the plot correspond to the average uncertainty on k_{600}, estimated using the individual standard error on the slope of the regression of pCO_2 in the floating chamber against time (from which the CO_2 flux was computed see the Materials and Methods) and assuming an error on ΔpCO_2 of ±3%. The Raymond and Cole (2001) relationship ($k_{600} = 1.91 \exp(0.35u_{10})$) is based on a compilation of published k_{600} values in various rivers and estuaries and obtained using different methods (floating chamber, natural tracers [CFC, ^{222}Rn], and purposeful tracer [SF_6]). The Clark et al. (1995) relationship ($k_{600} = 2 + 0.24u_{10}^2$) is based on a dual tracer (^3He and SF_6) release experiment in the Hudson River estuary and ^{222}Rn mass balance in San Francisco Bay from Hartman and Hammond (1984). Note that the Clark et al. (1995) and the Raymond and Cole (2001) relationships are constrained by data obtained at wind speeds below 6.5 m s^{-1} (bold in the plot). The Zappa et al. (2003) data are based on gradient flux technique measurements in Plum Island Sound (Parker River) estuary during a half tidal cycle at constant low wind speeds (1.9 m s^{-1}) (Z03; open circles). Solid lines correspond to the linear regression functions of $k_{600observed}$ and $k_{600wind}$ (Eqs. 2 and 13, respectively).

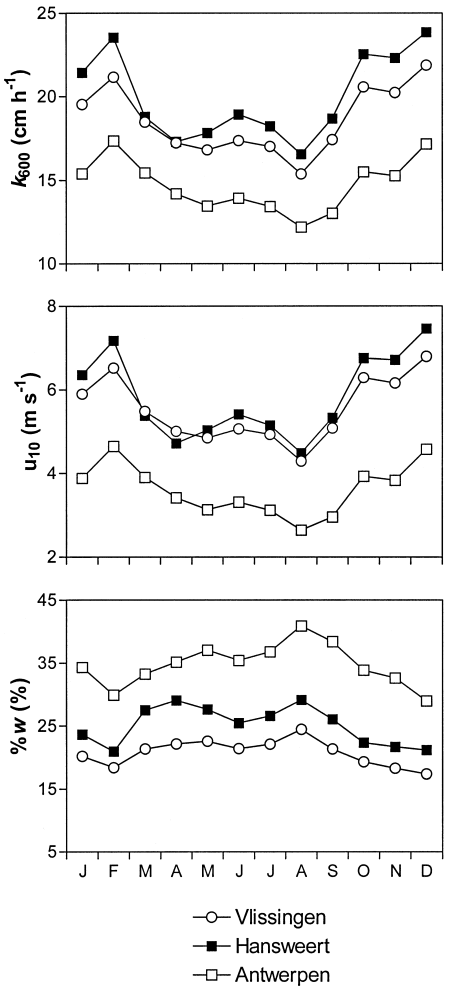

FIG. 3. Monthly averages for 1997–2001 of the gas transfer velocity of CO_2 (k_{600} in cm h^{-1}) computed from Eq. 14 from hourly wind speed measurements (u_{10} in m s^{-1}) and modelled water currents at three reference stations (Vlissingen, Hansweert, and Antwerpen; see Table 3 for geographical positions), and the percentage of contribution of water currents to the gas transfer velocity of CO_2 (%w).

pCO_2 in the chamber were written down every 30 s during 5 min. The flux was computed from the slope of the linear regression of pCO_2 against time (r^2 usually ≥ 0.99) according to Frankignoulle (1988). The uncertainty of the flux computation due to the standard error on the regression slope is on average $\pm 3\%$. The gas transfer velocity of CO_2 was computed from the interfacial CO_2 flux and ΔpCO_2 measurements (atmospheric pCO_2 was measured and recorded at the start of each flux measurement), using the CO_2 solubility coefficient formulated by Weiss (1974) and normalized to a Schmidt number (Sc) of 600 (k_{600}), assuming a dependency of the gas transfer velocity proportional to $Sc^{-0.5}$. The Schmidt number was computed for a given salinity from the formulations for salinity 0 and 35 given by Wanninkhof (1992) and assuming that Schmidt number varies linearly with salinity.

During both cruises, wind speed was measured at 18 m height with a Friedrichs 4034.000 BG cup anemometer, and, recorded every 10 s. Winds speeds were referenced to a height of 10 m (u_{10}) according to Smith (1988), using concomitant air and water temperature measurements and were averaged for the period of each flux measurement. Water current speeds in subsurface waters measured with an Aanderaa RCM7 were recorded every minute and were also averaged for the period of each flux measurement.

Temporal series of hourly u_{10} measurements were provided by the Koninklijk Nederlands Meteorologish Instituut at Vlissingen and Hansweert and by Belgocontrol at Antwerpen. At these three reference stations, hourly water currents were computed using a 1-dimensional hydrodynamic model of the Scheldt estuary (CONTRASTE, Regnier et al. 1997). The boundary conditions for the simulation are obtained from a tide prediction routine taking into account the spring-neap oscillation at the estuarine mouth and from the daily value of the freshwater discharge measured at the upper limit of the tidal rivers.

TABLE 2. Equations of fits of the gas transfer velocity of CO_2 (k_{600} in cm h^{-1}) as a function of wind speed at 10 m height (u_{10} in m s^{-1}), using various functions, in the Scheldt estuary (November 2002 and April 2003). ABS = absolute sum of residuals squares. r^2 and ABS of the three best fits discussed in text are in bold.

Equation Type	Equation Formulation	Eq.	r^2	ABS
$y = a + bx$	$k_{600} = 4.045 + 2.580u_{10}$	2	**0.955**	**24.9**
$y = a + bx^2$	$k_{600} = 10.07 + 0.201u_{10}^2$	3	0.892	59.6
$y = ax^2$	$k_{600} = 0.3501u_{10}^2$	4	0.095	499.0
$y = a + bx^3$	$k_{600} = 13.10 + 0.0179u_{10}^3$	5	0.807	106.6
$y = ax^3$	$k_{600} = 0.0355u_{10}^3$	6	0.000	987.2
$y = a + bx^c$	$k_{600} = -3.065 + 7.302u_{10}^{0.646}$	7	**0.961**	**21.48**
$y = ax^c$	$k_{600} = 5.141u_{10}^{0.758}$	8	**0.960**	**21.85**
$y = a + b.\exp(cx)$	$k_{600} = -897.5 + 901.6\exp(0.0687u_{10})$	9	0.954	25.13
$y = a.\exp(bx)$	$k_{600} = 8.7\exp(0.01503u_{10})$	10	0.914	47.69

TABLE 3. Average (± standard deviation) of time series (1997–2001) of tidal amplitude, water current (w), and wind speed (u_{10}) at three reference stations in the Scheldt estuary.

Station and Coordinates	Mean Water level (m)	Tidal Amplitude (m)	w (cm s^{-1})	u_{10} (m s^{-1})
Vlissingen 3.579°E 51.421°N	14.7	4.9 (0.4)	60.3 (28.9)	5.5 (2.8)
Hansweert 4.007°E 51.424°N	8.6	4.8 (0.8)	53.7 (22.1)	5.9 (3.1)
Antwerpen 4.418°E 51.228°N	10.8	5.5 (1.0)	73.3 (26.6)	3.6 (0.6)

Results and Discussion

Data Set Overview

A total of 295 CO_2 flux measurements were carried out for both cruises, at 9 stations in the Scheldt estuary (Table 1). A large fraction of the salinity gradient was covered during both cruises with values ranging from 0.4 to 21. Oversaturation of CO_2 of surface waters with respect to atmospheric equilibrium was systematically observed during both cruises with pCO_2 values ranging from 716 to 7,553 ppm. The largest difference between the two cruises in the distribution of pCO_2 versus salinity (not shown) was observed in the upper estuary, with pCO_2 values on average higher at salinity 0.4 during the November 2002 cruise (Table 1). Atmospheric pCO_2 values ranged from 368 to 422 ppm, and values for both cruises were on average 9 ppm above the uncontaminated pCO_2 signal from Weather Station Mike (66.00°N, 2.00°E), representative of the open North Sea waters (from the National Oceanic and Atmospheric Administration, Climate Monitoring and Diagnostics Laboratory air samples network, available from the internet at http://www.cmdl.noaa.gov/). The interfacial CO_2 fluxes were positive during both cruises, ranging from 31 to 2,189 mmol m^{-2} d^{-1}. Wind speed values ranged from 1.6 to 11.0 m s^{-1}. About 61% of the interfacial CO_2 flux measurements were obtained at wind speeds ranging from 3.0 to 7.0 m s^{-1}. About 1.4% and 4.4% of the interfacial CO_2 flux measurements were obtained at wind speeds below 2 m s^{-1} and above 10 m s^{-1}, respectively. Water currents ranged from 1 to 130 cm s^{-1} and unlike wind speed, the CO_2 flux measurements were regularly distributed over the water current range of variation.

Gas Transfer Velocity Parameterization as a Function of Wind Speed

Figure 2 shows the averaged k_{600} over wind speed bins of 1 m s^{-1} versus wind speed. A steady increase of k_{600} with wind speed is observed, and for wind speeds above 6 m s^{-1}, the k_{600} values fall within the range of values from existing parameterizations of k_{600} in estuaries. For wind speeds below 6 m s^{-1}, the k_{600} values are above any of the published parameterizations of k_{600} as a function of wind speed. At a wind speed of 2 m s^{-1}, k_{600} values in the Scheldt are within the range of values reported by Zappa et al. (2003) based on the gradient flux technique, during a half tidal cycle, in Plum Island Sound estuary where peak flow values of 80 cm s^{-1} were reported.

We tested various functions (linear, power-law, and exponential) that have been used in literature to parameterize k_{600} as a function of wind speed (Table 2). Based on r^2 and the absolute sum of residuals squares, the three best fits to the data are

TABLE 4. Average (± standard deviation) of water current (w), wind speed (u_{10}), gas transfer velocity of CO_2 (k_{600}), percentage of contribution of water currents to the gas transfer velocity of CO_2 (%w) and percentage of contribution of wind speed to the gas transfer velocity of CO_2 (%u_{10}), computed according to Eq. 14, using hourly observed wind speed and modelled water current data series at three reference stations in the Scheldt estuary 1997–2001.

	Vlissingen					Hansweert		
Year	w (cm s^{-1})	u_{10} (m s^{-1})	k_{600} (cm h^{-1})	%w (%)	%u_{10} (%)	w (cm s^{-1})	u_{10} (m s^{-1})	k_{600} (cm h^{-1})
1997	60.8 (29.0)	5.2 (2.7)	17.7 (7.2)	21.9 (10.4)	78.1 (10.4)	54.0 (22.1)	5.4 (3.1)	19.0 (8.2)
1998	60.8 (28.9)	5.7 (2.9)	19.1 (7.5)	20.2 (9.9)	79.8 (9.9)	54.0 (22.0)	6.2 (3.2)	20.8 (8.5)
1999	60.3 (29.0)	5.5 (2.8)	18.5 (7.3)	20.8 (10.5)	79.2 (10.5)	53.6 (22.2)	5.9 (3.1)	20.3 (8.2)
2000	59.6 (28.7)	5.7 (2.8)	19.0 (7.4)	20.3 (10.3)	79.7 (10.3)	53.0 (22.0)	6.2 (3.1)	20.7 (8.3)
2001	59.6 (28.5)	5.3 (2.6)	18.1 (6.8)	21.1 (10.2)	78.9 (10.2)	53.1 (21.9)	5.9 (2.9)	20.3 (7.6)
Mean	60.2 (28.8)	5.5 (2.8)	18.5 (7.2)	20.8 (10.3)	79.2 (10.3)	53.6 (22.0)	5.9 (3.1)	20.2 (8.2)

given by Eqs. 7, 8, and 2 in Table 2. Equation 7 gives the best fit, but for a null wind speed predicts a negative k_{600}, which is physically inconsistent. For null wind speeds, Eq. 8 predicts a null k_{600} while Eq. 2 predicts a k_{600} of 4 cm h^{-1}. From the present data set, it is not possible to check the validity of these two equations at very low wind speeds because all measurements were obtained at wind speeds above 1.6 m s^{-1}. In the more extensive data set described by Borges et al. (2004), 15 measurements are reported for wind speeds ranging between 0.4 and 0.9 m s^{-1} and give an average value for k_{600} of 8.9 cm h^{-1}. For the corresponding average wind speed (0.8 m s^{-1}), Eqs. 8 and 2 predict a k_{600} of 3.4 and 6.1 cm h^{-1}, respectively. Equation 2 predicts a k_{600} value closer to the observations at wind speeds below 1 m s^{-1}. Also, the k_{600} values predicted at zero wind speed by Eqs. 2 and 9 are identical, Eq. 9 being the next best fit to the data. We conclude that a simple linear regression gives the most consistent fit to the data.

Contribution of Water Current to the Gas Transfer Velocity

The contribution of the water current to the gas transfer velocity was estimated from the frequently referenced conceptual relationship of O'Connor and Dobbins (1958). The validity for estuarine environments of this relationship developed for streams has recently been confirmed by Zappa et al. (2003) based on k measurements using various micrometeorological methods in Plum Island Sound estuary and by Borges et al. (2004) based on floating dome measurements in the Randers Fjord. The O'Connor and Dobbins (1958) conceptual relationship gives the oxygen reaeration rate (R in d^{-1}) according to:

$$R = 0.439w^{0.5}h^{-1.5} \quad (11)$$

where w is the water current (cm s^{-1}) and h is the depth (m).

Equation 11 can be used to express the gas transfer velocity of CO_2, using the Schmidt number formulations given by Wanninkhof (1992), and assuming a dependency of k proportional to $Sc^{-0.5}$, according to:

$$k_{600current} = 1.719w^{0.5}h^{-0.5} \quad (12)$$

where $k_{600current}$ is the gas transfer velocity of CO_2 (cm h^{-1}), w is the water current (cm s^{-1}), and h is the depth (m).

From water current measurements concomitant to those of the interfacial CO_2 flux, the contribution of water current to the gas transfer velocity of CO_2 ($k_{600current}$) was computed according to Eq. 12 and was removed from the observed k_{600} ($k_{600observed}$). This gives the contribution to k_{600} of wind speed alone ($k_{600wind} = k_{600observed} - k_{600current}$), assuming that both contributions to water turbulence are linearly additive. The averaged $k_{600wind}$ over wind speed bins of 1 m s^{-1} are significantly lower than the $k_{600observed}$ values (Fig. 2). For a wind speed of 2 m s^{-1} $k_{600observed}$ is about 1.7 times higher than $k_{600wind}$, and for a wind speed of 11 m s^{-1}, $k_{600observed}$ is about 1.1 times higher than $k_{600wind}$. This confirms the conclusion from a previous study: the contribution to k of turbulence derived from the water current is very significant in the Scheldt but decreases with increasing wind speeds (Borges et al. 2004) in accordance with the theoretical analysis of Cerco (1989). Note that the $k_{600wind}$ are closer than $k_{600observed}$ to the values from published parameterizations even at low wind speeds (Fig. 2). The linear regression of $k_{600wind}$ as a function of wind speed is also highly significant and yields:

$$k_{600wind} = 1.0 + 2.58u_{10}$$
$$(r^2 = 0.960, p < 0.0001, n = 10) \quad (13)$$

where $k_{600observed}$ (cm h^{-1}) is the gas transfer velocity of CO_2 and u_{10} (m s^{-1}) is wind speed at 10 m height.

Note that the y-intercept of Eq. 13 is significantly different (0.96 ± 1.24 cm h^{-1}) than the one from Eq. 2. Assuming that the contributions of wind and

TABLE 4. Extended.

Hansweert		Antwerpen				
%w (%)	%u_{10} (%)	w (cm s^{-1})	u_{10} (m s^{-1})	k_{600} (cm h^{-1})	%w (%)	%u_{10} (%)
26.6 (14.2)	73.4 (14.2)	77.2 (27.0)	3.3 (2.2)	14.0 (5.8)	37.3 (16.1)	62.7 (16.1)
24.0 (13.3)	76.0 (13.3)	77.3 (27.1)	3.8 (2.3)	15.3 (6.0)	33.8 (14.4)	66.2 (14.4)
24.4 (12.8)	75.6 (12.8)	76.8 (27.2)	3.6 (2.3)	14.9 (6.0)	35.3 (16.5)	64.7 (16.5)
24.1 (13.9)	75.9 (13.9)	75.8 (26.9)	3.7 (2.2)	15.0 (5.7)	34.3 (15.5)	65.7 (15.5)
23.5 (11.0)	76.5 (11.0)	76.0 (27.2)	3.5 (2.0)	14.4 (5.3)	35.3 (15.4)	64.7 (15.4)
24.5 (13.0)	75.5 (13.0)	76.6 (27.1)	3.6 (2.2)	14.7 (5.8)	35.2 (15.6)	64.8 (15.6)

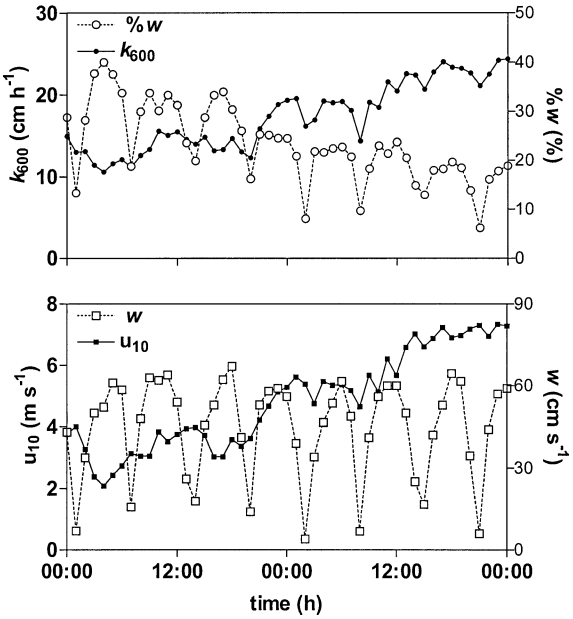

FIG. 4. Hourly variations of the gas transfer velocity of CO_2 (k_{600} in cm h^{-1}) computed from Eq. 14, using hourly wind speed measurements (u_{10} in m s^{-1}) and modelled water currents (w in cm s^{-1}), and the percentage of contribution of water currents to the gas transfer velocity of CO_2 (%w) at the Hansweert reference station, January 2–3, 1997.

water current to water turbulence are additive, an equation that accounts for both wind speed and water current speed can be constructed by summing Eqs. 12 and 13:

$$k_{600} = 1.0 + 1.719w^{0.5}h^{-0.5} + 2.58u_{10} \quad (14)$$

where k_{600} is the gas transfer velocity of CO_2 (cm h^{-1}), w is the water current (cm s^{-1}), h is the depth (m), and u_{10} (m s^{-1}) is the wind speed at 10 m height.

Spatial and Temporal Variability of the Gas Transfer Velocity in the Scheldt Estuary

At three reference stations—Vlissingen, Hansweert, and Antwerpen—that correspond to the lower, middle, and upper Scheldt estuary, respectively, the k_{600} was computed from Eq. 14, using the hourly time series of measured u_{10} and modelled w for the years 1997 to 2001 (Tables 3 and 4). On an annual basis, the contribution of w to k_{600} (%w) is highly significant at the three reference stations, ranging from about 20% to 35% for Vlissingen and Antwerpen, respectively (Table 4). The Antwerpen station is characterized on an annual basis by significantly lower k_{600} values than the two other stations (Table 4). This is mainly due to the significantly lower wind speeds at Antwerpen (Tables 3 and 4). The mean value for the 1997–2001 period of $k_{600current}$ is relatively similar at the three stations: 5.2, 4.2, and 3.9 cm h^{-1} for Antwerpen, Hansweert, and Vlissingen, respectively (refer to k_{600} and %w in Table 4). The higher contribution of w to k_{600} at Antwerpen compared to the two other locations is mainly due to the lower wind speeds, although mean tidal currents are highest at this station (Table 3).

The highest annual k_{600} values were computed at Hansweert (Table 4). This is related to the higher contribution of w to k_{600} at Hansweert compared to Vlissingen (Table 4), since wind speeds are very similar at both stations (Tables 3 and 4). The higher contribution of w to k_{600} (%w) at Hansweert is due to the fact that this location is shallower than Vlissingen where tidal currents are in fact stronger (Table 3).

Important seasonal variations of k_{600} are also apparent at the three reference stations (Fig. 3). For 1997–2001, lower monthly wind speed averages are observed during spring and summer compared to fall and winter. During spring and summer, k_{600} values are lower and the contribution of w to k_{600} increases. The differences between the three stations, discussed above, based on the annual means are also apparent at seasonal scale.

As for the annual and seasonal variability, the impact of wind speed is preponderant on k_{600} variations at daily scale. As an example, hourly variations of the computed k_{600} at Hansweert January 2–3, 1997, are shown in Fig. 4. During the 48 h, a steady increase of k_{600} and a general decrease of the contribution of w to k_{600} are observed in relation to the increase of wind speed. Note that k_{600} systematically decreases at the tide slack due to the reduction of %w. The evolution of %w follows well the one of w.

Although important spatial and temporal variations of k_{600} are found in the Scheldt, the overall intensity of the flux of CO_2 across the air-water interface will largely depend on the ΔpCO_2 values that are known to present extremely large spatial gradients in this estuary (Frankignoulle et al. 1996b, 1998; Frankignoulle and Borges 2001; Table 1). Based on a data set of 20 cruises carried out 1993–2003, covering the full annual cycle, we computed annual average ΔpCO_2 values of 5,550 (±1,078 standard deviation, SD), 577 (±170 SD), and 136 (±143 SD) ppm at Antwerpen, Hansweert, and Vlissingen, respectively. Based on the average values of k_{600} reported in Table 4, the corresponding mean annual interfacial CO_2 fluxes are 1,008 (±153 SD), 139 (±49 SD), and 30 (±28 SD) mmol m^{-2} d^{-1} at Antwerpen, Hansweert, and Vlissingen, respectively. The interfacial CO_2 flux is on average 34 times higher at Antwerpen compared to Vlissingen, although the k_{600} at Antwerpen corresponds to 75% of the one at Vlissingen.

The average CO_2 emission from Scheldt can be estimated to 164 mmol m^{-2} d^{-1}, assuming that the Antwerpen, Hansweert, and Vlissingen stations are representative of a surface area of 20, 90, and 110 km^2, respectively, based on the geometry of the estuary. This emission corresponds to 158×10^3 tons of carbon per year (t C yr^{-1}), which is consistent with the estimate of 170×10^3 t C yr^{-1} given by Frankignoulle et al. (1998) and with the net CO_2 production term of 197×10^3 t C yr^{-1} from the CO_2 budget given by Abril et al. (2000). The discrepancy between our CO_2 emission estimate and the net CO_2 production term based on the budget of Abril et al. (2000) can be reconciled if an error of ±17% is assumed on each of the terms of CO_2 budget (CO_2 production from nitrification and from net aerobic metabolism [primary production—respiration], input of CO_2 from tributaries, and output of CO_2 to the North Sea). This is a fairly reasonable uncertainty estimate considering the large spatial and temporal variability of biogeochemical processes in the Scheldt estuary. For an uncertainty of ±17% on each of the terms of the CO_2 budget given by Abril et al. (2000), the corresponding variability on the net CO_2 production term is about ±35 mmol m^{-2} d^{-1} that would result in an error on k_{600} of ±4 cm h^{-1}. An indirect budget of CO_2 fluxes cannot be used to verify the validity of a gas transfer velocity parameterization since the interfacial CO_2 flux computed indirectly from this approach is prone to large uncertainty. Such an approach gives invaluable information on the major biogeochemical processes controlling the interfacial CO_2 fluxes.

On a seasonal scale, the flux of CO_2 is modulated by both k_{600} and ΔpCO_2 variations. An annual cycle of ΔpCO_2 at Antwerpen was constructed from the data set of 20 cruises carried out from 1993 to 2003 (Fig. 5). Although this reconstructed annual cycle probably includes interannual variability, a distinct pattern in the ΔpCO_2 evolution is apparent. ΔpCO_2 increases relatively regularly from January to July and it decreases from July to December. This is probably due to the seasonal temperature cycle (not shown) that effects ΔpCO_2 by two processes: the variation of temperature effects the equilibrium constants of dissolved inorganic carbon, in particular the CO_2 solubility coefficient, so that pCO_2 rises about 4% for a temperature increase of 1°C; and a rise of temperature induces an increase of bacterial metabolism, leading to an increase CO_2 production. The CO_2 flux to the atmosphere shows surprisingly little seasonal variability; the emission values are relatively constant, except for an extreme value in February. From May to July, the CO_2 flux values are relatively constant because the decrease of k_{600} is compensated by the increase of ΔpCO_2 values. The apparent lack of seasonality in the CO_2 flux is probably biased by interannual variability, since the ΔpCO_2 seasonal evolution was constructed from data from different years. This matter can only be addressed by the continuous monitoring of pCO_2 at a fixed station in the Scheldt estuary that at present time is lacking.

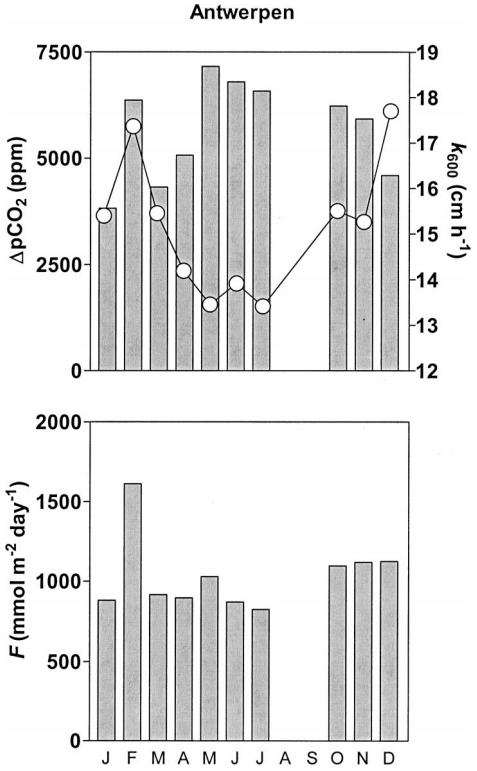

FIG. 5. Seasonal variations at Antwerpen of the air-water gradient of CO_2 (ΔpCO_2 in ppm, bars in top panel), the gas transfer velocity of CO_2 (k_{600} in cm h^{-1}, open circles), and the air-water flux of CO_2 (F in mmol m^{-2} d^{-1}, bars in bottom panel). The seasonal cycle of ΔpCO_2 was constructed from a data set of 20 cruises in the Scheldt estuary carried out from 1993 to 2003. The k_{600} values are monthly averages for 1997–2001, computed from Eq. 14, using hourly wind speed measurements and modelled water currents, using wind speed measurements and modelled water currents.

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