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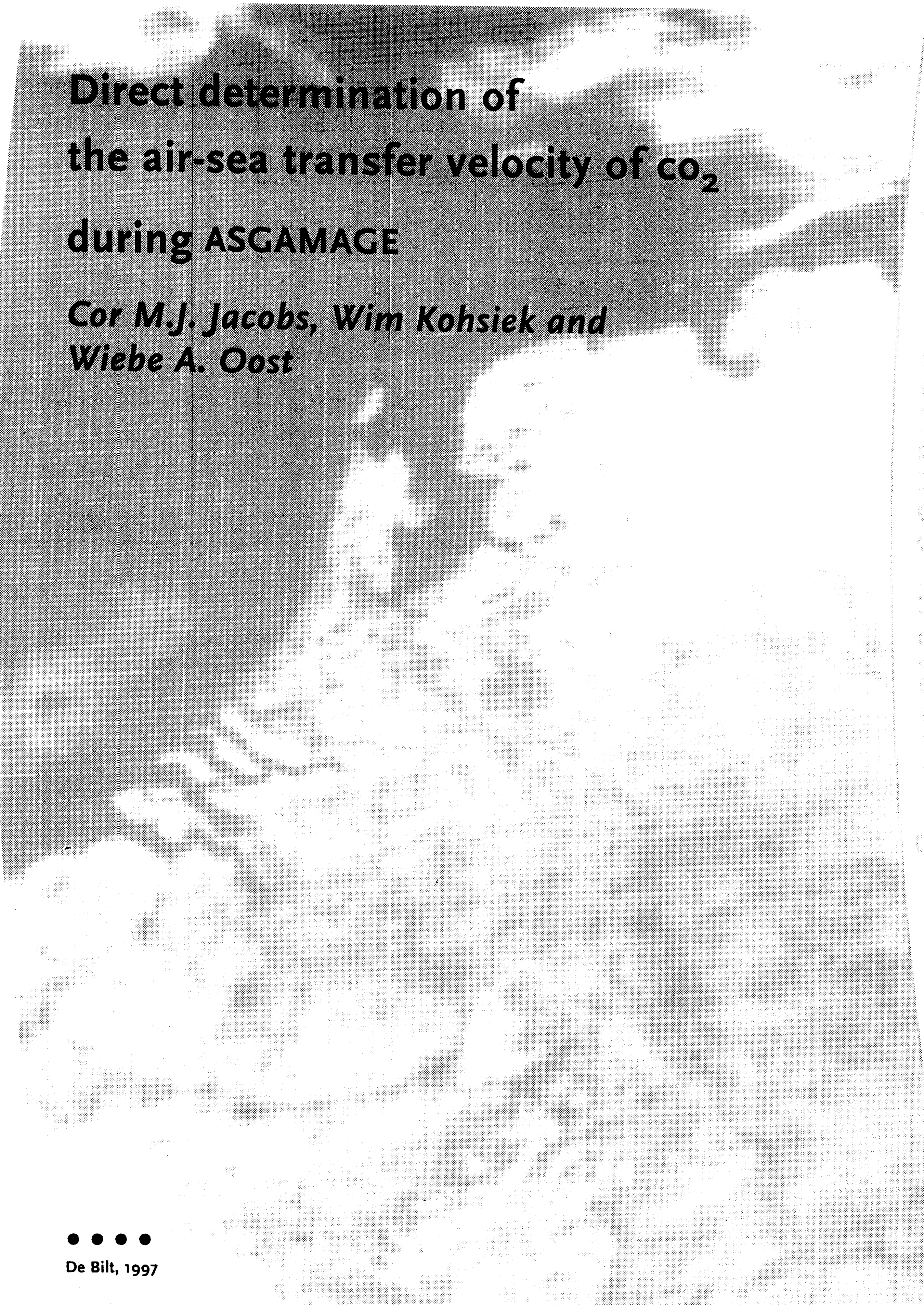

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Koninklijk Nederlands Meteorologisch Instituut

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PO Box 201
3730 AE De Bilt
Wilhelminalaan 10
De Bilt
The Netherlands
Telephone + 31(0)30-220 69 11
Telefax + 31 (0)30-221 04 07

Authors: C.M.J. Jacobs, W Kohsiek and
W.A. Oost

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Abstract

In the year 1996 the experimental phase of the Air Sea GAs exchange in the framework of the Marine Aerosol and Gas Exchange program (ASGAMAGE) of the International Global Atmospheric Chemistry project (IGAC) was carried out. This report mainly focuses on the efforts of the Royal Netherlands Meteorological Institute (KNMI) to determine the air-sea transfer velocity of CO_2, k_w. The measurements reported on here 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). During two intensive observation periods, in May and October, respectively, CO_2 fluxes were determined by means of the eddy correlation technique. Special care was taken in the data treatment to avoid the effect of cross-talk on the CO_2 fluxes. The air-sea CO_2 concentration difference was measured simultaneously. Occasionally, mostly during slack tide, the vertical CO_2 concentration profile within the water was determined. On these occasions no significant gradients of CO_2 concentration in the water column between 0.5 and 15 m below mean sea level were found. The combination of flux data and air-sea concentration difference allowed us to compute k_w for CO_2 directly. Results from the two observation periods, one with downward CO_2 fluxes (May) and one with upward CO_2 fluxes (October), are consistent. A relation with the wind speed adjusted to a height of 10 m and neutral stratification, $U_{N,10}$, was determined for the pooled data from the two experimental phases. The relation recommended here reads: $k_w = 0.53 U_{N,10}^2$ cm h^{-1}, with $U_{N,10}$ in m s^{-1}. Relations with other geophysical parameters could so far not be found from the present data set.

Contents

1. Introduction

The role of the oceans in absorbing or releasing atmospheric constituents has received considerable attention during the last few decades because of the environmental problems man is facing. One important example is the possible global warming as a result of the antropogenic release of radiatively active gases. The global fate of most of the greenhouse gases, such as carbon dioxide (CO_2) and nitrogen oxide (N_2O), is at present poorly understood. One of the reasons is the large uncertainty as to the sink or source strength of the oceans (Houghton *et al*, 1995). Another example is the so-called "global distillation" process by which semi-volatile pollutants that are relatively resistant to biological, physical and chemical degradation tend to accumulate in the colder regions at high latitudes. Deposition onto and accumulation in the waters of these regions is an important pathway in the global distillation process (Wania and Mackay, 1993; Simonich and Hites, 1995).

Gas transfer across the atmosphere-ocean interface appears to be a key process in both examples given above. For this reason, much scientific attention has been paid to an estimation of the gaseous air-water fluxes.

Traditionally, the flux, F, is described by means of the transfer velocity, K, defined by (Liss, 1983; Liss and Merlivat, 1986):

$$F = K\Delta c \tag{1.1}$$

where Δc is the concentration difference that drives the flux. The transfer velocity consists of an atmospheric part, k_a, and a water phase part, k_w, so that $1/K=1/k_a + 1/k_w$. However, for many gases, for example CO_2, K is almost exclusively controlled by the speed of transport in the water phase (Liss, 1983), that is, $k_w << k_a$, so that $K \approx k_w$. Therefore, taking the concentration difference to be the water phase concentration difference, the flux of such gases is given by:

$$F = k_w(c_w - c_{eq}) \tag{1.2}$$

where c_w is the actual concentration in the bulk of the water, and c_{eq} is the equilibrium concentration in the water. By virtue of Henry's law, c_{eq} 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 is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T is absolute temperature.

The transfer velocity k_w is generally taken to be a function of wind speed (Liss and Merlivat, 1986; Wanninkhof, 1992). However, in reality k_w may be influenced by a variety of processes, such as wave breaking (enhanced turbulence, bubble gas transfer, disrupter of the skin layer, that is, the layer where molecular transport dominates), the presence of surface active material, rainfall, biochemical processes, special flow conditions in the water (Langmuir circulations, downbursts) *etceteras*. The behaviour of k_w as a function of these features is far from established. Thus, in practice the value of k_w is only known approximately.

Part of the uncertainty with respect to k_w is that many data have been obtained in wind-tunnels and wind-wave tanks. Because scaled wave properties and breaking characteristics in wind tunnel experiments are generally different from those observed in the field, results of such experiments must be applied with caution (Donelan, 1990; Woolf, 1993; Wu, 1996).

In the field, most of the results for CO_2 were obtained using indirect techniques such as the dual tracer technique (Wanninkhof *et al*, 1993; see Liss (1983) and Liss and Merlivat, (1986) for a discussion of other methods). Such methods rely heavily on the assumption that the diffusivity of gaseous substances can be related by the Schmidt number (*Sc*), which is the ratio of the molecular diffusivity and the kinematic viscosity. Then, k_w becomes proportional to Sc^{-n}. Often, n = $^1/_2$ to $^2/_3$ is taken (Liss and Merlivat, 1986), but values of n down to $^1/_3$ and up to 1 have also been used. Also, given the role of bubble mediated gas transfer, it is not entirely clear whether or not these methods are handicapped by the fact that they ignore control of the physico-chemical properties such as solubility on bubble mediated gas transfer (Merlivat and Memery, 1983; Woolf, 1993).

A potentially powerful method to determine k_w is to measure the fluxes directly by means of the eddy-correlation (EC) technique, in combination with a measurement of the concentration difference between the air and the water. Then, k_w can be computed directly from observations in the field, without Schmidt number dependence. Interestingly, results for CO_2 that were obtained during the late seventies and the early eighties show k_w values obtained with the EC-technique that are generally much larger than values obtained with the indirect methods (Broecker *et al*, 1986; Smith and Jones, 1986; Wesely, 1986).

The results from the EC-method have been criticised because none of the EC measurements were made on open sea, nor were they accompanied by accurate direct measurements of the air-sea concentration difference. Furthermore, their ability to measure small fluxes is limited. Finally, large corrections should be applied (e.g., the "Webb correction"; Webb *et al.*, 1980) and there is a possible lack of stationarity during the measurements (Liss, 1983; Broecker et al, 1986). However, previous experiences have led to improved technological applications in the EC instruments and new insights into the quality of the data and into the corrections to be applied. Thus, to date the EC-technique may be regarded as a reasonably reliable method for determining fluxes over sea.

In order to try to fill some of the gaps in our knowledge of air-sea gas exchange, the ASGAsex-MAGE project (Air-Sea GAS EXchange; MAGE is the Marine Aerosol and Gas Exchange subgroup of IGAC) was started. Four main goals have been defined for ASGAMAGE (Oost and Huebert, 1995):

- To test new methods for the measurement of air-sea fluxes of CO_2, N_2O, CH_4 and DMS
- To compare these methods with established methods for estimating transfer velocities of trace gases over sea
- To find relationships between the transport coefficients for the gas fluxes and relevant geophysical parameters
- To investigate whether significant vertical CO_2 concentration gradients can exist in the upper meters of the water column.

ASGAMAGE was set up to investigate air-sea gas transfer both experimentally and theoretically. It was started in 1996 and relies on the co-operation of 14 research groups from Europe, Canada and the United States of America. Appendix 1 lists the names of the contributing institutes and the acronyms used here to refer to these institutes. The present report focuses mainly on the contribution of the Royal Netherlands Meteorological Institute (KNMI) to ASGAMAGE, and is restricted to our efforts to determine the CO_2 transfer velocity. Some data from the Netherlands Institute for Sea Research (NIOZ) and TNO Physics and Electronics Laboratory (TNO-FEL) will be used here as well.

In order to determine k_w values for CO_2, the flux as well as the CO_2 concentration difference between the air and the sea were measured *directly*. Thus, k_w can be computed directly from the data. Although various methods to determine the fluxes were applied, only results from the EC method will be discussed here. The CO_2 concentration of the water was determined at various depths, which allows us to investigate the vertical stratification with respect to CO_2 as well. Experimental details are given in Chapter 2. Next, in Chapter 3, results will be presented and analysed. Finally, Chapter 4 presents some conclusions and recommendations.

2. Experimental set up

2.1. General

Two intensive observation periods of five weeks each were the core of the experimental phase of ASGAMAGE. The first period, ASGAMAGE-A, started on 6 May 1996. During this period, the CO_2 concentration in the water was expected to be low due to algal bloom. Thus, downward fluxes of CO_2 where anticipated. The second period, ASGAMAGE-B, started on 7 October 1996. During this period, respiratory release of CO_2 was expected to be dominant over photosynthetic consumption. Thus, a relatively high CO_2 concentration in the water was foreseen, accompanied by upward CO_2 fluxes.

A considerable portion of the experimental part of ASGAMAGE was 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). The platform was also used for HEXOS (Katsaros *et al.*, 1987; Smith *et al.*, 1994) and ASGASEX (Oost, 1995). Near the platform, the water reaches an average depth of about 18 m. During the B-phase measurements were also made from the UK ship RRS "Challenger" during a cruise in the area near MPN. Here, k_w was determined indirectly using the differential tracer technique (see, for example, Wanninkhof *et al*, 1993, for a description of this technique).

Because one of the main goals of ASGAMAGE was to determine k_w from direct measurements, the air-sea concentration difference as well as the CO_2 flux were measured simultaneously. In order to determine the air-sea concentration difference sample water taken from various depths and air samples taken at various heights were analysed at laboratory level (about 12 m above sea level) for their CO_2 concentration. Details on these analyses are given in Section 2.2. Four institutes were involved in determining the CO_2 concentration difference, viz. KNMI, MPIC, NIOZ and TNO-FEL. At the time of writing, the MPIC data were not available. Therefore, the description of these measurements will be confined to those of the other institutes. The fluxes of CO_2 were determined in various ways (Oost and Huebert, 1995), but here we restrict ourselves to the results from the EC-measurements performed by KNMI. More details on these EC measurements are given in Section 2.3.

In addition to the data needed to compute k_w directly, a number of geophysical variables were monitored continuously. These measurements included the measurements of whitecap coverage by visual as well as by acoustic techniques, observations on bubble clouds within the water, wave height and speed, and sea water temperature. Measurements furthermore included various meteorological variables such as wind speed and direction, global radiation, air temperature and humidity. These measurements are not described in detail, except where necessary for the discussion.

Incidentally some extra observations were made. These measurements include Planetary Boundary Layer observations by means of Lidar (Light detection and ranging), and CTD (Conductivity Temperature Depth) scans during slack tide.

Measurement runs were initiated if the wind direction was expected to be between South and North (180 ° - 360°). For this wind direction, flow distortion due to the presence of MPN is minimal and can be corrected for (Oost *et al*, 1994). Each run lasted somewhat less than 55 minutes. 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. Determination of the CO_2 concentration difference between air and water

CO_2 concentration in air

Air was sampled at various heights between sea level and a height of 30 m and analysed for its CO_2 content. KNMI sampled air at a height of about 12 m. During the A-phase, an ADC Mk3 infrared gas analyser (IRGA; The Analytical Development Company, 1988) was applied to determine the CO_2 concentration. For the B-phase an LI-6262 IRGA (LiCor, 1991) was installed to measure CO_2 content. Air samples analysed by NIOZ were taken from a height of 20 m. Air analysed by TNO-FEL was taken from a height of 12 m above mean sea level during the ASGAMAGE-A. During the B-phase air was sampled at 30 m, 12 m, 6 m and 2 m above mean sea level, respectively. In all cases, NIOZ and TNO-FEL determined CO_2 concentration by means of an LI-6262 IRGA.

CO_2 concentration in water

In order to determine the CO_2 concentration in water, submerged pumps were used to obtain water from a depth of 2, 3.5, 5, 7, 11 and 15 m below mean sea level, respectively. During ASGAMAGE-A, an additional level of 0.5 m below sea surface was sampled. Marine water was pumped simultaneously from two of these depths at all times. The sampled water was led to the laboratory level, about 12 m above sea level. 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. The sample levels were controlled manually. MPIC continuously analysed for CO_2 concentration at 0.5 m (A-phase) or 2 m (B-phase). KNMI, NIOZ and TNO-FEL, usually determined the concentration at one other depth, but these measurements were interspersed by short excursions to other depths.

Preferably around slack tide, profile measurements were made by switching the inlet depths along all the available levels (See Appendix 2 for more information about these profile runs). On these occasions, each level remained connected for 15-30 minutes, in order to allow the CO_2 measurement system to reach a new equilibrium. As illustrated in Appendix 3, the response time of the system was a few minutes only.

In order to determine the CO_2 concentration of the samples, the water was sprayed continuously into an equilibrator. Usually after five to ten minutes of spraying, the air in the equilibrator and the sample water were assumed to be in equilibrium (cf. Appendix 3). Then, the concentration in the water flowing through the equilibrator, c_w^{eq}, can be computed from the partial pressure of CO_2 in the equilibrator air, pCO_2^{eq}, because under equilibrium conditions the following relation holds:

$$pCO_2^{eq} = H c_w^{eq} \tag{2.1}$$

where H denotes the Henry coefficient, which is a function of temperature and salinity (Weiss, 1974). For CO_2, H is about 2400 $\text{Pa}\cdot\text{m}^3\,\text{mol}^{-1}$ ($\approx$24 $\text{atm}\cdot\text{l}\,\text{mol}^{-1}$) at 12°C and a salinity of $31^0/_{00}$. The corresponding solubility (=1/H) is about $4.2\text{x}10^{-4}$ $\text{mol}\,\text{m}^{-3}\,\text{Pa}^{-1}$ ($\approx 4.2\text{x}10^{-2}$ $\text{mol}\,\text{l}^{-1}\,\text{atm}^{-1}$).

The temperature dependence of the solubility also implies that a correction to the data may be necessary if the temperature difference between the water in the sea and the water in the equilibrator becomes too large. Therefore, the temperature of the sample water in the equilibrator was monitored as well. Furthermore, in order to avoid temperature differences as much as possible, the equilibrator was isolated and the pumping rate was kept high (see above). Comparisons between the temperature of the sample water with sea water temperatures that had been measured *in situ* showed that the temperature differences remained very small and could be neglected.

Sampling sequence and calibration of the IRGA

During both experimental phases, the IRGA operated by KNMI was calibrated on a daily basis for CO_2 by means of a span gas (358 ppm CO_2) and a CO_2-free nitrogen gas. Generally, only minor adjustments were needed during calibration to obtain the correct values for the calibration gases. Most of the time, the KNMI IRGA was set to analyse equilibrator air. Only on a few occasions outside air was analysed.

During the B-phase, the water vapour content of the sample air was also measured and used to correct for the influence of water vapour on the CO_2 concentration measurements. The corrections applied here are related to the effect of pressure broadening and to water vapour dilution. The internal software of the LI-6262 was used to correct for this effect *in situ* (LiCor, 1991). During the A-period only a dilution correction was applied afterwards. According to the manufacturer's specification, the error in the measured CO_2 molar fraction due to interference with water vapour is about 2% of the water vapour molar fraction, corresponding to less than 0.5 ppm CO_2 in the data from ASGAMAGE-A.

The TNO-FEL measurements were performed in an automated sampling and calibration cycle. Calibration was performed every two hours, using span gases of 248 and 454 ppm respectively, and using CO_2-free nitrogen gas. Between two calibrations, samples from the equilibrator air and outside air were sequentially analysed in cycles of 20 minutes, thereby flushing the measurement system prior to each separate analysis. The instrumental software correction provided with the IRGA was used to account for the influence of water vapour. More details on these measurements are given in Kunz and De Leeuw (1997).

NIOZ also used a fully automated sampling and calibration cycle. The cycle was completed in about 25 minutes. The instrument was calibrated using span gases of 250, 368 and 444 ppm, respectively. A second-order polynomial response curve was fitted through the calibration data and this calibration curve was used to analyse the samples. Sample air was dried completely in order to avoid the influence of water vapour on the measurements. During each cycle, the CO_2 concentration in the equilibrator air usually was determined five times, whereas the concentration of the outside air was determined once.

2.3. Eddy Correlation measurements

Principle

The instantaneous vertical transport of a species *x* is the product of its concentration, c_x, and the vertical velocity, *w*. The average of this product over a given time interval yields the average flux over that time interval. Upon applying Reynolds averaging, the average flux, F_x, is given by:

$$F_x = \overline{w}\,\overline{c_x} + \overline{w' c_x'} \qquad (2.2)$$

where overbars denote time averages. Defining the vertical turbulent flux as the transport perpendicular to the mean wind, and assuming $\overline{w} = 0$, the kinematic turbulent flux is equal to $\overline{w' c_x'}$ (see, for example, Wyngaard, 1991). Actually $\overline{w} \neq 0$ and a correction to account for this feature may be required (Webb *et al.*, 1980). The impact of this correction - known as the "Webb correction" - can be quite large. Its influence on our data is discussed in Section 2.4.

The Eddy Correlation technique directly relates to the flux definition (2.2). It requires the simultaneous measurement of *w* and c_x at a sampling frequency that allows the fluctuations contributing to the flux to be determined. In the atmospheric surface layer, eddies having frequencies between, roughly, 0.001 and 10 Hz are known to carry most of the flux (McBean, 1972; Kaimal *et al*, 1972). In order to resolve the highest frequency in this range, a sampling frequency of 20 Hz is required.

EC-devices used by KNMI during ASGAMAGE

During ASGAMAGE, wind velocity was measured by a three-dimensional Sonic Anemometer (Solent, Gill Instruments Ltd., Lymington, Hampshire, UK) as well as by a Pressure Anemometer (PA), an instrument developed at KNMI (Oost *et al*, 1991). Temperature was determined using a thin-wire thermocouple. The concentration of water vapour and CO_2 was measured by means of the Infrared Fluctuation Meter (IFM), developed at KNMI in co-operation with the US National Center for Atmospheric Research (NCAR) in Boulder, Colorado (Kohsiek, 1991).

The combination IFM/Sonic was intended to be the principle EC device for CO_2 flux measurements and were mounted near each other (separation distance about 0.3 m). The PA was foreseen for momentum flux measurements mainly. It was mounted some 1.8 m below the sonic anemometer and the IFM. Data from the PA/IFM combination are therefore less relevant in the present context and will not be presented here.

CO_2 flux devices: sonic anemometer and IFM

The sonic anemometer observes the travel time of sound pulse over a fixed distance. Because the speed of sound is influenced by the wind speed, the wind velocity can be obtained. Using sound pulses in three directions, the wind speed can be determined in any direction.

The IFM is an open path infrared sensor for the simultaneous measurement of the water vapour and CO_2 concentration. It consists of a box with the IR source, the detector, chopper/filter wheel and some electronics. The sensing head contains a folded open absorption path, enclosed by a ventilated perspex cylinder that protects the sensing head from rain. Two optical fibre cables transport the optical signals.

Although fast fluctuations are damped somewhat by the cylinder around the sensing head, fluctuations relevant to CO_2 flux (< 1 Hz, in our situation) can be sampled with confidence. Thus, the damping effect can be neglected.

Two optical filters pairs on a spinning filter wheel are applied to measure the concentration of water vapour (H_2O) and CO_2, enabling the measurement in four optical wavelength bands. 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. Usually, the filter pair of 4.2 and 3.9 μm is used to measure CO_2, and the filter pair of 2.6 and 2.3 μm for H_2O. However, as explained in Section 2.4, during ASGAMAGE special efforts were made to deal with cross-talk between CO_2 and H_2O. Therefore, other filter combinations were used as well (see Table 1, Section 2.4). The optics of the IFM sensing head are heated somewhat in order to avoid the formation of water films at high relative humidity. Furthermore, during the second part of ASGAMAGE-B the sensor optics were cleaned on a regular basis.

All EC 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. This position is outside the region where flow distortion due to the presence of MPN has a noticeable effect (Oost *et al*, 1994). Samples from the EC devices were taken at a frequency of 40 Hz and stored on the data handling system developed at the KNMI.

2.4. Processing of the data and determination of transfer velocity

Initial processing and selection of runs for further processing

The samples stored on the data handling system were processed by means of the software package DADiSP^{TM} (DSP Development Corporation, 1995). First, the 40 Hz samples were converted to their 20 Hz equivalents. From these samples, turbulence characteristics and the turbulent flux of momentum, sensible and latent heat and CO_2 were computed.

The data were corrected for instrumental flow distortion and flow distortion by MPN, following Oost (1991) and Oost *et al* (1994). Furthermore, corrections were applied for sensor separation and instrumental tilt. Next, some secondary, derived data were computed such as: Monin-Obukhov length (L); aerodynamic roughness length (z_o); wind speed at a height of 10 m, adjusted to neutral stratification ($U_{N,10}$; see section 3.4 for a definition of this quantity). All secondary data were computed using run-averaged primary data and stored on a run-by-run basis.

Runs were considered to be unsuitable for further processing if the run-averaged wind direction was less than 200 degrees (to be on the safe side with respect to wind direction), in case of a suspect $u'w'$ cospectrum (where u denotes wind speed along the x-axis), in case of rain during a substantial portion of the run, or in case of malfunctioning of various instruments. Applying these criteria, 107 runs could be retained for ASGAMAGE-A and 194 for ASGAMAGE-B.

Further processing of the CO_2 fluxes; Webb correction and correction for cross-talk

A further selection of runs was made to exclude data problematic with respect to the CO_2 measurements. In this selection, runs were rejected if the data were thought to be affected by dirty optics of the IFM, in case of insufficient pCO_2 data (no air or water pCO_2), or in case of malfunctioning of the IFM during a significant portion of the run. After application of these criteria, 66 ASGAMAGE-A runs were found to be suitable to compute k_w values and 128 runs from ASGAMAGE-B.

The CO_2 fluxes were corrected for the effect of heat and water vapour on the density of air, which cause $\overline{w} \neq 0$ (Webb *et al*, 1980). For CO_2 flux, the correction reads:

$$\overline{w'c'}_c = \overline{w'c'}_u + \mu(\bar{c}/\overline{\rho_a})\overline{w'\rho_v'} + (1+\mu(\overline{\rho_v}/\overline{\rho_a})(\bar{c}/T)\overline{w'T'} \qquad (2.3)$$

where the subscript c denotes "corrected," the subscript u denotes "not corrected," μ is the ratio of the average molecular mass of air to that of water, ρ_a is the density of dry air, and ρ_v the water vapour concentration.

Another, potentially large source of error to the CO_2 flux measurements is the effect of liquid water and water vapour on the CO_2 concentration measurements. This error is called cross-talk and can be related to the following processes:

❶ A water film occurring on the optics of the instrument. This problem can supposedly be aggravated with the presence of sea salt in the environment.

❷ Absorption of IR light by water vapour (lines or continuum) in the passband of the CO_2 absorption and/or reference filter.

❸ Pressure broadening, related to collisions of CO_2 with other molecules; among them is H_2O.

The first effect could be partly avoided by slightly heating the optics of the IFM. Furthermore, later in the experiment the optics were cleaned regularly. The second effect is thought to be negligible (Wolfe and Zissis, 1985) except if the 2.3 μm reference filter is used. The third effect might be considerable (Li-Cor, 1991).

The cross-talk was investigated by means of an additional laboratory study. A significant influence was found, which was presumably caused by a combination of the first (water film) and third (pressure broadening) effect. The impact of cross-talk was strongly affected by the filter combination used in the IFM.

Fortunately, it appeared possible to correct the CO_2 fluxes. The corrections to be applied are in the form:

$$\overline{w'c'_c} = \overline{w'c'_u} - \varepsilon \overline{w'\rho_v'} \tag{2.4}$$

where ε is the cross-talk factor. Table 1 lists the values of ε for the different filter combinations and the ASGAMAGE runs where a particular filter combination was used. It can be seen that in some cases, the cross-talk correction is negative. This negative value is probably due to cross-talk from the 2.6 μm channel into the 2.3 μm channel.

The Webb correction (2.3) was applied prior to the cross-talk correction (2.4). The impact of both corrections is illustrated in Figure 1, which shows data from the B-period. It can be seen that the Webb correction is by far the largest of the two corrections. This

Table 1 *IFM filter combinations used during ASGAMAGE and related cross-talk factor, ε. The second filter of each filter pair denotes the reference filter. For the 4.2 μm CO_2 filter (s) and (b) denote small passband and broad passband, respectively. Runs are labelled* Annn *and* Bnnn *for the A and the B phase respectively. Note: during runs 158-159 the H_2O channel was replaced by a second CO_2 channel (data not used).*

Filters (μm)		**Runs**	**Cross-talk factor, ε**
CO_2	H_2O		
4.2 (b) / 2.3	2.6 / 2.3	A001-A130	-2.6×10^{-4}
4.2 (s) / 2.3	2.6 / 2.3	B001-B112; B118-B122	-2.9×10^{-4}
4.2 (s) / 3.9	2.6 / 2.3	B113-B117; B123-B153; B155-B157; B160-B167; B204-B282	3.9×10^{-4}
4.2 (s) / 4.2 (b)	2.6/4.2 (b)	B154; B168-B203	4.3×10^{-4}

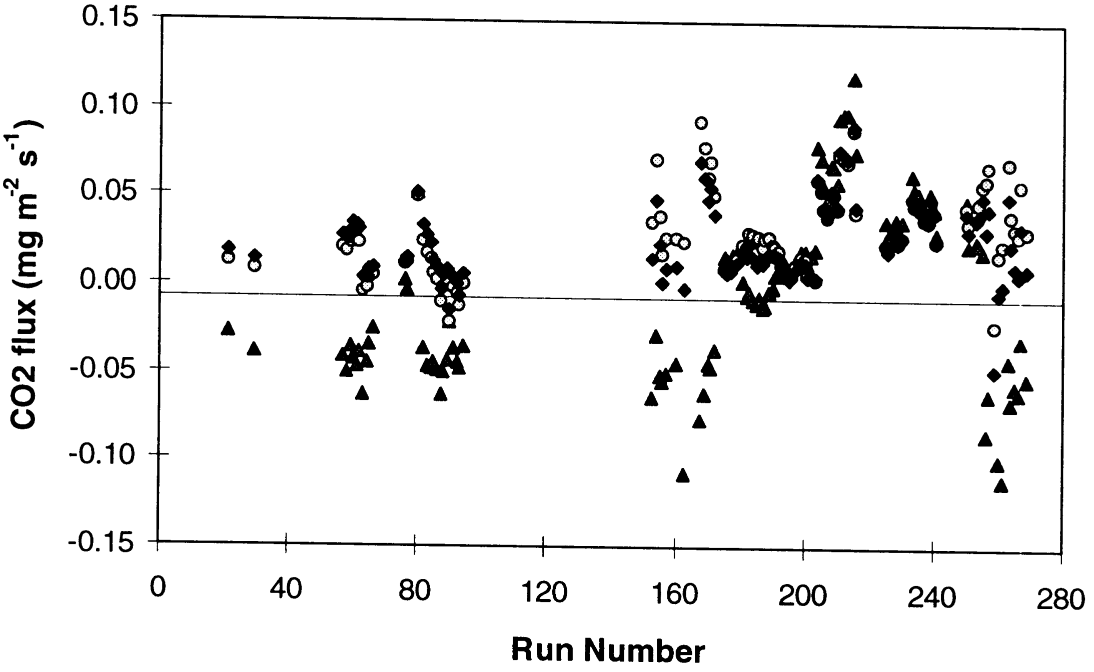

Figure 1. *Illustration of the impact of the Webb-correction (Webb* et al., *1980) and of the cross-talk correction on the CO_2 fluxes measured during ASGAMAGE-B. The correction for cross-talk was applied after the Webb correction. Triangles: raw fluxes; circles: Webb correction applied; diamonds: Webb and cross-talk correction applied.*

correction sometimes has a dramatic influence on the CO_2 flux. Most negative (downward) CO_2 fluxes became positive (upward) after the Webb correction had been applied. Recall that positive fluxes are to be expected for the B-period (also see Section 3.2). The effect of the cross-talk correction is less dramatic, but still significant.

Despite the care taken to avoid or correct for cross-talk, some data at very high relative humidity (> 96%) were presumably affected too strongly by the presence of water films on the optics. Therefore, data that were obtained at a relative humidity of over 95% were also excluded from further processing, which left 53 runs from ASGAMAGE-A and 123 from ASGAMAGE-B to compute k_w.

Further processing of the pCO_2 data and computation of k_w

The solubility, represented by H in (2.1), was computed from the temperature dependence suggested by Weiss (1974), using the sea water temperature measured near the platform. This temperature was measured using a PT100 resistance thermometer just below the water surface, at a maximum depth of 30 cm.

The temperature measured at this particular depth can be considered as representative for all depths. This conclusion is based on a number of CTD scans taken near the platform, which showed a temperature stratification insignificant to the problem of determining k_w values. Usually, temperature differences over the entire depth near the platform were within 0.1 °C, and occasionally up to 0.3 °C.

Most scans also showed a salinity stratification that may be considered as insignificant if the aim is to compute k_w. Differences usually were within $0.1^0/_{00}$. Only in one extreme case a difference of about $3^0/_{00}$ was observed between the upper 3 meters of the water and the water below this layer. The salinity used in all computations of H was derived from these CTD scans and taken to be $31^0/_{00}$. In the range of salinities observed during ASGAMAGE the effect of salinity on H is only of secondary importance, so that our choice to use a fixed salinity will only cause very small errors in the computed k_w.

To determine k_w, the CO_2 concentration in the outside air and in the equilibrator air were computed from the pCO_2 data, using

$$c_a^x = m \; pCO_2^x \, / \, RT^x \tag{2.5}$$

where c_a is CO_2 concentration in air (in g m^{-3}), the superscript 'x' is 'a' for outside air or 'eq' for equilibrator air, m denotes the molecular mass of CO_2 (44 g mol^{-1}) and pCO_2 is in Pa.

The outside air temperature was measured at a height of 12 m by means of a Väisälä aspirated thermo-hygrometer. The temperature of the equilibrator air was taken equal to the water temperature. Next, k_w was computed as

$$k_w = \overline{w'c'_c} K_H \, / \, (c_a^{eq} - c_a^a) \tag{2.6}$$

Recall that K_H is the dimensionless Henry coefficient H/RT (≈ 1 for CO_2 in the case of sea water of 12 °C and a salinity of $31^o/_{oo}$). Also, note that the CO_2 concentration in water is given by $c_w = c_a^{eq}/K_H$, while the equilibrium concentration is given by $c_{eq} = c_a^a/K_H$. Thus, (2.6) is fully consistent with (1.2) because $F \equiv \overline{w'c'}$.

3. Results

3.1. Vertical stratification with respect to CO_2

First, the CO_2 profiles in the water near the platform were examined. Results are shown in Figure 2 for the KNMI data. The profile names refer to the observation period (A or B) and runs are numbered chronologically. (Note that these run numbers are different from those of the flux measurements.) Details on the date and the time of the day for which the profiles are valid are given in Appendix 2. The graph shows the molar fraction of CO_2 in the equilibrator air.

In 20 out of 26 cases the differences in CO_2 content remained within 16 ppm over the entire depth. In five cases, the differences were 21 to 27 ppm. Only in one exceptional case (A15) a difference of 50 ppm was observed. The latter profile is probably highly influenced by industrial exhaust products carried with the river Scheldt into the North Sea. Given the rather long period over which the profiles had to be taken and given the error of typically 5 - 10 ppm in the measurement method, the observed differences cannot be considered as significant. We therefore conclude that it is allowed to treat the water near the platform as well-mixed with respect to CO_2 in the calculation of k_w. Note that profile A15 was taken after the regular runs had stopped, so that this particular profile does not influence the results presented below.

3.2. Evolution of CO_2 concentration in water and air

Figure 3 shows the evolution of the CO_2 concentration in water and of the equilibrium concentration ($c_{eq} = c_a^a / K_H$) as observed during ASGAMAGE. The concentrations during the A-phase (left panel) have been derived from KNMI data only. The concentrations shown for the B-phase are a combination of data from KNMI, NIOZ, TNO-FEL. The reason to combine the latter data is that the NIOZ data covered mostly the first part of the observation period CO_2, whereas the reliable KNMI and TNO-FEL data covered mostly the second part of the period. A comparison of the results from the different institutes showed that the results generally agreed within about 10 ppm ($\approx$18 mg m^{-3}) for the CO_2 content of outside air and about 20 ppm ($\approx$36 mg m^{-3}) for CO_2 content of equilibrator air and that the differences were systematic to a large extent (Jacobs *et al.*, 1997). In cases where more data points per run were available, the CO_2 content was computed as the average of all data.

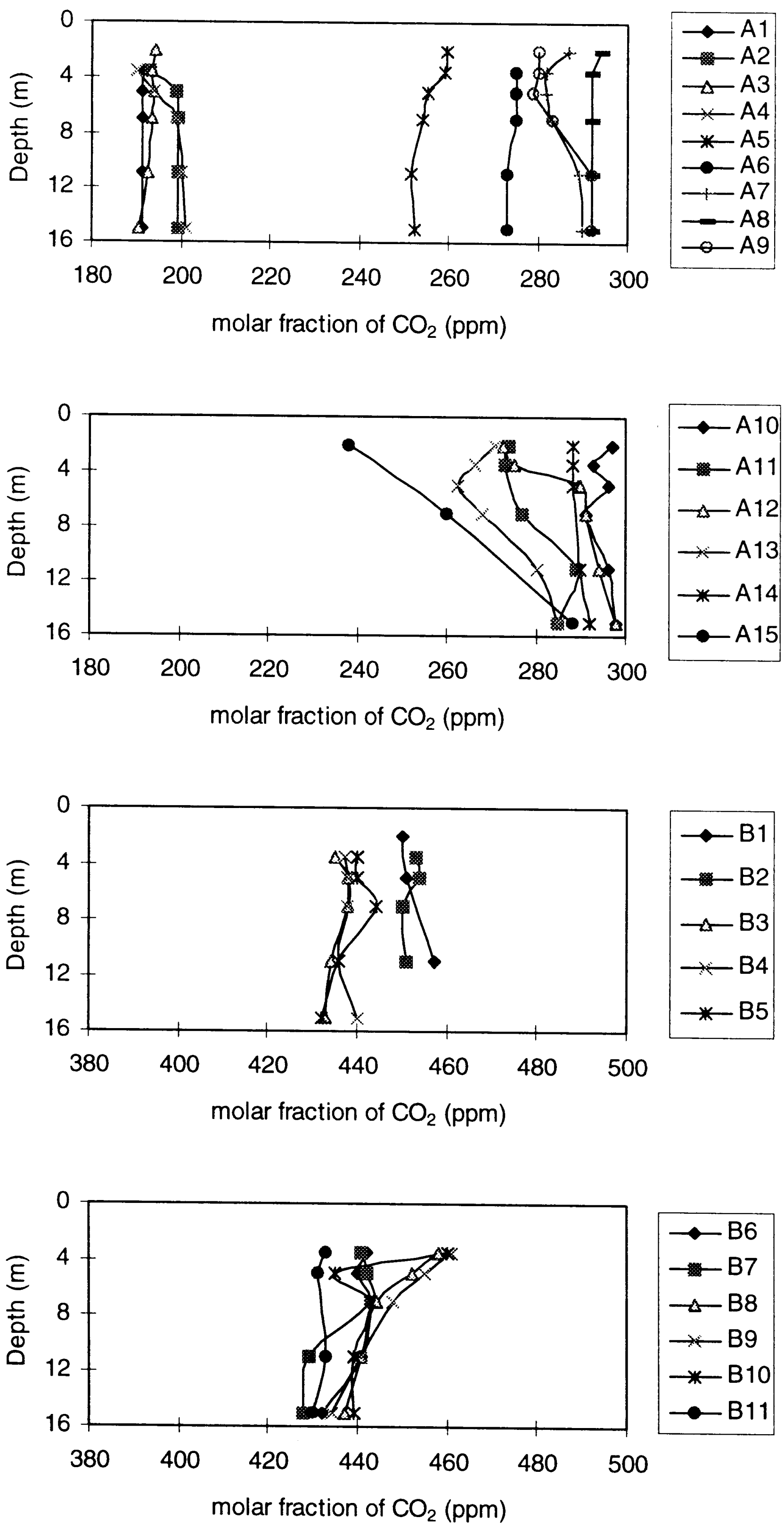

Figure 2. Observed profiles of the CO_2 content of the water, expressed as the molar fraction of CO_2 in the equilibrator air. The codes correspond to profile runs during the A-phase (Ann) and the B-phase (Bnn), respectively (see Appendix 2 for more details). Note the difference in scaling between the upper and the lower panels.

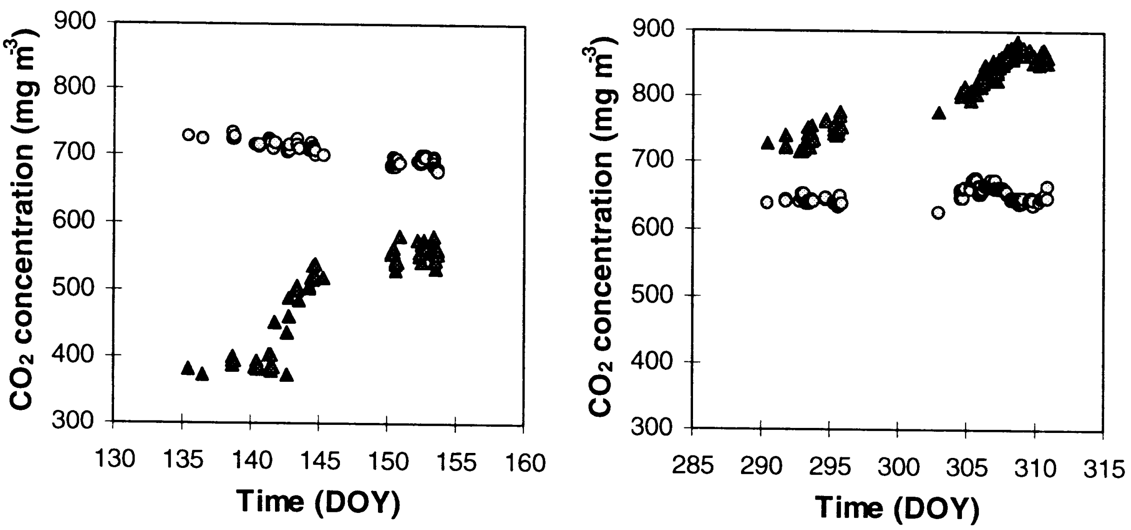

Figure 3. Observed CO_2 concentration in water (c_w, triangles) and equilibrium concentration (c_{eq} ; circles) for ASGAMAGE-A (left) and ASGAMAGE-B (right). Time is in Day Of Year (DOY).

The concentration difference that can be derived from Fig. 3, $\Delta[CO_2]= c_w - c_{eq}$, is the concentration difference that drives the CO_2 flux and is used to compute k_w (Eq 2.5). The air-sea concentration difference is positive during the A-phase, and negative during the B-phase. The sign of the air-sea concentration difference changes during summer, but this transition and the expected accompanying change in CO_2 flux direction was not captured by the ASGAMAGE experiments.

The equilibrium concentration slowly decreased during the ASGAMAGE-A period, due to the rising water temperature which causes the solubility to decrease. During the B-phase, c_{eq} appears to be at a minimum, with c_{eq} being approximately constant throughout the period.

From the combination of the data from ASGAMAGE A and B, it can be seen that the water concentration gradually increased from about 400 mg m^{-3} in May, up to about 850 mg m^{-3} in November. The concentration changed relatively fast during the observational periods. The observed evolution of c_w probably reflects the biological activity in the water near the platform. In May, there is an algal bloom accompanied by high photosynthetic activity. Next, because of a decreasing light intensity and an increasing respiratory activity, the respiratory processes will gradually become dominant over the photosynthetic activity and c_w increases.

3.3. CO_2 flux

Figure 4 shows the CO_2 fluxes corresponding to the concentrations depicted in Fig. 3. Most fluxes fall within the range between -0.05 and 0.05 mg m^{-2} s^{-1}. The fluxes do not show a clear trend consistent with the concentration difference shown in Fig. 3, except that the sign of the flux and the air-sea concentration difference correspond correctly in most cases.

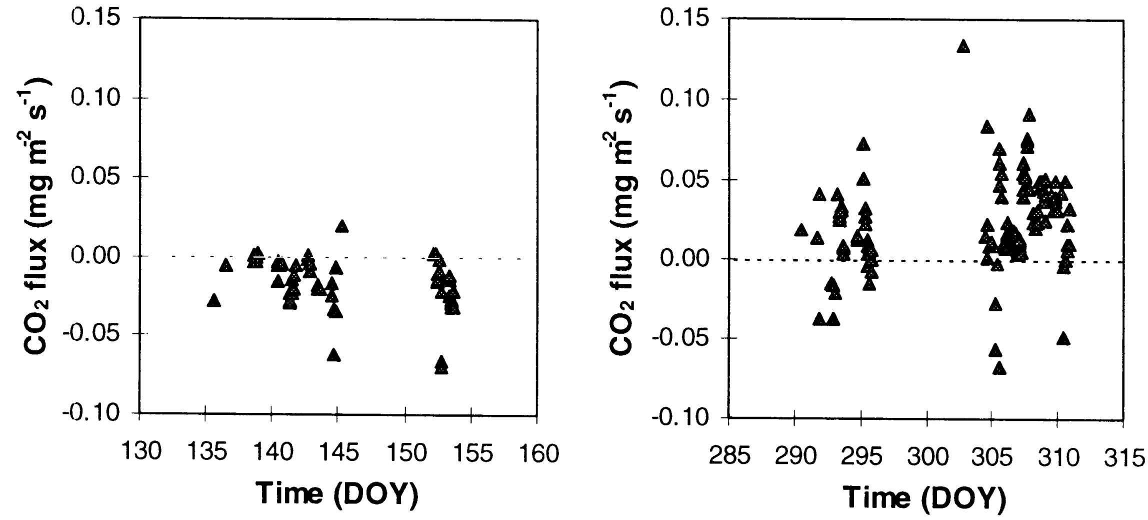

Figure 4. Observed CO_2 flux for ASGAMAGE-A (left) and ASGAMAGE-B (right). Time is in Day Of Year (DOY).

However, a better impression of the quality of the data than from Fig. 4 can be obtained if the fluxes are plotted versus the neutral wind speed at 10 m (see the next section for a precise definition of this quantity). This is shown in Figure 5, for both ASGAMAGE-A (triangles) and ASGAMAGE-B (circles). The crosses refer to fluxes that result in values of k_w that can statistically be considered as outliers (see below). More than half of the outliers are related to cases where the flux and the concentration difference are inconsistent with respect to their sign. Without these outliers, the flux data reduce to two

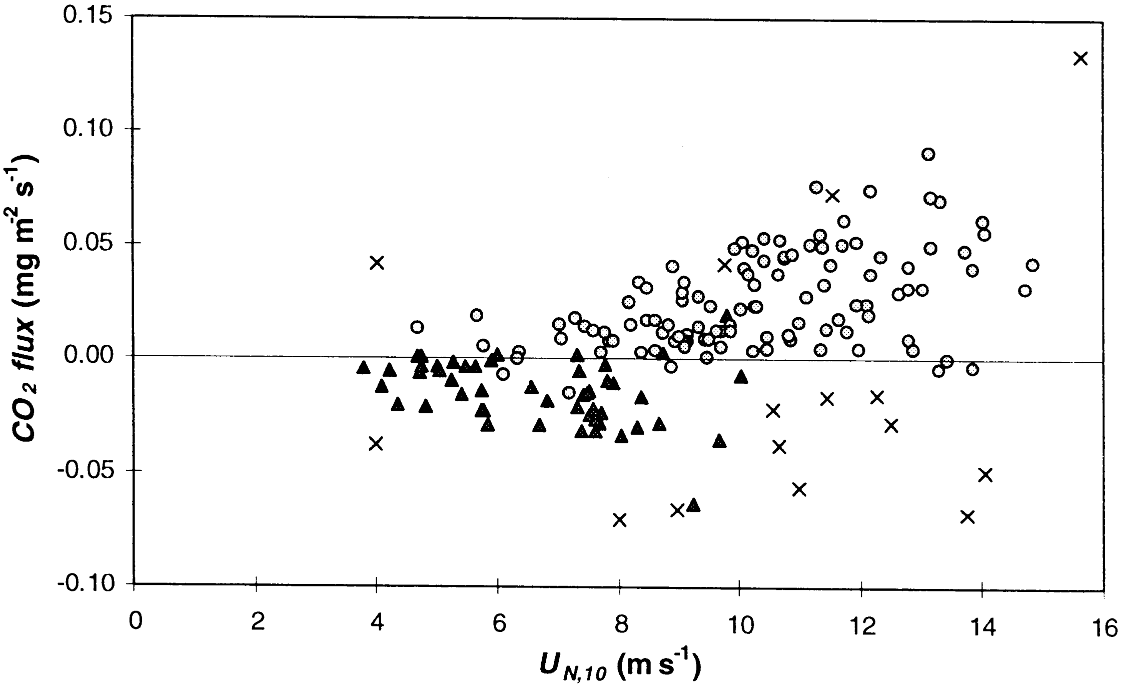

Figure 5. CO_2 flux versus neutral wind speed at 10 m. Triangles: ASGAMAGE-A; Circles: ASGAMAGE-B; crosses: rejected upon k_w analysis (see Section 3.4).

bands (positive and negative flux, respectively) with limited scatter. The data then give the impression of having a reasonable quality.

3.4. CO_2 transfer velocity k_w

From the data shown in Figs. 3 ($\Delta[CO_2]$) and 4 (flux) k_w was computed. The results were normalised to a water 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}):

$$k_w(@20) = k_w \left(\frac{Sc}{660}\right)^{-0.5} \tag{3.1}$$

where @20 denotes "at a temperature of 20 °C" and 660 is the Schmidt number for CO_2 for salt water with a temperature of 20 °C. The dependence of Sc on temperature was computed using the fit tabulated by Wanninkhof (1992). The fits therein are for a salinity of 35 $^o/_{oo}$ instead of the 31 $^o/_{oo}$ encountered near MPN, but the error involved is rather small. Note that some authors use Sc(@20) = 600, which applies to fresh water.

The resulting k_w values will be depicted as a function of "the neutral wind speed at 10 m" ($U_{N,10}$). This is the wind speed that would be measured under neutral conditions, at a height of 10 m, assuming that the logarithmic wind profile applies with the observed friction velocity, u_*, and the observed roughness length, z_o:

$$U_{N,10} = \frac{u_*}{\kappa} \ln\left(\frac{10}{z_o}\right) \tag{3.2}$$

with κ being the Von Kármán constant (0.4). Friction velocity, u_*, was computed from the data using $u_*^2 = -\overline{u'w'}$, with the observed wind speed fluctuations transformed such that $\overline{v} = 0$ (where v is the wind speed along the y-axis of the sonic). Furthermore, z_o was computed from the data as:

$$z_o = z_u \exp - [\kappa\, u(z_u) / u_* + \Psi(z_u / L)] \tag{3.3}$$

where z_u is the height of the sonic, u is the average wind speed, Ψ is the integrated stability correction for the flux-profile relationship for momentum (Paulson, 1970; Dyer and Hicks, 1970), and L is the Monin-Obukhov length defined by:

$$L = \frac{\theta_v}{\kappa g} \frac{u_*^3}{\overline{w'\theta'_v}} \tag{3.4}$$

Here, g is the acceleration of gravity (9.81 m s^{-2}), and θ_v is the virtual potential temperature = $\theta(1 + 0.61q)$, with q the specific humidity in kg kg^{-1} and θ the potential temperature in K.

Figure 6 shows the resulting k_w values as a function of $U_{N,10}$, for the combined (A+B) data set. The data cover a wide range of wind speeds (4-15 m s^{-1}). The scatter, that now includes the scatter in the flux data as well as the scatter in $\Delta[CO_2]$ is rather large and tends to increase with wind speed. Nevertheless a trend of k_w increasing with wind speed can be observed. Furthermore, it can be seen that the data from the two ASGAMAGE phases are consistent. Therefore, further analyses were performed using the pooled data.

Two methods were applied to determine the coefficient that relates k_w to $U^2_{N,10}$ (cf. Wanninkhof, 1992). In the first method, k_w, was related directly to the square of $U_{N,10}$ by fitting

$$k_w = a + bU^2_{N,10} \tag{3.5}$$

with a and b regression coefficients. This procedure minimises the deviation between the fit and the observed values of k_w. In the second method, deviations from the observed flux were minimised by fitting

$$F = (a + bU^2_{N,10})(Sc / 660)^{-0.5} \Delta[CO_2] \tag{3.6}$$

In both cases, calculations were made in which the coefficient a was either chosen zero or

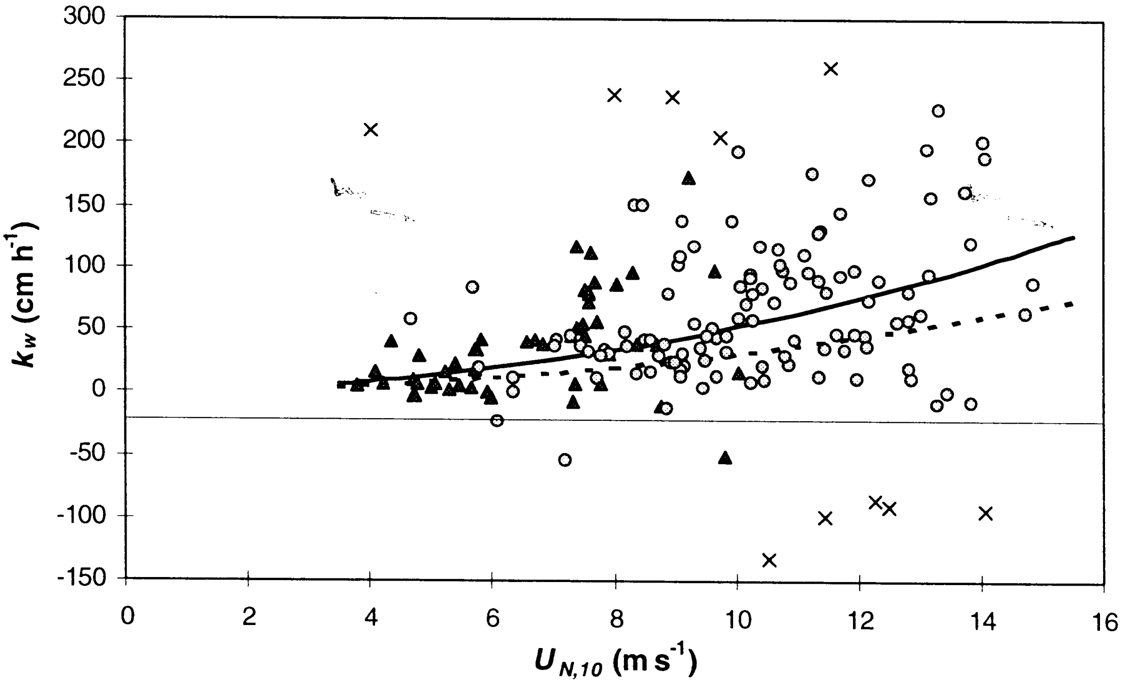

Figure 6. Computed k_w at 20 °C for the ASGAMAGE data set. Triangles: ASGAMAGE-A; Circles: ASGAMAGE-B; Crosses: outliers according to the Chauvenet criterion, not used in the fits as discussed in the text (not shown: four outliers with $k_w < -150$ cm h^{-1} and one with $k_w > 300$ cm h^{-1}). A quadratic fit through the data, $k_w = 0.527\, U^2_{N,10}$ is also shown (solid line), along with the Wanninkhof (1992) fit, $k_w = 0.31 U^2_{N,10}$ (dashed line). See text and Table 2 for more information about the quadratic fit.

left free. Note that for most scientific purposes it will be desirable to correctly model the *flux*, so a fit based on (3.6) is preferable to one that is obtained using (3.5).

First, (3.5) was fitted to the data with the coefficient *a* left free to obtain the best fit. To remove outliers, Chauvenet's criterion (Kotz and Johnson, 1982) was applied repeatedly, using the standard deviation of the residuals from the fit. Applying this criterion while optimising (3.5) to fit k_w-values removes erroneous combinations of the flux and $\Delta[CO_2]$.

The remaining data set (n = 161) was used to determine the coefficients *a* and *b* according to the other methods as well. Results for all the fits are summarised in Table 2. The fit (3.6) with $a = 0$ is plotted in Fig. 6, along with the fit proposed by Wanninkhof (1992). Figure 7 shows the 95% confidence region for the coefficients *a* and *b*, using the k_w optimisation procedure (3.5) and the flux optimisation procedure (3.6) respectively. The circles display the values of the best fits, while the results obtained with *a* set to zero are depicted by means of the diamonds. The combination of values proposed by Wanninkhof (1992), $a = 0$ and $b = 0.31$, is shown as well.

Depending on the method used the slope varies between about 0.45 and 0.60. This is still high as compared to the coefficient proposed by Wanninkhof (1992), but there is no order of magnitude difference. The coefficient of determination (R^2) given in Table 2 shows that in all cases, the fraction of the variance of k_w explained by (3.5)-(3.6) is rather low (18-21%). A little more than 55% of the flux variance can be reproduced by assuming a dependence of k_w on $U_{N,10}^2$.

The results from ASGAMAGE are significantly ($p < 0.001$) different from Wanninkhof (1992) ($a = 0$ and $b = 0.31$; see also Fig. 7). The 95% confidence interval for *b* with $a = 0$ extends from 0.526 to 0.663 using (3.5), and from 0.467 to 0.588 using (3.6). For the present set of data, a slope of 0.32 would be statistically possible, but an intercept of 20-30 cm h^{-1} would then be required. This seems not physically plausible. Similarly, the present best fits lead to rather high intercepts of 12.3 and 8.8 m s^{-1} respectively.

The fits with $a = 0$ are not significantly different from those with *a* free. On the other hand, $a = 0$ requires larger slopes *b*. Note that the current values of the coefficient *a* will be not very reliable, as reflected in the large vertical extent of the 95% confidence region,

Table 2 *Fits of (3.5) and (3.6) to the ASGAMAGE data set (n = 161).* R^2 *is the fraction of the variance in* k_w *(subscript k) or the* CO_2 *flux (subscript F) explained by the fits.*

Equation	***a*** $[cm\ h^{-1}]$	***b*** $[(cm\ h^{-1})(s^2 m^{-1})^{-1}]$	R^2_k	R^2_F
(3.5)	0.0	0.595	0.1911	0.5534
(3.5)	12.3	0.489	0.2034	0.5591
(3.6)	0.0	0.527	0.1735	0.5665
(3.6)	8.8	0.453	0.1856	0.5723

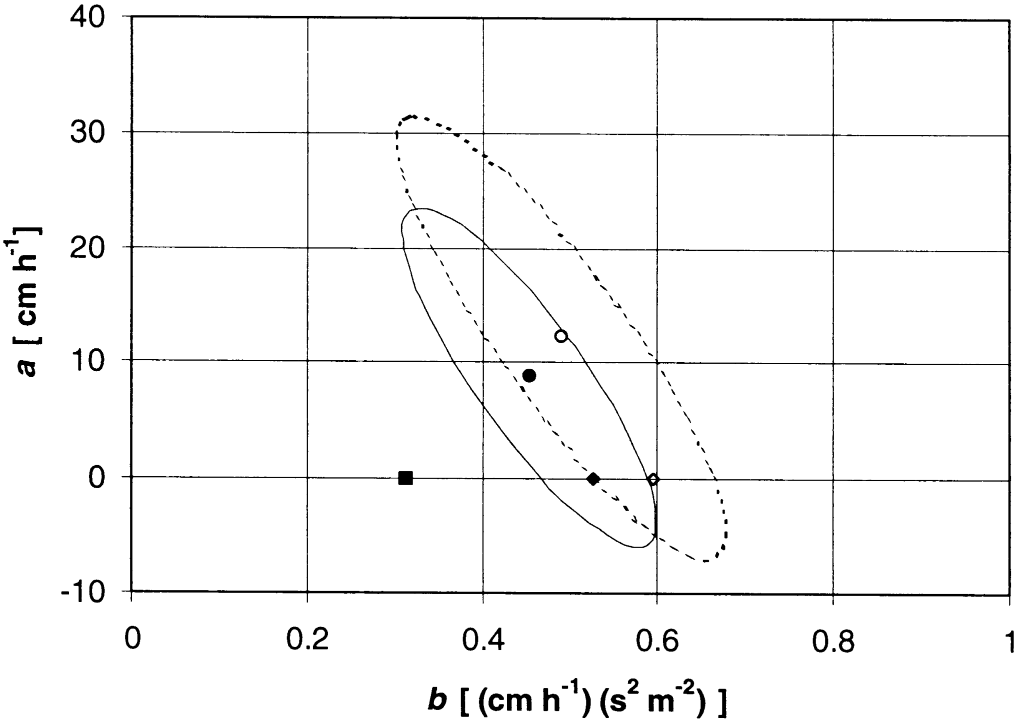

Figure 7. Coefficient a and b resulting from fits of (3.5)-(3.6) to the pooled ASGAMAGE data set. Open circle: best fit of (3.5); Open diamond: fit of(3.5) with a = 0; Filled circle: best fit of (3.6); Filled diamond: fit of (3.6) with a = 0; Filled square: Wanninkhof (1992); Dashed line: 95% confidence region for best fit of (3.5); Solid line: 95% confidence region for best fit of (3.6). See also Table 2.

because of the lack of data between $U_{N,10}$ = 0 m s^{-1} and 4 m s^{-1} in combination with the large scatter of the data. 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 chemical enhancement might be required, leading to a small offset at $U_{N,10}$=0 (Wanninkhof, 1992).

The deviations between the fit (3.5) and the observations of k_w were also investigated. The correlation between the various data and the residuals was computed for the ASGAMAGE-A and B data sets separately, and for the combined data set. Apart from a slight correlation with global radiation (r ≈ 0.3), no other correlations were found that were consistent for the two datasets and that were not autocorrelations (flux and $\Delta[CO_2]$). The weak correlation with global radiation might arise because the radiation affects the CO_2 flux. One reason for such an impact on the CO_2 flux might be the influence of light on photosynthetic activity and other biochemical activities (Sieburth, 1983). Another reason might be the effect of light absorption in the water on the vertical stratification of the water column.

4. Concluding remarks

During ASGAMAGE the eddy correlation technique to determine fluxes of CO_2 over sea has been applied with reasonable success. Special care has been taken to avoid the effects of cross-talk on the fluxes. The air-sea concentration difference, $\Delta[CO_2]$ was determined simultaneously, by directly determining the CO_2 concentration in atmospheric air and of air in equilibrium with sea water.

From the combination of CO_2 flux data and the measured concentration difference we were able to compute k_w directly. Although the resulting values for k_w show a considerable scatter, a first-order effect of wind speed on k_w could be determined. Furthermore, data from the two separate experimental periods (ASGAMAGE A and B) appeared to be consistent.

The results for k_w where fitted to the square of the wind speed using two different methods. The first method minimises the deviations of the observed k_w from the fit. The second method minimises the deviations of the flux computed using the fitted k_w, and the observed flux. Practical applications of k_w will mostly be aimed at predicting the flux correctly. Therefore, the use of the results of 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:

$$k_w = 0.53 U_{N,10}^2 \tag{4.1}$$

where k_w is in cm h^{-1} and $U_{N,10}$ in m s^{-1}. Equation (4.1) is valid at a Schmidt number of 660, that is, for CO_2 fluxes to or from salt water of 20°C. For other temperatures, a correction based on the Schmidt number dependence suggested by, for example, Wanninkhof (1992) has to be applied. Statistically, the 95% confidence interval of the coefficient in (4.1) extends from 0.45 up to 0.60, or 0.53 ± 12%. Note that the exponent in (4.1) has been based on the work by Wanninkhof (1992). For the present data set, the optimum fit with zero intercept and the exponent of (4.1) left free is $1.74 U_{N,10}^{1.5}$, but this fit is not significantly different from the one represented by (4.1).

Values for k_w obtained with (4.1) are significantly higher ($p < 0.001$) than those 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 even bigger. The latter parameterisation is a piecewise linear fit of k_w to $U_{N,10}$, which can be approximated by $k_w = 0.164 U_{N,10}^2$ for wind speeds up to about 25 m/s. Results from the direct method so far yielded k_w values larger than those from the indirect techniques such as the dual or triple tracer technique, or the radiocarbon and Radon deficiency method, the differences being one order of magnitude or more (Broecker et al, 1986; Smith and Jones, 1986; Wesely, 1986). Results from the present data set now start to approach the parameterisations based on the mass balance methods. Ongoing theoretical research in the framework of ASGAMAGE is aimed at resolving the nature of the remaining difference.

The fits given here may require some slight adjustment in the future and should therefore be used with caution. As discussed in Section 3.2 and by Jacobs *et al.* (1997), the results for CO_2 concentration from the different participating groups did not fully agree. Here, we have chosen to average the results from the different groups. However, as agreed upon during the ASGAMAGE International Workshop (Oost, 1997) the results for CO_2 might be re-calibrated to obtain consensus values for $\Delta[CO_2]$. The value of the coefficient in (4.1) probably remains well within the present 95% confidence limits: a systematic experimental error of ± 28 mg m^{-3} in $\Delta[CO_2]$ (about 15 ppm) corresponds to the present 95% confidence limits on the coefficient. Due to the averaging of results from the participants, the deviation between the consensus concentration difference and that concentration difference used here is expected to be much smaller than 28 mg m^{-3}.

The present data set does not allow to distinguish relations between k_w and geophysical parameters other than $U_{N,10}$. Correlations between the residuals from the fit and other parameters, were found to be very low. The effect of some features, such as Langmuir circulations and the effect of bubble clouds is still to be investigated. Other parameters that might be important, such as surface tension and the presence of slicks (GESAMP, 1995), and wave-enhanced turbulence (e.g., Terray *et al*, 1996) have not been investigated. A further investigation of such features in the framework of experiments similar to ASGAMAGE is recommended.

The stratification of the water near the platform with respect to the CO_2 concentration has also been investigated. Given the experimental error in $\Delta[CO_2]$ (typically about 20-30 mg m^{-3}, corresponding to 11 - 16 ppm) and given the time needed to perform a profile measurement, the CO_2 concentration differences found in the water may be considered as insignificant and can be neglected in computations of k_w. Recall that a systematic error of ± 28 mg m^{-3} in $\Delta[CO_2]$ corresponds almost exactly to the statistical 95% confidence interval for the coefficient in (4.1).

The ASGAMAGE results with respect to CO_2 content of the water column also show that the stratification observed during ASGASEX (Oost *et al*, 1995) was probably exceptional. The cause of the stratification reported by these authors is probably not of a purely physical nature, but related to the release of exhaust products by the River Scheldt into the North Sea. However, a concentration gradient very close to the surface must be expected on theoretical grounds: without such a gradient, a flux into the water 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 still not be excluded on the basis of the present data set. Such a gradient could greatly influence the results of direct methods to determine k_w. Theoretical research into this subject within the framework of ASGAMAGE will further address this issue. It furthermore should be noted that most of the profile measurements were performed around slack tide. Larger gradients at other times, due to horizontal advection, can still not be excluded.

Acknowledgements

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Appendix 1 ASGAMAGE Participants

Institute	***Acronym***
Bedford Institute of Oceanography, Ocean Circulation Division, *Canada*	BIO
Max Planck Institute for Chemistry, Biochemical Department, *Germany*	MPIC
National Center for Atmospheric Research, *USA*	NCAR
NOAA Atlantic Oceanographic and Meteorology Laboratory, *USA*	AOML
NOAA Climate Monitoring and Diagnostics Laboratory, *USA*	CMDL
NOAA Environmental Technology Laboratory, *USA*	ETL
Netherlands Institute for Sea Research, *The Netherlands*	NIOZ
Risø Notional Laboratory, Dept. of Meteorology and Wind Energy, *Denmark*	RISØ
Royal Netherlands Meteorological Institute, Dept. Oceanographic Research, *The Netherlands*	KNMI
School of Environmental Sciences, University of East Anglia, *United Kingdom*	UEA
Southampton University, Department of Oceanography, *United Kingdom*	SUDO
TNO Physics and Electronics Laboratory, *The Netherlands*	TNO-FEL
University Collage Galway, Department of Oceanography, *Ireland*	UCG
Univ. of Newcastle Upon Tyne, Dept. of Marine Sc. and Coastal Management, *United Kingdom*	NUT

Appendix 2 KNMI profile runs for CO_2 concentration in water

Code[1]	*Date and DOY*		*Time (UTC)*	*Depths (m)*					
				2	3.5	5	7	11	15
A1	19/05	140	9:00 - 11:40		•	•	•	•	•
A2	19/05	140	14:30 - 17:00		•	•	•	•	•
A3	20/05	141	14:10 - 16:35	•	•	•	•	•	•
A4	21/05	142	13:20 - 16:05		•	•	•	•	•
A5	23/05	144	10:35 - 13:35	•	•	•	•	•	•
A6	28/05	149	15:10 - 17:35		•	•	•	•	•
A7	31/05	152	10:45 - 12:30	•	•	•	•	•	•
A8	31/05	152	15:10 - 17:05	•	•	•	•	•	•
A9	01/06	153	10:40 - 12:15	•	•		•	•	•
A10	02/06	154	6:45 - 9:25	•	•	•	•	•	•
A11	02/06	154	12:55 - 15:15	•	•		•	•	•
A12	03/06	155	7:25 - 10:40	•	•	•	•	•	•
A13	03/06	155	12:50 - 14:22	•	•	•	•	•	•
A14	04/06	156	7:35 - 9:50	•	•	•	•	•	•
A15	04/06	156	13:35 - 14:20	•			•		•
B1	17/10	291	7:45 - 10:00	•		•		•	
B2	18/10	292	14:40 - 15:35		•	•	•	•	
B3	19/10	293	9:30 - 11:30		•	•	•	•	•
B4	20/10	294	10:45 - 11:55		•	•	•	•	•
B5	21/10	295	16:55 - 20:10		•	•	•	•	•
B6	22/10	296	7:00 - 9:00		•	•	•	•	•
B7	22/10	296	13:50 - 15:00		•	•	•	•	•
B8	23/10	297	8:45 - 10:00		•	•	•	•	•
B9	23/10	297	14:55 - 15:50		•	•	•	•	•
B10	24/10	298	9:35 - 11:05		•	•	•	•	•
B11	24/10	298	13:50 - 16:55		•	•		•	•

[1] A*nn* = ASGAMAGE-A period; B*nn* = ASGAMAGE-B period

Appendix 3 Illustration of equilibrator response

The following graph serves as an example of the response characteristic of the CO_2 measurement system of KNMI. Figure A1 shows results for CO_2 recorded during run 93 of ASGAMAGE-B. Each data point represents a 10 s average CO_2 content of equilibrator air. During the run, the inlet depths were switched three times to another level, as is clearly marked by the spikes in the signal. It can be seen the analysing equipment, which included the inlet tubes, the equilibrator and the IRGA, can safely be considered to have reached a new equilibrium after five to ten minutes.

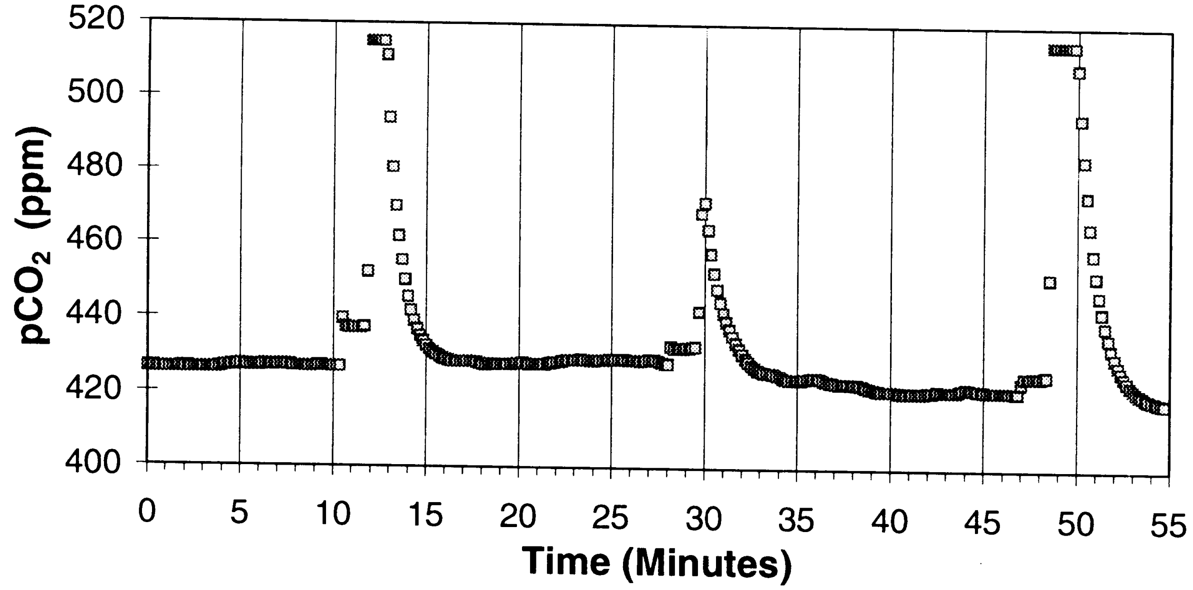

Figure A1 *Illustration of the response of the KNMI CO_2 measurement system: sequence of CO_2 content of equilibrator air recorded during run 93 of ASGAMAGE-B (21/10, 19:05-20:00 UTC, profile run B5).*

Abstract

The Air-Sea Gas exchange project in the framework of the Marine Aerosol and Gas Exchange program (ASGAMAGE) is designed to study air-sea gas-exchange both experimentally and theoretically. Within the project 14 research groups -one of which is Riso- from Europe, Canada and the United States of America co-operate. The experimental part of ASGAMAGE was carried out in May and October of the year 1996 and resulted in a wealth of data that should help us to better understand the nature of air-sea gas exchange. A considerable part of the experiment was performed at "Meetpost Noordwijk"(MPN), a research platform some 9 km off the Dutch coast in the North Sea. CO_2 fluxes were measured by means of the eddy correlation technique and the air-sea concentration difference was measured simultaneously. This combination of data allowed us to determine the air-sea transfer velocity of CO_2, k_w, directly. Results obtained by the Royal Netherlands Meteorological Institute (KNMI) will be shown. Data from the two experimental periods appeared to be consistent. A relation with wind speed could be determined for the pooled data set. The fit results in k_w values that are about a factor of two higher than those obtained by the traditional chemical methods. Significant relations with other geophysical parameters could so far not be found. Ongoing theoretical research within the framework of ASGAMAGE is aimed at a further interpretation of the data. A model is being developed that will be used to study gas fluxes theoretically. The model is a one-dimensional oceanic boundary layer model that includes the basic chemistry of the inorganic carbon system in water. The most important model features will be outlined and some preliminary results will be presented.