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Air–sea fluxes and transfer velocity of CO_2 over the North Sea: results from ASGAMAGE

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ABSTRACT

The paper presents an analysis, performed at the Royal Netherlands Meteorological Institute (KNMI), of data obtained at a research platform 9 km off the Dutch coast within the framework of the air–sea gas exchange program ASGAMAGE†. The air–sea transfer velocity of CO_2 was determined directly, that is, by observing CO_2 fluxes and air–sea concentration differences simultaneously. CO_2 fluxes were determined by means of the eddy correlation technique. Special care was taken to avoid the effects water vapour on the CO_2 flux measurements. The air and water near the air–sea interface were treated as well-mixed with respect to CO_2. The combination of flux and concentration data allowed the computation of the transfer velocity for CO_2 without recourse to other gases. Results for two observation periods, one with downward CO_2 fluxes (May) and one with upward CO_2 fluxes (October), are consistent. A relation with $U_{N,10}$, the wind speed adjusted to a height of 10 m and neutral stratification, was determined for the pooled data from the two experimental phases. The relation found was: $k_{660} = 0.54U_{N,10}^2$ cm h^{-1}, with k_{660} the CO_2 transfer velocity normalised to salt water (35‰) at a temperature of 20°C, and $U_{N,10}$ in m s^{-1}. The 95% confidence interval of the coefficient extends from 0.46 to 0.63. No relations with other geophysical parameters could be found from the present data set.

1. Introduction

The rate of gaseous transfer of CO_2 across the atmosphere–ocean interface, F_{CO_2}, is usually described by (Liss, 1983; Liss and Merlivat, 1986):

$$F_{CO_2} = k_w(c_w - c_E), \quad (1)$$

where k_w (m s^{-1}) is the air–sea transfer velocity, sometimes called the piston velocity, c_w is the concentration in the bulk of the water (g m^{-3}), and c_E is the equilibrium concentration in the water (g m^{-3}). By virtue of Henry's law, c_E may be taken equal to c_a/K_H, in which c_a is the concentration in the air and K_H is the dimensionless Henry coefficient $= H/(RT)$, where H is the Henry coefficient, R the universal gas constant, and T absolute temperature. Thus, c_E is the concentration in the water that would be in equilibrium with the concentration in the air. Gaseous exchange between water and air proceeds as long as the actual concentration in the water, c_w, differs from c_E. The subscript w of k_w indicates that the flux is mainly controlled by the water phase (Liss, 1983). Although parameterisations to estimate k_w as a function of geophysical parameters are available (Liss and Merlivat, 1986; Wanninkhof, 1992; Wu, 1996), the fundamental physical nature of k_w is poorly understood.

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† ASGAMAGE is a contraction of ASGASEX (for Air Sea Gas Exchange), an earlier experiment in this field, and MAGE, the Marine Aerosol and Gas Exchange activity of the International Global Atmospheric Chemistry program (IGAC).

There have been many attempts to determine k_w experimentally in the field. Most of the reported experiments involved indirect techniques, in which gases other than CO_2 are used to determine the behaviour of k_w for CO_2. The indirect methods include the dual tracer technique (Wanninkhof et al., 1993) and isotopic methods (Broecker and Peng, 1974). The reader is also referred to Liss (1983) and Liss and Merlivat (1986) for a review and discussion of these and other methods.

Crucial to indirect methods is the assumption that the diffusivities of different gases are related by the Schmidt number (*Sc*), the ratio of the kinematic viscosity and the molecular diffusivity. k_w is taken to be proportional to Sc^{-n}. At present, $n=\frac{1}{2}$ to $\frac{2}{3}$ is used most frequently (Liss and Merlivat, 1986), but values of n down to $\frac{1}{3}$ and up to 1 have also been used. One of the sources of uncertainty in the Schmidt number dependence is the possible effect of bubble mediated gas transfer (Merlivat and Memery, 1983; Woolf, 1993), which would give values of $n \neq 0.5$ (Wanninkhof et al., 1993; Asher and Wanninkhof, 1998). Furthermore, in the case of CO_2 special effects due to chemical reactions of dissolved carbon species are ignored. Such reactions include the possible catalysis of the hydration of CO_2 in the water by the enzyme carbonic anhydrase. This catalysis would enhance the effective rate of gas exchange for CO_2, but not for other gases (Liss et al., 1997). Finally, indirect methods generally use averaging periods of a day or more. Thus, a diurnal variation of k_w cannot be resolved. Furthermore, errors may be introduced if fluctuations in k_w on a timescale smaller than the averaging period correlate with variations in the air–sea concentration difference (Oost, 1998b).

A potentially powerful method to determine k_w is to measure the fluxes directly by means of the eddy correlation technique, in combination with a measurement of the concentration difference of the gas between the air and the water. Then, k_w can be computed directly from observations in the field, without Schmidt number dependence. The measured flux includes all special effects, such as bubble mediated transfer and catalytic reactions. Furthermore, fluxes obtained with the eddy correlation method are averages over 20–60 min only.

Results obtained with the eddy correlation technique during the late seventies and the early eighties show much larger values of k_w for CO_2 than results from the indirect methods (Broecker et al., 1986; Smith and Jones, 1986; Wesely, 1986). Differences amounted to a factor of 10 and more. The eddy correlation method has been criticised because none of the eddy correlation measurements was made in open sea, nor were they accompanied by accurate direct measurements of the air–sea concentration difference. Furthermore, the exceedingly small fluxes are at the very limit of detection. Finally, large corrections have to be applied (e.g., the "Webb correction"; Webb et al., 1980) and there is a possible lack of homogeneity in the CO_2 concentration field (Liss, 1983; Broecker et al., 1986). However, previous experiences have led to technologically improved eddy correlation instruments, especially with respect to the gas sensors, and to new insights into the quality of the data and the corrections to be applied. Thus, the eddy correlation technique may at present be regarded as a reasonably reliable method for determining fluxes over sea.

In order to try to reconcile results from the different methods of determining k_w the ASGAMAGE program was started (ASGAMAGE is a contraction of ASGASEX (for Air–Sea Gas Exchange), an earlier experiment in this field, and MAGE (Marine Aerosol and Gas Exchange, an activity of the International Global Atmospheric Chemistry program, IGAC.) In an international effort by 14 research groups from Europe, Canada and the USA, measurements were performed at 'Meetpost Noordwijk' (MPN), a research platform some 9 km off the Dutch coast in the North Sea (52°16′N, 04°18′E) and on the UK ship RRS "Challenger" during a cruise in the area near MPN. During the experiment, many geophysical parameters were determined, and many measurement techniques were applied. The reader is referred to Oost and Huebert (1996) and to Oost (1998a) for an overview of the experiment and for a presentation of preliminary results.

The present paper focuses on an attempt of the Royal Netherlands Meteorological Institute (KNMI) to determine the CO_2 transfer velocity directly, using the following data: (1) CO_2 flux from the eddy correlation method; (2) CO_2 concentration in the air; (3) CO_2 concentration in the water.

A significant part of the CO_2 concentration data used here were made available by courtesy of the TNO Physics and Electronics Laboratory (TNO-

FEL, The Netherlands), the Netherlands Institute for Sea Research (NIOZ) and the Max Planck Institut für Chemie (MPIC, Germany). Apart from the data on CO_2 flux and concentration, a set of additional data is required such as on sensible and latent heat flux, water temperature and salinity.

The description of the experimental set-up in Section 2 is restricted to some general information about the ASGAMAGE experiment and focuses on a description of the measurement of CO_2 flux and concentrations. A short description of the determination of other geophysical quantities is only given where relevant to the discussion that follows. Section 3 presents the results. A summary, discussion and conclusions are given in Section 4.

2. Experimental set-up

2.1. *Location and period*

The experimental part of ASGAMAGE reported on here was performed at MPN. Near the platform, the water reaches an average depth of about 18 m. Observations were carried out during two periods of five weeks each. The first one, ASGAMAGE-A, started on 6 May 1996; the second period, ASGAMAGE-B, started on 7 October 1996.

Measurement runs were initiated if the wind direction was expected to be between South and North (180°–360°). Each run lasted somewhat less than 55 min. The number of runs performed during ASGAMAGE was 412, of which 130 runs were performed during ASGAMAGE-A and 282 during ASGAMAGE-B.

2.2. *CO_2 concentration in air, c_a*

Air was sampled at various heights up to 30 m above mean sea level (MSL). Infrared gas analysers (IRGA) were used to determine the CO_2 concentration of the samples (ADC Mk3, The Analytical Development Company, 1988; LI6252 and LI6262, LiCor, 1991). Data obtained with the ADC Mk3 were corrected for the effect of water vapour dilution using the measured water vapour pressure of outside air. In most cases where the LiCor was used the water vapour content of the samples was determined by means of the IRGA. The manufacturer's software was then applied to correct for the influence of water vapour on the CO_2 concentration in situ. Another set of LiCor data required no correction at all because the samples were dried completely before analysis. Air concentration data from the different institutes were screened and converted to consensus values as described in Jacobs et al. (1998b).

In the analyses reported on below, we ignored a possible gradient of CO_2 concentration in the air. For our goal, that is, the determination of k_w using the concentration difference between air and water, this approximation is justified by the fact that concentration differences between a height of 30 m and 6 m were generally less than 1 ppm or 2 mg m^{-3} (Kunz et al., 1998). More details on the determination of c_a can be found in Jacobs et al. (1998) and in Kunz et al. (1998).

2.3. *CO_2 concentration in water, c_w*

To determine the CO_2 concentration in water, submerged pumps were used to obtain water from depths of 2, 3.5, 5, 7, 11 or 15 m below MSL. During ASGAMAGE-A, samples from an additional level at 0.5 m below the actual sea level could be obtained. The sample levels were controlled manually, and usually remained at a particular level between 3.5 and 11 m for many hours.

The sampled water was led to the laboratory level, located about 12 m above MSL. At the standard pumping rate of about 3.3 $m^3 h^{-1}$, it took less than 20 s for water from the deepest level to reach the analysing equipment. To determine the CO_2 concentration of the samples, water was sprayed continuously into an equilibrator. After 5 to 10 min of spraying, the air in the equilibrator and the sample water were assumed to be in equilibrium with each other (Jacobs et al., 1998a; Kunz et al., 1998). The actual CO_2 concentration in the water, c_w, can then be computed from the CO_2 concentration in the equilibrator air, c_{eq} (see Subsection 2.6).

The concentration in the equilibrator air was determined using the instruments and procedures outlined in Subsection 2.2, a minor difference being that some data from the A-phase were corrected for the influence of water vapour dilution assuming that the air in the equilibrator is saturated with water vapour at the measured sea water temperature.

Data from the different research groups were

screened and converted to consensus values. More details about this procedure and about the c_w measurements may be found in Jacobs et al. (1998b).

On some occasions, preferably around slack tide, CO_2 concentration profiles were measured by switching along all available levels. In 20 out of 26 cases (data not shown) the differences, expressed as differences in c_{eq}, remained within 16 ppm over the entire sampling depth. In five cases, the differences were 21 to 27 ppm. Only in one exceptional case a difference of 50 ppm was observed. The latter profile was accompanied by relatively large gradients in temperature and salinity, and is presumably influenced by industrial exhaust products carried with the rivers Scheldt, Rhine and Meuse into the North Sea (Hoppema, 1991; Frankignoulle et al., 1996). Because one profile measurement took about two hours and because the experimental error in c_w can be estimated at ± 15 ppm (Jacobs et al., 1998b), it was concluded that for our purpose it is allowed to treat the water near the platform as well-mixed with respect to CO_2. The validity of this assumption will be further assessed in Subsection 3.2.

2.4. *Turbulent fluxes; initial processing of flux data and selection of runs*

The fluxes of momentum, heat, water vapour and CO_2 were determined by means of the eddy correlation technique. Wind velocity fluctuations were obtained using a 3-dimensional Sonic Anemometer (Solent, Gill Instruments Ltd., Lymington, Hampshire, UK). Air temperature fluctuations were determined using a thin-wire thermocouple shielded by a tube to avoid the notorious cold spikes due to sea salt on the wire as much as possible.

The concentration of water vapour and CO_2 was measured by means of an Infrared Fluctuation Meter (IFM; Kohsiek, 1991). The IFM is an infrared sensor with a folded open absorption path, enclosed by a ventilated cylinder that protects the sensing head from rain. The damping effect of the cylinder is very small and is corrected for. Two optical filter pairs on a spinning filter wheel are applied to measure the concentration of water vapour and CO_2. Each pair contains an absorption filter, that allows the measurement within the IR absorption band of H_2O or CO_2, and one reference filter just outside the absorption bands. The relation between concentration and the ratio of the signals from a filter pair is determined by empirical calibration.

The effect of cross-talk, that is, the effect of interference of H_2O and CO_2 during the measurements, was avoided as much as possible. The optics of the IFM were heated slightly to avoid cross-talk occasioned by water films on the optics. Later during the experiment the optics were also cleaned frequently.

More details on the most advanced type of the IFM, used during ASGAMAGE, can be found in Kohsiek (1998) and in Jacobs et al. (1997). The eddy correlation devices were mounted at the end of a boom of 21 m length, at the West side of the MPN, some 5–6 meters above sea level (Fig. 1). For this position and the applied angle of acceptance of the average wind direction (180°–360°) effects of flow distortion due to the presence of MPN may be neglected (Oost et al., 1994).

Turbulence characteristics and the turbulent fluxes of momentum, sensible heat, latent heat and CO_2 were computed from samples obtained at 20 Hz. The data were corrected for flow distortion, due to small obstacles near the sensor, following Oost et al. (1994). Furthermore, corrections were applied for instrument tilt and sensor separation. For typical conditions at MPN (near neutral stability and wind speeds over 5 m/s) and the instruments used here, corrections for CO_2 flux loss due to line averaging can be shown (Moore, 1986) to be very small and were not applied. All processed data were stored on a run-by-run basis, as 55-min averages.

Runs were rejected in case of a suspect $u'w'$ cospectrum (where u denotes wind speed along the mean wind, w is the vertical wind speed and primes denote deviations from the average), in case of rain during a substantial portion of the run, or in case of malfunctioning of various instruments. More details are given by Jacobs et al. (1997, 1998a).

2.5. *Further processing of the CO_2 fluxes*

A further selection of runs was made in which runs were rejected if the data were thought to be affected by dirty optics of the IFM, in case of lacking CO_2 concentration data (no air or water concentration), or in case of malfunctioning of the

Fig. 1. Photographic view of eddy correlation devices mounted at the end of the West-boom at MPN. Marked: KNMI devices from which the data where used in the present analysis. A: Solent sonic anemometer; B: Infrared Fluctuation Meter (IFM).

IFM during a significant portion of the run. Air concentrations obtained at a wind direction of less than 220° might have been affected by CO_2 sources over land (Kunz et al., 1998), in which case there may be some doubt about the homogeneity of c_a. Therefore, runs performed under such conditions were rejected as well. Finally, a few runs from ASGAMAGE-A were rejected because there was evidence of strong inhomogeneities in the air as well as in the water. In these cases, an exceptionally strong peak in the time record of c_a and the sea water temperature was accompanied by a dip in c_w.

CO_2 fluxes were corrected for the effect of heat and water vapour on the density of air, following Webb et al. (1980). Cross-talk due to radiative absorption by water vapour in the passband of CO_2 absorption was further investigated afterwards, in a controlled laboratory experiment described by Kohsiek (1998). Corrections were based on results from this experiment and applied in the form:

$$F^c_{CO_2} = F^u_{CO_2} - \varepsilon F_{H_2O}, \tag{2}$$

where F_{CO_2} and F_{H_2O} are the fluxes of CO_2 and H_2O, respectively ($g\,m^{-2}\,s^{-1}$), and the superscripts c and u denote the corrected and the uncorrected flux. The cross-talk factor, ε, varies between -2.9×10^{-4} and $+4.3 \times 10^{-4}$, depending on the filter combination used in the IFM (Kohsiek, 1998). Eq. (2) can be regarded as a simplified form of the correction proposed by Leuning and Moncrieff (1990).

The impact of both the Webb correction and the cross-talk correction is illustrated in Fig. 2, which shows CO_2 fluxes from the B-period. It can be seen that the Webb correction is by far the larger of the two corrections. This correction sometimes has a dramatic effect on the CO_2 flux. Most uncorrected negative (downward) CO_2 fluxes became positive (upward) after the Webb correction had been applied. Positive fluxes

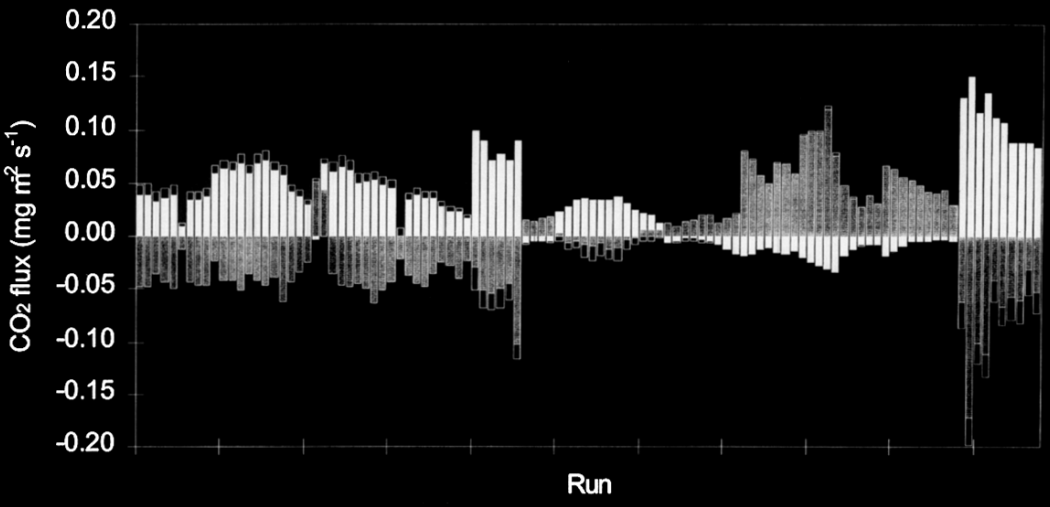

Fig. 2. Illustration of the impact of the Webb-correction (Webb et al., 1980) and of the cross-talk correction on the CO_2 fluxes measured during ASGAMAGE-B. The correction for cross-talk was applied after the Webb correction. Light shaded areas: raw fluxes; dark shaded areas: Webb correction; blank area: cross-talk correction. The sum of the contributions yields the total flux of a run.

were to be expected for the B-period (see Subsection 3.1). The effect of the cross-talk correction is less dramatic, but still significant. In general, the sensible and latent heat fluxes were much smaller during ASGAMAGE-A, so that the corrections to be applied were much smaller as well.

Despite the care taken to avoid or correct for cross-talk, a strong correlation was found between the water vapour flux and the CO_2 flux for data obtained at very high relative humidity (>96%). These data were presumably affected too strongly by the presence of water in the optical path of the IFM. Therefore, data that were obtained at a relative humidity of over 95% were also excluded from further processing.

2.6. *Determination of k_w*

To compute k_w from $F^c_{CO_2}$, c_a, and c_{eq}, we applied the following form of (1):

$$k_w = \frac{F^c_{CO_2} K_H}{c_{eq} - c_a}, \tag{3}$$

where we used the fact that $c_E = c_a/K_H$ and $c_w = c_{eq}/K_H$. The dimensionless Henry coefficient K_H was computed as a function of temperature and salinity, using the solubility data of Weiss (1974). Note that the solubility S, and K_H are related by $K_H = 1/(SRT)$. The fits proposed by Weiss (1974) result in $K_H \approx 1$ for CO_2 in the case of sea water of 12°C with a salinity of 31‰.

In all computations, we used the sea water temperature observed in situ near the platform. This temperature was measured using a PT100 resistance thermometer just below the water surface, at a maximum depth of 30 cm below the sea surface. A number of CTD (Conductivity, Temperature Depth) casts taken near the platform (made available by courtesy of the Department of Oceanography of the University College Galway, UCG, Ireland, and the Southampton Oceanographic Centre, SOC, UK) showed that the temperature measured at this particular depth can be considered as representative for all depths: temperature differences over the entire depth near the platform were within 0.1 K, only occasionally up to 0.3 K. To avoid temperature differences between the water at the sampling level and in the equilibrator as much as possible, the pumping rate was kept high (see Subsection 2.3). Furthermore, the equilibrator was placed in a vessel that was continuously flushed with the sample water. Comparison of the temperature of the sample water and the in situ sea water temperature showed that temperature differences were at most 0.1 K.

The effect of salinity on K_H is of secondary importance only. Therefore, in all cases the salinity was taken to be 31‰. This value was derived from the CTD casts. The salinity stratification appeared to be insignificant if the aim is to compute k_w: differences usually were within 0.1‰. Only in one extreme case a difference of about 3‰ was observed between the upper 3 m of the water and the water at deeper layers.

Results for k_w were normalised to salt water at a temperature of 20°C by means of the Schmidt-number dependence suggested by Wanninkhof (1992), valid for the wind speed range observed during ASGAMAGE (3.5–15 m s^{-1}):

$$k_{660} = k_w \left(\frac{660}{Sc}\right)^{-0.5}, \quad (4)$$

where k_{660} denotes the normalised value of k_w and 660 is the Schmidt number for CO_2 in salt water at a temperature of 20°C. The dependence of Sc on temperature was computed using the fit for sea water (with salinity 35‰) given by Wanninkhof (1992). Note that many authors normalise k_w using a Schmidt number of 600, which applies to fresh water.

3. Results

3.1. c_w, c_E and CO_2 fluxes

Fig. 3 shows the evolution of the actual CO_2 concentration in water, c_w, and of the equilibrium concentration ($c_E = c_a/K_H$) observed during ASGAMAGE, along with the corresponding CO_2 fluxes.

The concentration difference $\Delta c = c_w - c_E$ drives the CO_2 flux and is used to compute k_w (see Subsection 2.6). Note that the concentration has been converted to units of mg m^{-3}. Δc was positive during the A-phase and negative during the B-phase. The accompanying fluxes have the correct sign in most cases. However, within the respective observation periods no strong correlation with Δc can be observed. This is an indication of the strong influence of other factors on the CO_2 flux. Most fluxes are between −0.05 and 0.05 mg m^{-2} s^{-1}.

Due to the rising water temperature which causes the solubility to decrease (data not shown) c_E slowly decreased during the ASGAMAGE-A period. During the B-phase, c_E tended to increase because of the decreasing water temperature.

The actual water concentration, c_w, gradually increased from about 400 mg m^{-3} in May to about 850 mg m^{-3} in November. The ASGAMAGE data are in reasonable agreement with the data reported by Hoppema (1991), who presented evidence that the seasonal trend observed near the Dutch coast may well be related to biological processes. In this region of the North Sea, c_w is occasionally affected by exhaust products from the rivers Scheldt, Rhine and Meuse (Hoppema, 1991; Frankignoulle et al., 1996).

3.2. Air–sea transfer velocity, k_w

The resulting values of k_{660} for the combined (A + B) data set are depicted in Fig. 4 as a function of $U_{N,10}$, the wind speed adjusted to a height of 10 m and neutral atmospheric conditions, taken relative to the velocity of the water. The data cover a wide range of wind speeds (3.5–15 m s^{-1}). The scatter is rather large because it includes the scatter in the flux data as well as in the concentration difference. Nevertheless a trend of k_{660} increasing with wind speed can be observed.

We will analyse the results in terms of a fit of k_{660} to $U^2_{N,10}$. As such our result can be directly compared to the well-known relation suggested by Wanninkhof (1992), who proposed $k_{660} = 0.31U^2_{N,10}$ cm h^{-1}. An alternative would be to follow Liss and Merlivat (1986) and to derive a piecewise linear fit to the data, but such a fit can also be represented by a quadratic fit. Within the ASGAMAGE wind speed range the Liss and Merlivat (1986) fit can be approximated by $k_{660} \approx 0.17U^2_{N,10}$ cm h^{-1}.

A first analysis showed that fits of k_{660} to $U^2_{N,10}$ could not be considered as statistically different for the A and the B phase ($p > 0.05$, with p denoting probability). Therefore, further analyses were performed using the pooled data set.

Two methods were now applied to determine the coefficient that relates k_{660} to $U^2_{N,10}$. The first method relates k_{660} directly to the square of $U_{N,10}$ by fitting

$$k_{660} = a + bU^2_{N,10}$$

with a and b regression coefficients. This procedure minimises the deviation between the fit and the observed values of k_{660}. The second method

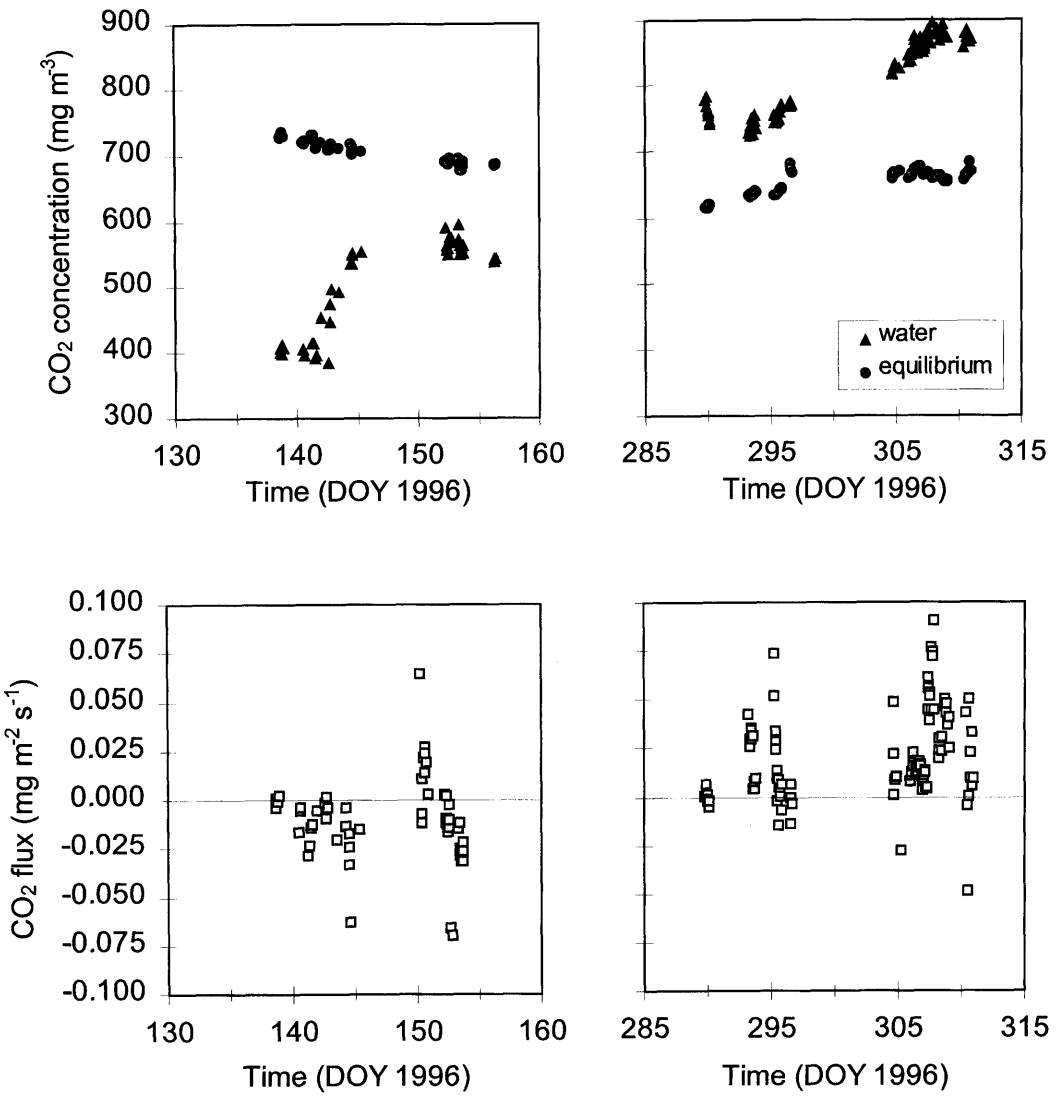

Fig. 3. Observed CO_2 concentration in water (c_w, triangles) and equilibrium concentration ($c_E = c_a/K_H$; circles) (upper panels), and CO_2 fluxes (lower panels, squares) for ASGAMAGE-A (left) and ASGAMAGE-B (right). Time is in Day of Year 1996 (DOY 1996).

minimises deviations from the observed CO_2 flux by fitting

$$F^c_{CO_2} = (a + bU^2_{N,10})(\mathrm{Sc}/660)^{-0.5}\Delta c. \quad (6)$$

In both cases, calculations were made in which the coefficient a in (5) and (6) was either chosen zero or calculated to obtain the best least squares fit. Note that for most purposes it will be desirable to correctly model the flux, so a fit based on (6) is preferable to one that is obtained using (5).

First, the best fit of (5) to the data was determined. Outliers were marked by applying Chauvenet's criterion (Wieringa, 1973) repeatedly, using the standard deviation of the residuals from the fit. They are shown in Fig. 4 as crosses, but were not used to determine the coefficients of the

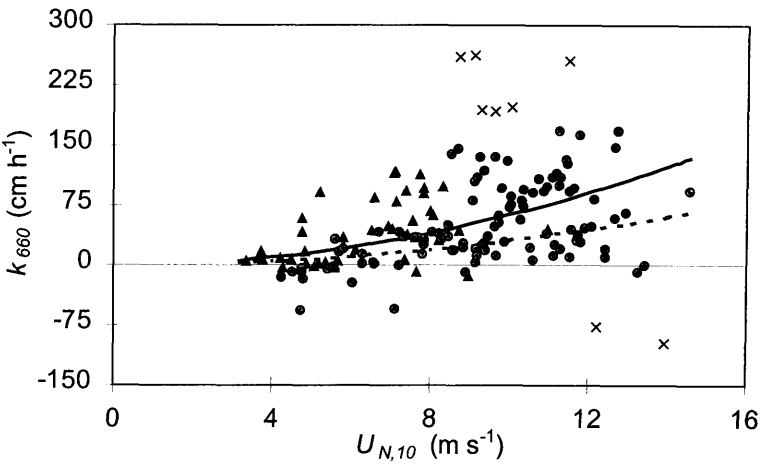

Fig. 4. Computed k_w normalised to salt water at 20°C, k_{660}, for the ASGAMAGE data set: Triangles: ASGAMAGE-A; Circles: ASGAMAGE-B; Crosses: outliers according to the Chauvenet criterion, not used in the fits as discussed in the text. A quadratic fit through the data, $k_{660} = 0.54U^2_{N,10}$ is also shown (solid line), along with the Wanninkhof (1992) fit, $k_{660} = 0.31U^2_{N,10}$ (dashed line). See text and Table 1 for more information about the quadratic fit.

fits. Thus, the influence of presumably erroneous combinations of flux and Δc was removed.

The remaining data set ($n = 147$) was used to determine the coefficients a and b according to the other methods as well. Results for all fits are summarised in Table 1. The fit (6) with $a = 0$, $k_{660} = 0.54$, is plotted in Fig. 4, along with the fit proposed by Wanninkhof (1992). Fig. 5 shows the 95% confidence region for the coefficients a and b, using the k_{660} optimisation procedure (eq. (5); solid line) and the flux optimisation procedure (eq. (6); dashed line) respectively, along with the best fits (circles), the fits with $a = 0$ (diamonds) and the Wanninkhof (1992) fit, $a = 0$ and $b = 0.31$ (filled square).

Depending on the method used, the coefficient b of the optimum fit varies between about 0.47 and 0.58, but the differences are not statistically significant ($p > 0.05$). The 95% confidence interval for b with $a = 0$ extends from 0.479 to 0.672 (cm h^{-1} s^2 m^{-2}) using (5), and from 0.459 to 0.625 (cm h^{-1} s^2 m^{-2}) using (6). For the present set of data, b could statistically attain a minimum value of 0.270 or 0.320 (cm h^{-1}s^2 m^{-2}), but then an intercept of, respectively, 26.6 and 19.6 cm h^{-1} would be required. This does not seem physically plausible. The present best fits lead to intercepts of 10.9 and 6.7 cm h^{-1}, respectively. The fraction of variance in k_{660} explained by the various fits, R^2_k is also given in Table 1. R^2_k is rather low in all cases (17–19%). In spite of that, the hypothesis that there is no relation with $U_{N,10}$ must be rejected ($p < 0.001$). The fraction of the flux variance that can be reproduced by assuming a dependence of k_{660} on $U^2_{N,10}$, R^2_F, lies between 57% and 58%.

Table 1. *Fits of (5) and (6) to the ASGAMAGE data set ($n = 147$). R^2 is the fraction of the variance in k_{660} (subscript k) or the CO_2 flux (subscript F) explained by the fits*

Eq.	a (cm h^{-1})	b (cm h^{-1} s^2 m^{-2})	R^2_k	R^2_F
(5)	0.0	0.576	0.1764	0.5721
(5)	10.9	0.469	0.1893	0.5753
(6)	0.0	0.542	0.1722	0.5750
(6)	6.7	0.480	0.1841	0.5785

In all cases, the results from ASGAMAGE are significantly ($p < 0.001$) different from Wanninkhof (1992) ($a = 0$ and $b = 0.31$ (cm h^{-1} s^2 m^{-2}); see also Fig. 5). Differences with the parameterisation proposed by Liss and Merlivat (1986) ($a = 0$ and $b \approx 0.17$ (cm h^{-1} s^2 m^{-2}) are greater. However, there is no order of magnitude difference as with earlier results from eddy correlation measurements.

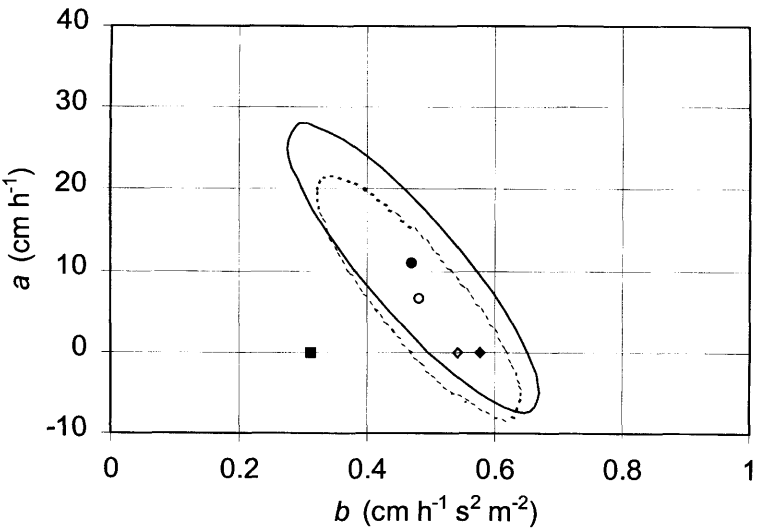

Fig. 5. Coefficients a and b resulting from fits of (5)–(6) to the pooled ASGAMAGE data set: Open circle: best fit of (5); Open diamond: fit of (5) with $a = 0$; Filled circle: best fit of (6); filled diamond: fit of (6) with $a = 0$; filled square: Wanninkhof (1992); dashed line: 95% confidence region for (a, b) from (5); solid line: 95% confidence region for (a, b) from (6).

The fits with $a = 0$ are not significantly different from those with a free to vary. On the other hand, $a = 0$ requires larger slopes b. The current values of the coefficient a will not be very reliable. The vertical extent of the 95% confidence region is very large, due to the lack of data between $U_{N,10} =$ 0 m s^{-1} and 4 m s^{-1} and the large scatter at higher wind speeds. Therefore, it is suggested to use $a =$ 0, at least for a wind speed over 4 m s^{-1}. For smaller wind speeds, a correction due to, e.g., chemical enhancement might be required, leading to a small offset at $U_{N,10} = 0$ (Wanninkhof, 1992).

The exponent in the relationship between k_{660} and $U_{N,10}$ has been based on the work of Wanninkhof (1992). As an alternative, a fit with zero intercept and the exponent optimised, instead of 2, was determined using the flux optimisation procedure. The relation then becomes $k_{660} =$ 1.75 cm h^{-1} ($R_k^2 = 0.2005$, $R_F^2 = 0.5851$) but this fit is not significantly different from the one represented by (6) with $a = 0$.

The possible error introduced by the assumption that the atmosphere as well as the water are well-mixed was also investigated. In most cases, the observed CO_2 concentration differences (see Subsection 2.4) in the water, expressed as c_{eq}, were within 27 ppm, whereas concentration differences in the air were at most some 2 ppm (Kunz et al., 1998). Increasing the absolute value of the observed Δc systematically by 29 ppm (≈ 52 mg m^{-3}) leads to $b = 0.428$ (cm h^{-1} s^2 m^{-2}) using (6) with $a = 0$; a systematic reduction of the observed Δc by the same amount results in $b =$ 0.730 (cm h^{-1} s^2 m^{-2}). However, the observed gradients were not systematic, and the maximum observed difference (29 ppm) was used in these calculations. Therefore, it is very unlikely that the present results could be reconciled with previous results from the indirect techniques by assuming a strong stratification with respect to CO_2 concentration in water or air (cf. Oost et al., 1995).

Finally, deviations between the fit (6) and the actual k_{660} were investigated. The correlation between the various data and the residuals was computed for the ASGAMAGE-A and B data sets separately, as well as for the combined data set. Apart from a slight correlation with global radiation ($r \approx 0.3$), no other correlations were found that were consistent for the two data sets and not autocorrelations (for example, k_{660}, flux). The resulting weak correlation with global radiation may arise from an interplay between several factors, such as the impact of light on photosynthetic activity and various other biochemical activities

(Sieburth, 1983), water temperature with its effect on solubility and static stability of the water column (Soloviev and Schlüssel, 1996). The present data set does not allow to draw more firm conclusions about a possible effect of light on k_{660} or k_w.

4. Concluding remarks

During ASGAMAGE the eddy correlation technique to determine fluxes of CO_2 over sea has been applied by KNMI with reasonable success. Special care was taken to avoid the effects of cross-talk on the fluxes. The difference $\Delta c = c_w - c_E$, was determined simultaneously by KNMI, TNO-FEL, NIOZ and MPIC. A set of consensus values of c_E and c_w was constructed from the contributions of the various institutes (Jacobs et al., 1998b) and these data were combined with the KNMI CO_2 flux data.

From the combination of CO_2 flux data and Δc we were able to compute the air–sea transfer velocity of CO_2, k_w, directly, without the need to use a Schmidt number dependence. Values of k_w were normalised to k_{660}, which applies to sea water at a temperature of 20°C and with salinity 35‰. Although k_{660} shows a considerable scatter, a first-order effect of wind speed on k_{660} could be determined. Furthermore, data from the two separate experimental periods with opposite direction of the flux (ASGAMAGE A and B) were consistent.

The results for k_{660} were fitted to the square of the wind speed using two different methods. The first method minimises the deviations of the observed k_{660} from the fit to wind speed. The second method minimises the deviations between the observed flux and the flux that can be computed using the fitted k_{660}, and the observed Δc. Practical applications will mostly be aimed at predicting the flux correctly. Therefore, the use of results from the second method is recommended. Because the transfer of CO_2 at zero wind speed may be expected to be very small (see, for example, Wanninkhof, 1992), fits with zero intercept are preferred. Then, the following parameterisation can be based on the present data set:

$$k_{660} = 0.54 U_{N,10}^2, \tag{7}$$

where k_{660} is in cm h^{-1} and $U_{N,10}$ in m s^{-1}. If (7) is used to obtain the actual value of k_w, a correction based on the Schmidt number dependence suggested by, for example, Wanninkhof (1992) has to be applied.

The 95% confidence interval of the coefficient in (7) extends from 0.46 to 0.63, or $0.54 \pm 15\%$. The coefficient in (7) is significantly higher ($p < 0.001$) than the one from the parameterisation of Wanninkhof (1992), who found a coefficient of 0.31. The difference with the parameterisation proposed by Liss and Merlivat (1986) is larger. Thus, results from the direct method again lead to k_{660} values larger than those from the indirect techniques such as the dual tracer technique (Wanninkhof et al., 1993) or isotopic methods (Broecker and Peng, 1974). However, the difference is now within a factor of 2 to 3. We believe that the remaining difference between the eddy correlation results and those from the indirect method can no longer be attributed simply to technical inadequacies. We therefore assume that the primary cause of the remaining discrepancy of roughly a factor of three therefore has to be found in either the extent to which the basic assumptions for both methods are fulfilled or in differences in the actual implementation of these methods that make their results difficult to compare. Further research, aimed at resolving the nature of the remaining difference, is needed because reliable estimates of atmospheric trends of CO_2 concentration require reasonably accurate estimates of air–sea fluxes of CO_2 and therefore of k_w.

It is unlikely that the present results are affected to a large extent by stratification with respect to CO_2 concentration in the water or the air (cf. Oost et al., 1995). However, on theoretical grounds concentration gradients close to the air–sea interface must be expected: without such gradients, fluxes cannot be maintained. Generally, such a gradient is thought to be confined to the skin layer, of which the depth is in the order of 10^{-3} to 10^{-5} m (GESAMP, 1995). A concentration gradient beyond the skin layer, as suggested by, for example, Kitaigorodskii (1984) can not be excluded. Such a CO_2 concentration gradient might help to explain differences between direct and indirect methods to determine k_w. Theoretical research into this subject within the framework of ASGAMAGE will further address this issue.

The present data set does not allow definition of relations between k_{660} and geophysical para-

meters other than $U_{N,10}$. Correlations between the residuals from the fit and other parameters, were found to be very low. Possible effects of other features, such as CO_2 gradients in the water or the air, Langmuir circulations, wave-enhanced turbulence, bubble clouds, the presence of surface active material and rain are the subject of further research.

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