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Dissolved carbon dioxide in Dutch coastal waters

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Abstract

The role of shelf seas in global carbon cycling is poorly understood. The dissolved inorganic carbon system and air–sea exchange of carbon dioxide (CO_2) are described for the Dutch coastal zone in September 1993. The inorganic carbon chemistry was affected by tidal mixing, wind speed, wind direction, freshwater input, stratification and coastal upwelling. Surface water had a variable fugacity of carbon dioxide (f_{CO_2}) between 300 and 800 μatm with short-term changes partly related to the tidal cycle. High contents of dissolved inorganic carbon (DIC) and CO_2 in relatively saline water probably originated from mineralisation of accumulated organic matter in water and sediments farther out at sea and transport of water enriched in DIC into the coastal zone by upwelling. Air–sea exchange of CO_2 ranged from -20 to $60 \text{ mmol m}^{-2} \text{ day}^{-1}$. These fluxes are critically discussed in the light of potential stratification. It is not possible to assess from this study whether the Dutch coastal zone is a net sink or source for atmospheric CO_2 .

Keywords: dissolved carbon dioxide; coastal waters; North Sea; inorganic carbon chemistry

1. Introduction

1.1. Research objectives

The role of shelf seas in global carbon cycling is poorly understood (e.g., Frankignoulle et al., 1996a,b; Kempe and Pegler, 1991). Of particular importance is the question, whether shelf seas act as a sink or source for carbon dioxide (CO_2). S.V. Smith and Hollibaugh (1993) concluded that coastal seas were a net source for atmospheric CO_2 in preindustrial

times. In the current era the world ocean is generally considered a net sink of fossil fuel CO_2 (Schimel et al., 1995), but the source or sink function is not known for the part consisting of coastal seas (Hopema and De Baar, 1991; Kempe, 1995).

In the open ocean air–sea exchange of CO_2 is driven by warming and cooling of surface waters, wax and wane of plankton blooms, wind velocity (Bakker et al., 1996), lateral advection and upwelling. In coastal seas the same processes take place, yet with more intensity and variability. In addition, the content of dissolved inorganic carbon (DIC) is highly variable as a consequence of river input and more dominant tidal forcing. Moreover, exchanges with the shallow sediments strongly affect the carbon budget of the water column. Finally, the nearby regional sources and sinks on land may cause

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large variations of the atmospheric CO_2 value as function of wind direction.

The dissolved inorganic carbon chemistry in Dutch coastal waters is discussed in relation to the outflow of fresh water, tidal mixing, wind speed, wind direction and coastal upwelling. Attention is paid to the effect of hydrography on the estimated air–sea fluxes of CO_2 . The research was conducted in September 1993 at Measuring Platform Noordwijk as part of the Air–Sea Gas Exchange (ASGASEX) experiment.

1.2. Inorganic carbon chemistry and air–sea exchange of CO_2

Dissolved CO_2 constitutes $\sim 1\%$ of the dissolved inorganic carbon content of seawater, which otherwise mainly consists of bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and a negligible amount of carbonic acid (H_2CO_3):

$$\text{DIC} = [\text{CO}_{2(\text{aq})}] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (1)$$

A concentration difference of carbon dioxide (CO_2) across the air–water interface drives the net gas exchange (Liss and Slater, 1974). A common assumption is that a concentration gradient of CO_2 exists only near the air–water interface and that the gas is well mixed in bulk air and bulk water. In practice, contents of CO_2 in air and water are determined at a certain height above and depth below the sea surface. Then the flux F can be expressed as:

$$F = k([\text{CO}'_{2(\text{aq})}]_{\text{bulk}} - K_0 f_{\text{CO}_2(\text{air})}) \quad (2)$$

The gas transfer velocity, k , is taken as a function of the gas, wind speed, salinity and temperature (Liss and Merlivat, 1986; Wanninkhof, 1992). The concentration of dissolved CO_2 in bulk surface water, $[\text{CO}'_{2(\text{aq})}]_{\text{bulk}}$, includes the small amount of carbonic acid (H_2CO_3), as denoted by the accent. The fugacity of CO_2 in air, $f_{\text{CO}_2(\text{air})}$ (μatm), is the partial pressure of CO_2 corrected for the slightly non-ideal behaviour of the gas. The solubility of CO_2 in seawater, K_0 ($\text{mol kg}^{-1} \text{atm}^{-1}$), is mainly a function of temperature and salinity (Weiss, 1974):

$$[\text{CO}'_{2(\text{aq})}] = K_0 f_{\text{CO}_2} \quad (3)$$

Air–sea exchange slowly brings the concentration of dissolved CO_2 in surface water towards equilibrium with the atmospheric CO_2 content. More rapid physical and biological disturbances of the concentration of CO_2 in water generally prevent this equilibrium from being established.

1.3. Measuring Platform Noordwijk

Measuring Platform Noordwijk ($52^\circ 16' \text{N}$, $04^\circ 18' \text{E}$), sometimes called ‘‘Tower Noordwijk’’, is situated in water of 18-m depth in the Dutch coastal zone. The platform is 9 km offshore from the town of Noordwijk, which is 35 km north of the river Rhine outflow and 25 km south of the mouth of the North Sea Channel (Noordzeekanaal) (Fig. 1). The vast industrial areas of Velsen and Europoort and the

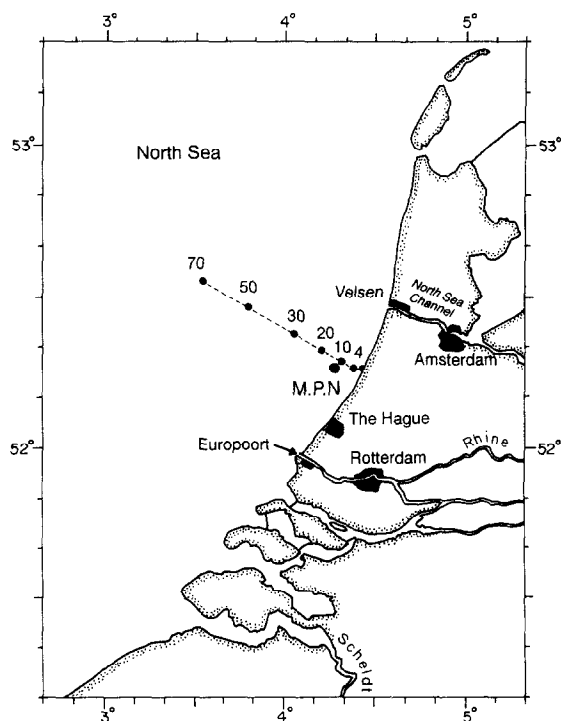


Fig. 1. The Dutch coastal zone with Measuring Platform Noordwijk (M.P.N.), the cruise track (dashed line) and CTD stations (black dots) of R.V. ‘‘Holland’’ on 29 September 1986. Eastern longitude and northern latitude are on the x-axis and y-axis, respectively. Numbers next to the CTD stations refer to the distance offshore in kilometres. Also indicated are the vast industrial areas of Europoort and Velsen, and the cities of Rotterdam, The Hague and Amsterdam.

cities of Amsterdam, The Hague and Rotterdam are situated on nearby land, northeast to southwest of the platform. These and the industrial regions of Germany and Belgium are deemed to be major sources of fossil fuel CO_2 .

Water in the Dutch coastal zone mainly originates from the English Channel ($\sim 95\%$) and the outflow of the Rhine–Meuse Estuary ($\sim 5\%$) (Van der Giessen et al., 1990). The fresh water of the Rhine builds a narrow coastal boundary current, which flows towards the northeast with most transport of fresh water within 15–20 km offshore (De Ruijter et al., 1992). Point sources along the coast add additional fresh water.

2. Methods

2.1. Meteorological and hydrographic parameters

Wind speed, wind direction, air temperature, atmospheric moisture content and atmospheric pressure were recorded every 10 min at 27.6 m above mean sea level on the southeastern side of the platform. Wind speed was corrected to an undisturbed wind field at 10 m above mean sea level by dividing the detected wind speed by 1.142, a factor close to the value derived from the correction for height advised by WMO (1983) (Benschop, 1996). Current direction and current velocity at 5 m below mean sea level, tidal height and wave height were detected every 10 min on the southwestern side of the platform. Alongshore and cross-shore components were calculated for wind speed and tidal currents. Residual alongshore and cross-shore current velocities were obtained by filtering the current components with a running average of 149 values.

Salinity, at the practical salinity scale, was calculated from water temperature and conductivity (UNESCO, 1981) detected by two thermosalinographs at 5- and 7-m depth on the southwestern side of the platform. Average salinity of both thermosalinographs was used for calibration, which was carried out at 19°C with 25 samples collected throughout September. Accuracy was ± 0.2 for the calibrated values.

Water was pumped at a large flow rate to the laboratory level by a submerged pump from 5 m

below mean sea level on the southern side of the platform. Water temperature was registered with a Pt-100 sensor attached to the inlet. Water was sampled in parallel for determination of f_{CO_2} , DIC and calibration of the thermosalinographs.

A CTD section was conducted perpendicular to the coast by R.V. ‘Holland’ on 29 September (Fig. 1; Rijkswaterstaat, 1994). CTD casts were made to the bottom at 2, 4, 10, 20, 30, 50 and 70 km offshore from Noordwijk.

2.2. Parameters of the inorganic carbon system

For detection of f_{CO_2} water from 5 m below mean sea level was continuously sprayed through a showerhead into an equilibrator (Robertson et al., 1993; Bakker et al., 1996). The temperature change of the water between the inlet and the equilibrator was typically between -0.1° and 0.5°C with an average of 0.2°C ($\sigma_{n-1} = 0.1^\circ\text{C}$, $n = 1006$), as determined from the difference of two Pt-100 sensors. The headspace of the equilibrator was sampled after ample flushing. Marine air was obtained from 6 m above mean sea level on the western side of the platform. Air and head-space samples were dried with silica gel before analysis. In the gas chromatograph two Hayesep D columns separated CO_2 from other components. A nickel catalyst converted CO_2 to methane, which was detected by the flame ionisation detector (FID). A cycle of 18 min contained three calibration gases of 261.1, 361.3 and $476.5 \mu\text{mol mol}^{-1} \text{CO}_2$ in artificial dry air, an air sample and a head-space sample. Calibration gases had been calibrated against NOAA standards of 254.71, 326.32, 374.13 and $446.46 \mu\text{mol mol}^{-1} \text{CO}_2$ in dry air.

The fugacity of CO_2 in bulk water was obtained from the detected mixing ratio of CO_2 in the head space, atmospheric pressure, the Weiss (1974) formulae and the temperature correction of Copin-Montégut (1988, 1989). For flux calculations an atmospheric humidity of 100% was assumed in the equilibrator and at the sea surface. The air–sea flux of CO_2 was calculated from the concentration difference of CO_2 between bulk air and bulk water, in situ 10-minute wind speed and atmospheric pressure with the relationship of Wanninkhof (1992) for shipboard measurements. Choice of this relationship rather than

that of Liss and Merlivat (1986) is somewhat arbitrary, as both are well suited for instantaneous flux assessment (Wanninkhof, 1992). Potential temperature differences between the sea surface and the water inlet at 5 m below mean sea level were neglected. The highly variable CO₂ contents of air and water made it difficult to estimate precision and accuracy of the CO₂ measurements. During an earlier cruise the overall precision of the mixing ratios of CO₂ in air was estimated as $\pm 0.6 \mu\text{mol mol}^{-1}$ or $\pm 0.2\%$ with an accuracy of better than $\pm 0.5\%$. The precision of f_{CO_2} in surface water was then estimated as $\pm 0.7 \mu\text{atm}$ or $\pm 0.2\%$ (Bakker et al., 1996). Measurements at the platform may have had a slightly lower precision and accuracy as a result of introduction of the drying agent and the larger moisture correction at higher ambient temperatures.

The content of DIC in water from 5 m below mean sea level was determined with a coulometer (Stoll, 1994), modified for semi-continuous operation. A subsample was acidified with 8.5% phosphoric acid and sparged with nitrogen. The evolving CO₂ was captured in an ethanol–amine solution with an indicator. The solution was photometrically backtitrated by the coulometer (Johnson et al., 1987). Accuracy of the coulometer in the continuous mode was estimated as $\pm 5 \mu\text{eq kg}^{-1}$, precision as $\pm 1.5 \mu\text{mol kg}^{-1}$ (after Stoll, 1994). Alkalinity was calculated from f_{CO_2} and DIC using the constants of Goyet and Poisson (1989).

Upon request the complete set of meteorological, hydrographic and CO₂ variables is available from the Netherlands Institute for Sea Research.

3. Results

3.1. Meteorology and hydrography

Between 8 and 25 September a spell of fine weather contained light to strong, offshore winds mainly from the northeast to south (Fig. 2a and b). Wave heights remained lower than 1.5 m (Fig. 3a). From 25 to 27 September strong winds from the northwest with a maximum of 16 m s^{-1} increased wave heights up to 3.5 m and pushed water towards the coast (Figs. 2a, b and 3a, c). Discharge of the river Rhine at Lobith was approximately 1500 m^3

s^{-1} to 14 September and between 1600 and $2100 \text{ m}^3 \text{ s}^{-1}$ for the second half of September (data from Rijkswaterstaat); slightly below the annual mean river discharge of $2000 \text{ m}^3 \text{ s}^{-1}$ (Van der Giessen et al., 1990).

Strong semi-diurnal tidal currents ran mainly parallel to the coast. Neap tides were on 11 and 24 September, spring tides on 3 and 18 September and 1 October. Tidal amplitude varied from 0.6 m for neap tides to 1.0 m for the spring tide of 18 September (Fig. 3c). High water coincided with the maximum velocity of the flood current directed towards the northeast. Low water was shortly after the maximum strength of the ebb current towards the southwest (Fig. 3b and c). Tidal excursion was 4–10 km in alongshore direction, and 0–1 km in cross-shore direction (from Fig. 3b).

The residual alongshore current was often directed towards the northeast, parallel to the alongshore wind component (Fig. 4a and b). The current reversed twice towards the southwest, namely on 12 September and between 23 and 27 September. In the first case the residual alongshore current was not clearly related to the weak alongshore wind component. In the second case persistent winds from the northwest changed the direction of the current towards the southwest. As wind strength decreased on 27 September, the current turned towards the northeast again. Daily residual alongshore transport ranged from 7 km day^{-1} towards the northeast to 5 km day^{-1} towards the southwest (from Fig. 4a). The residual cross-shore current was generally shoreward, frequently opposite to the cross-shore wind component (Fig. 4c and d). Daily residual cross-shore transport was between 5 km day^{-1} in shoreward direction and 1 km day^{-1} in offshore direction (from Fig. 4c).

Salinity, temperature, DIC, alkalinity and f_{CO_2} varied at both short and long time scales throughout September (Fig. 5a–e). Variability of these parameters at short time scales was related to the tidal cycle. Patterns of salinity and temperature occasionally recurred after the turn of the tide in a reversed sequence. Between 11 and 20 September the flood current carried more saline, warmer water than the ebb current, as suggested by maxima and minima of salinity and temperature at the turn of tide. Recurring, shifting patterns of salinity indicated water

passing the platform over several tidal cycles for 23 to 27 September. Cooling of the water prevailed from 14 to 20 September and from 25 to 28 September (Fig. 5b). The four independent temperature sensors around the platform indicated similar tidal changes.

Salinity differences over the tidal cycle amounted to 2.4 and 1.0 close to neap tides, in contrast to 0.4 close to the spring tide of 18 September, when salinity variations became very regular (Figs. 3b, c and 5a). Wind mixing reduced the variability of salinity and temperature over the tidal cycle between

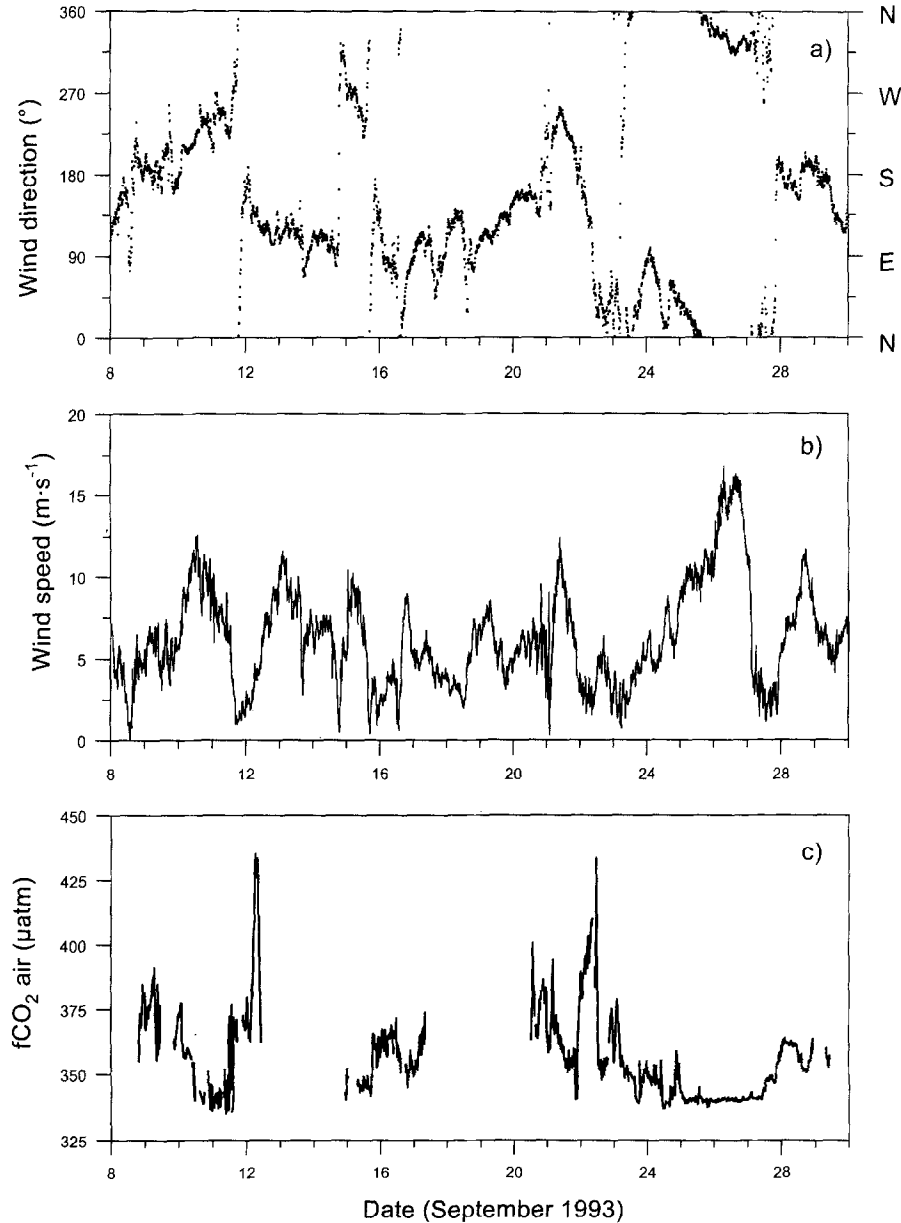


Fig. 2. Wind direction (a), wind speed (b), and the fugacity of CO₂ in air (c) of 8–30 September 1993 at Measuring Platform Noordwijk. Wind direction indicates where the wind is coming from.

25 and 28 September. Average salinity over the tidal cycle was generally between 31.0 and 31.5 with two exceptions. High average salinity of 32.3 occurred between 15 and 21 September, while salinity dropped to 29.0 after an intrusion of water with a relatively large content of fresh water on 28 September.

Salinity strongly increased from a value of 28.2 at 4 km offshore to 34.0 at 30 km offshore from

Noordwijk on 29 September (Figs. 1 and 6; after Rijkswaterstaat, 1994). Salinity gradually changed from 30.8 to 31.4 between 2.5- and 12.5-m depth in the CTD cast 10 km offshore. Temperature increased from 15.3° to 15.5°C from the coast to 30 km offshore, but did not have pronounced vertical gradients within this area. Hence, vertical gradients of density were largely determined by salinity.

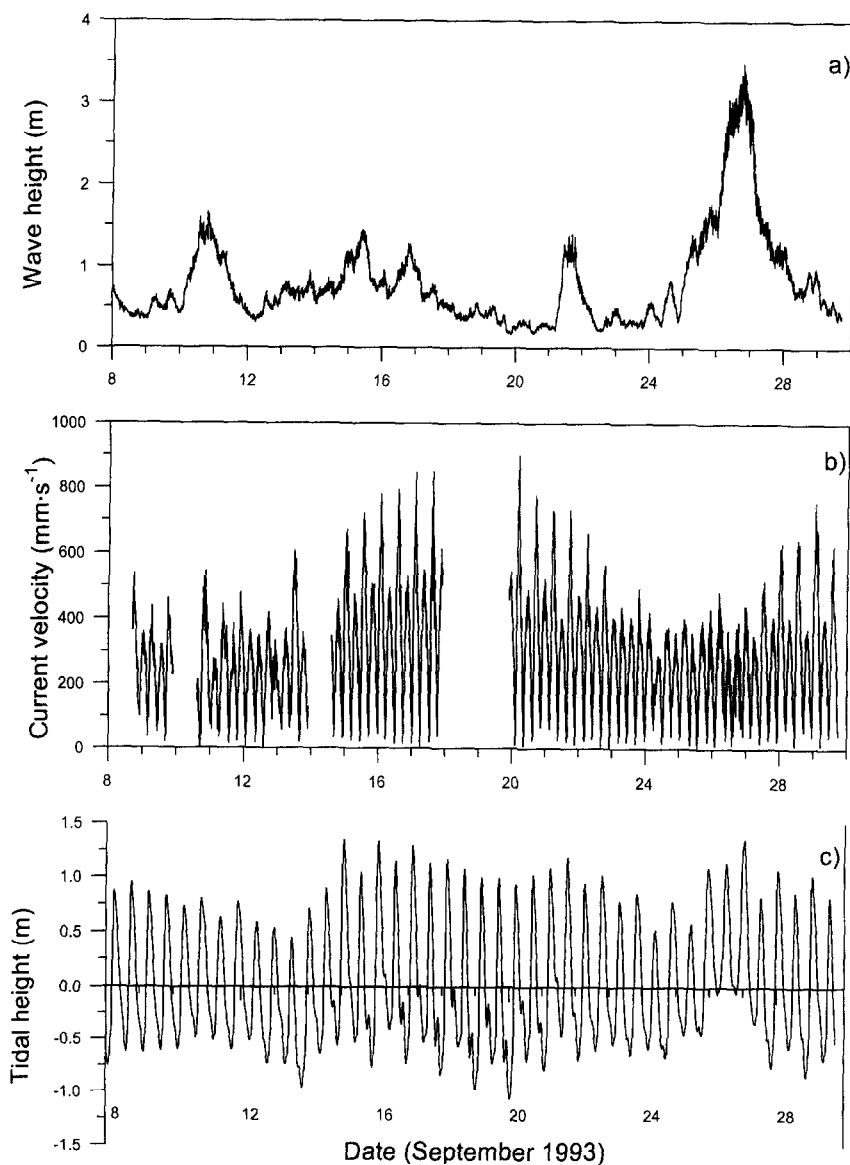


Fig. 3. Wave height (a), current velocity at 5 m below mean sea level (b), and tidal height (c) of 8–30 September 1993 at Measuring Platform Noordwijk.

3.2. Dissolved inorganic carbon chemistry

Low salinity accompanied high DIC within the tidal cycle on 11 September and from 21 to 28 September (Fig. 5a and c). The opposite, low salinity along with low DIC and high salinity with high DIC,

was observed in the relatively saline water between 15 and 17 September.

The content of dissolved CO_2 in surface water varied from close to equilibrium with the atmospheric CO_2 content to strong supersaturation for 12 to 24 September (Fig. 5e). Very high f_{CO_2} values of

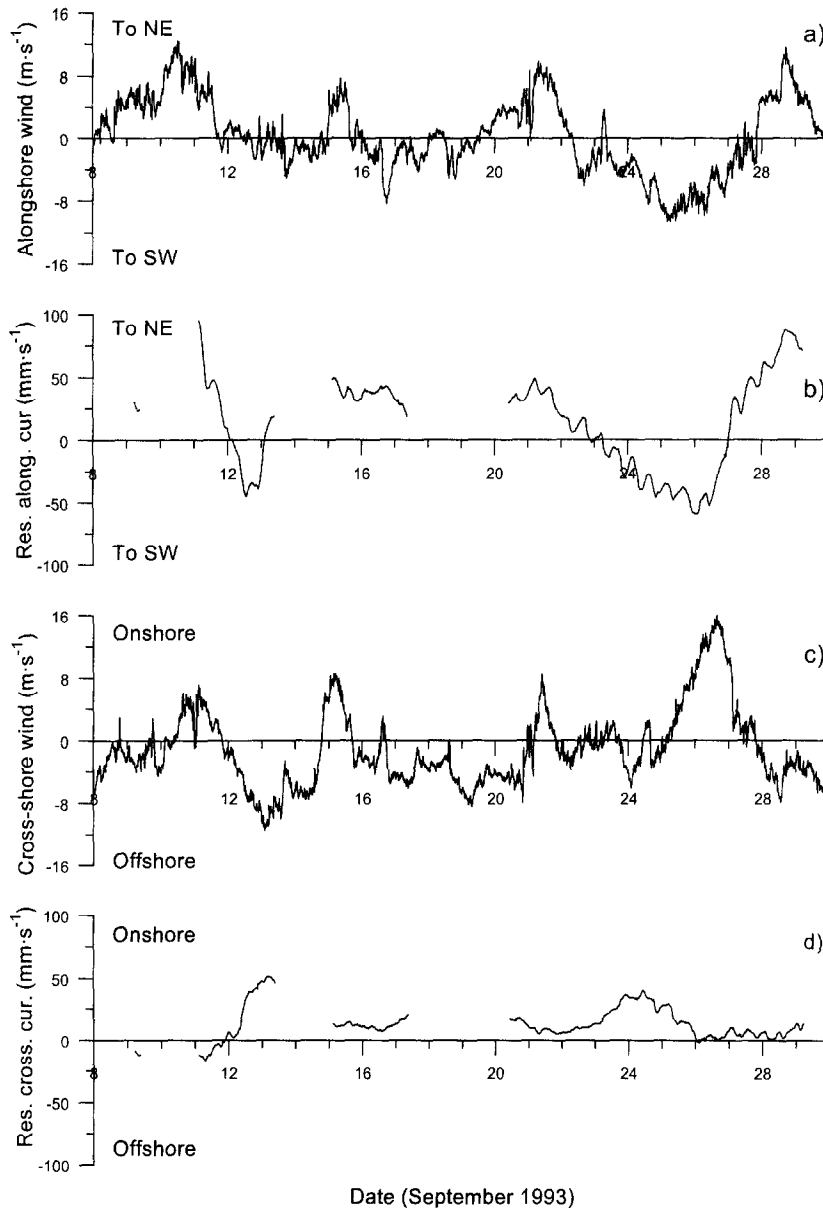


Fig. 4. Alongshore and cross-shore wind speeds (a, c) and residual alongshore and cross-shore current velocities at 5 m below mean sea level (b, d) of 8–30 September 1993 at Measuring Platform Noordwijk.

500 and 800 μatm occurred between 15 and 18 September, a period with relatively saline water, cooling and strong tidal mixing. These maxima of f_{CO_2} were partly related to maxima of salinity and temperature within the tidal cycle. On 24 September

the variable supersaturation of CO_2 abruptly changed to undersaturation with less variation over the tidal cycle. The water with low f_{CO_2} had intermediate salinity and DIC values. Frequent blockage of the showerhead of the equilibrator with algal material

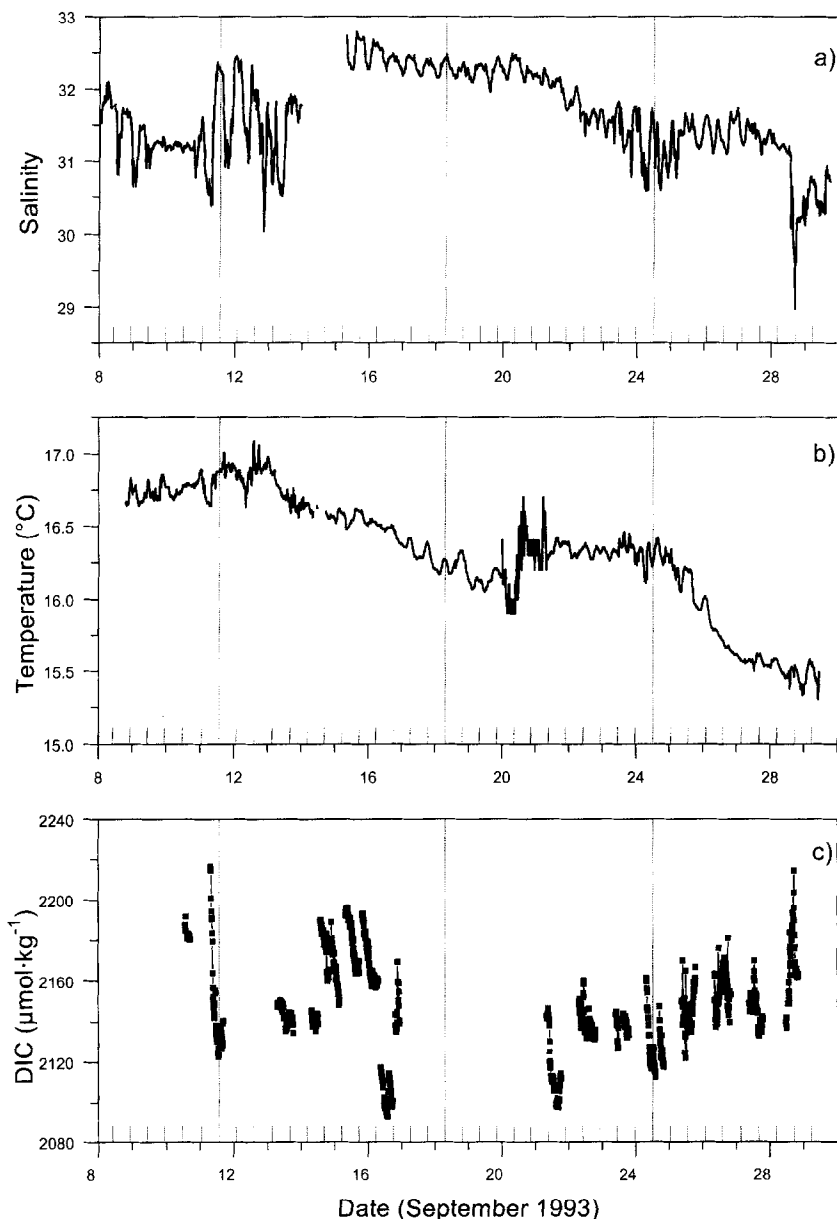


Fig. 5. Salinity (a), water temperature (b), the content of dissolved inorganic carbon (c), calculated alkalinity (d), f_{CO_2} in water (e), and air-sea exchange of CO_2 (f) of 8–30 September 1993 at Measuring Platform Noordwijk. The vertical marks on the x-axis denote the turns of the tide from flood current to ebb current, while the thin lines denote those after a neap or spring tide. The horizontal dashed line (e) indicates a fugacity of CO_2 in air of 340 μatm , as detected between 25 and 27 September.

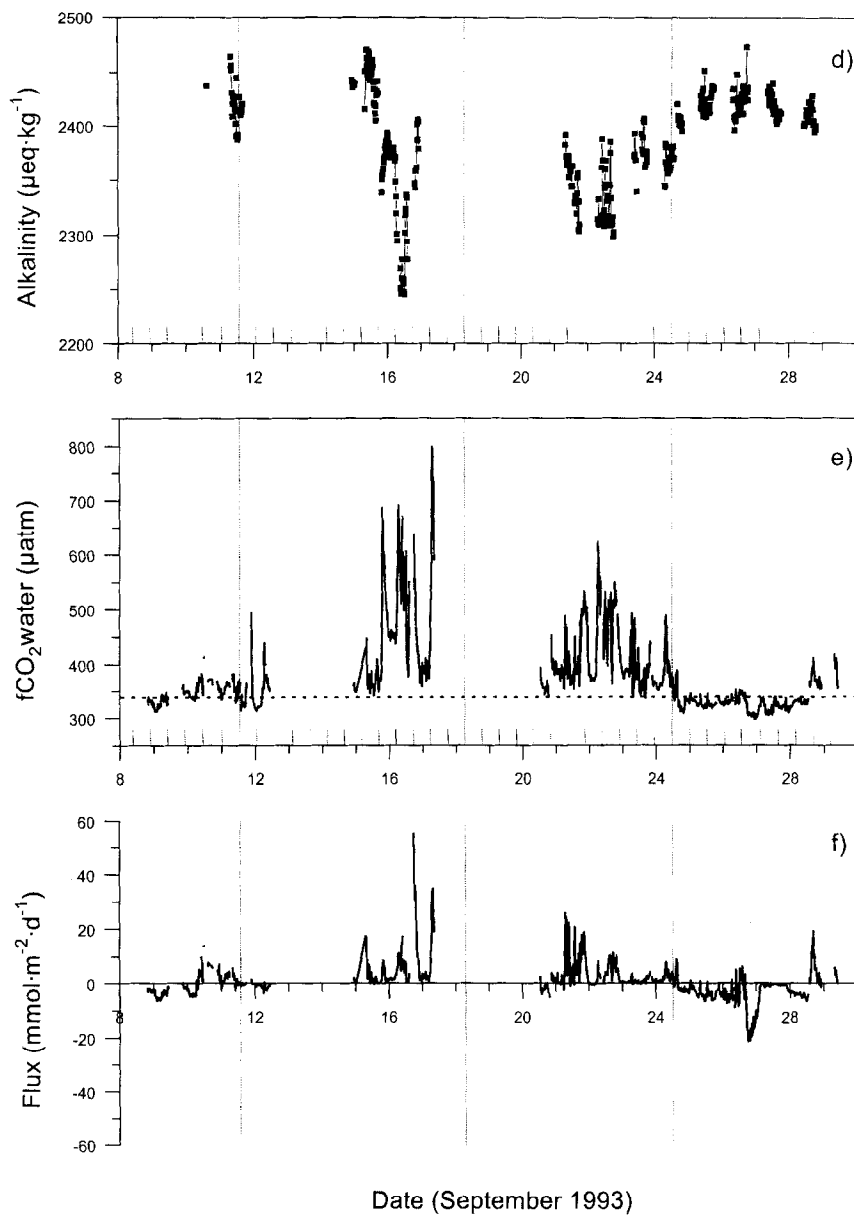


Fig. 5 (continued).

suggested the presence of an algal bloom in surface water.

The flood current carried relatively fresh water on 28 September. Minimum salinity of 29.0 and maxima of DIC ($2214 \mu\text{mol kg}^{-1}$) and $f\text{CO}_2$ ($411 \mu\text{atm}$) were observed at the turn of the tide. Alkalinity and temperature were not notably affected by the less

saline water. After the freshwater intrusion salinity increased with considerable small scale variation. On 29 September salinity values lower than 30 were only found within 5 km offshore (Fig. 6; from Rijkswaterstaat, 1994). After the appearance of the relatively fresh water the $f\text{CO}_2$ of the water was 0–60 μatm above that of the air.

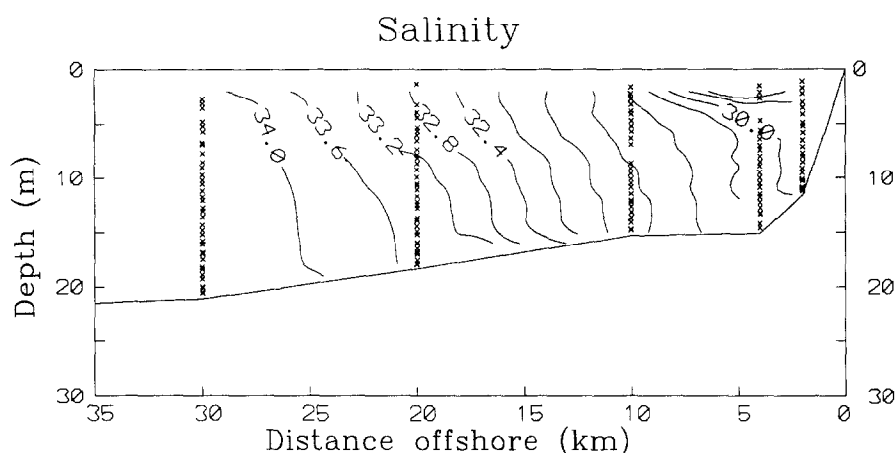


Fig. 6. Salinity in the CTD section offshore from Noordwijk by R.V. "Holland" on 29 September 1993. Crosses denote sampling points (after Rijkswaterstaat, 1994).

3.3. The atmospheric CO_2 content

The offshore winds carried air with variable and high f_{CO_2} ranging from 335 to 440 μatm to the platform between 8 and 25 September (Fig. 2a–c). Highest mixing ratios of CO_2 occurred during light winds from the northeast and southeast (Fig. 7a and b). Winds from the northwest had a more constant CO_2 content between 25 and 28 September. A diurnal trend in the mixing ratios could not be distinguished.

3.4. The air–sea flux of CO_2

The estimated air–sea flux of CO_2 reflected the variability of both wind speed and the concentration difference of CO_2 across the air–water interface (Figs. 2b and 5e, f). Very high f_{CO_2} in surface water caused considerable CO_2 release, even during light winds. Maximum release of CO_2 occurred on 16 and 17 September, when high f_{CO_2} in surface water was accompanied by moderate wind speed. On 25 and 26 September the combination of strong northwesterly

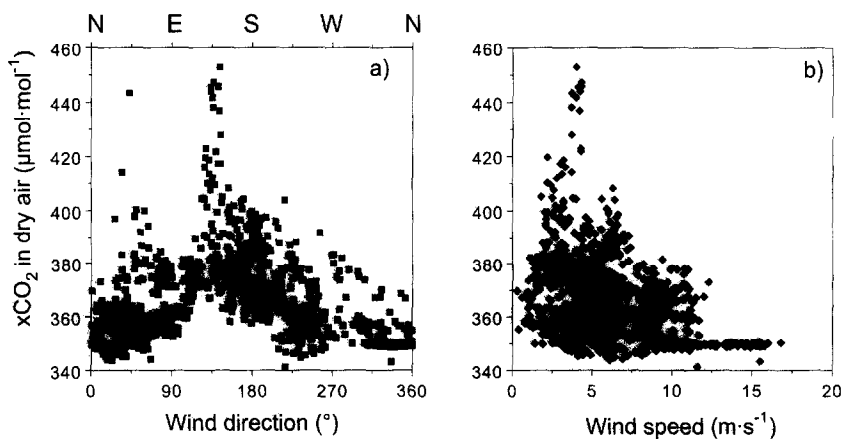


Fig. 7. Mixing ratio of CO_2 in dry air as function of wind direction (a) and wind speed (b) of 8–30 September 1993 at Measuring Platform Noordwijk. Wind direction is the direction where the wind is coming from.

winds and low f_{CO_2} in surface water induced moderate seawater uptake of CO_2 . Slight uptake of atmospheric CO_2 of $0.8 \text{ mmol m}^{-2} \text{ day}^{-1}$ occurred between 8 and 30 September.

The estimated air–sea exchange of CO_2 should be viewed critically in the light of the potential occurrence of stratification above the water inlet at 5 m below mean sea level, which will be discussed in Section 4.1. The method to determine the flux assumes perfect mixing of CO_2 throughout bulk water and bulk air, except for a gradient across the air–water interface. This assumption is violated in the case of stratification.

Measuring Platform Noordwijk provides a stable platform for the intercomparison of different techniques for estimating the air–sea flux of CO_2 (Kunz et al., 1995; Oost, 1995; Oost et al., 1995; S.D. Smith et al., 1995). Unfortunately, the dynamic and complex marine and atmospheric chemistry of CO_2 induce large variations in time and space of the true air–sea exchange of CO_2 at this coastal site. This is likely to cause incompatibility in sampling between the individual flux assessment techniques and strongly complicates any intercomparison.

4. Discussion

4.1. Residual currents, stratification and coastal upwelling

Water temperature decreased by seasonal cooling and as such behaved as a partly conservative tracer (De Ruijter et al., 1992). Temperature changes over the tidal cycle were similar for the four individual sensors. Artefacts of the different sampling positions around the platform or of the underwater structure of the platform on other parameters cannot be ruled out, however.

Spring-neaps switching influenced the variation of salinity over the tidal cycle (Figs. 3b, c and 5a). Minima and maxima of salinity and water temperature more often occurred at the turn of the tide than at low or high water (Figs. 3b, c and 5a, b). Patterns of salinity and temperature occasionally recurred in a reversed sequence after the turn of the tide. As a maximum amount of water had passed the platform in one direction at the turn of the tide, this indicated

that horizontal heterogeneity outweighed vertical stratification as a cause of the variability of the hydrographic parameters (De Wilde and Duyzer, 1995). This does not, however, exclude the presence of stratification. On 29 September vertical gradients of salinity pointed to stratification at 10 km offshore from Noordwijk, close to the platform.

The variability of the wind field affected the direction and strength of the residual current, which supports previous measurements (Van der Giessen et al., 1990). The residual alongshore current at 5 m below mean sea level was generally parallel to the alongshore wind component (Fig. 4a and b) in agreement with Van der Giessen et al. (1990). The residual cross-shore current remained directed towards the shore, often opposite to the cross-shore wind component (Fig. 4c and d). This is in apparent contrast to observations at 10 km offshore from Noordwijk that the residual current at 3 m below the lowest low water surface occasionally turned offshore in response to winds from the northeast to southeast (De Ruijter et al., 1992). Corresponding residual near-bottom currents generally had a shoreward component (Van der Giessen et al., 1990; De Ruijter et al., 1992). The observed shoreward residual current opposite to offshore winds suggests presence of stratification with a shallow wind-driven surface layer, below which water moved shoreward.

Periodic stratification is common in the region of freshwater influence of the river Rhine (Simpson et al., 1993) and has previously been observed in the coastal zone near Noordwijk (Van Alphen et al., 1988; Van der Giessen et al., 1990). Springs-neaps switching between mixed and stratified conditions occurred 20 km offshore from Noordwijk (Simpson et al., 1993). Semi-diurnal variation of stratification was detected close to the platform (Simpson and Souza, 1995; Souza and Simpson, 1996). Offshore, upwelling-favourable winds tend to maintain stratification and to promote restratification. Onshore winds may inhibit the development of stratification and are more effective than offshore winds in inducing wind mixing (Simpson and Souza, 1995).

Stratified conditions with a shallow wind mixed layer may well have been present during parts of the experiment, most likely between 8 and 15 September and 22 to 25 September, when offshore winds coincided with weak tidal mixing. Coastal upwelling

might have taken place, when winds came from the northeast to southeast. An indication of coastal upwelling might be the rather high salinity of the water between 15 and 21 September. Strong winds from the northwest would have destroyed any stratification present between 25 and 27 September.

Relatively fresh water penetrated near the platform on 28 September (Fig. 5a). An explanation for the appearance of this water could be instability in the coastal flow of less saline water, caused by the reversal of the residual alongshore current on 27 September.

4.2. Complex dissolved inorganic carbon chemistry

A mixing line can be drawn for salinity and DIC by exclusion of the 78 black squares, which represent water with high salinity and DIC from 7:50 U.T.C. at 15 September to 7:10 U.T.C. at 16 September (Fig. 8a):

$$\text{DIC} = 2909 - 24.4S \quad (4)$$

The line has 653 datapoints and a correlation coefficient of -0.67 . Its end-members are fresh water with a DIC content of $2909 \mu\text{mol kg}^{-1}$ and seawater with a salinity of 35 and a DIC content of $2056 \mu\text{mol kg}^{-1}$. Scatter around the line indicates that either the end-members did not have a constant composition or that additional processes occurred. High f_{CO_2} and DIC at a salinity of 31.1–31.5 and 32.3–32.8 suggest enrichment of relatively saline water with CO_2 and DIC (Fig. 8a and b). An explanation could be mineralisation of accumulated organic matter in water and (suspended) sediment further out at sea and subsequent transport of saline water enriched in CO_2 and DIC into the coastal zone by upwelling. Nevertheless, a straightforward relationship between DIC and f_{CO_2} was not present (Fig. 8c).

Cooling of the water did not induce the abrupt decrease of f_{CO_2} on 24 September, as cooling only started after the change had occurred (Fig. 5b and e). More likely algal uptake of CO_2 was responsible for the undersaturation between 24 and 28 September. The abrupt change of f_{CO_2} in surface water indicated arrival of a ‘‘new’’ water type in the area.

Calculated alkalinity varied from 2240 to 2470 $\mu\text{eq kg}^{-1}$, a larger range than previously observed

(Pegler and Kempe, 1988; Hoppema, 1991a,b; Table 1). The graph of alkalinity and salinity did not indicate conservative mixing of seawater and fresh water (Fig. 8d). Apparently either the fresh water did not have a constant alkalinity or other processes overshadowed the effect of mixing on alkalinity (Hoppema, 1991b). Dissolution of marine carbonates in nearby estuaries could have increased alkalinity (Kempe, 1982). Anaerobic mineralisation in sediments (Kempe, 1995) probably did not affect alkalinity in the coastal zone, as subsequent oxidation of reduced components in the water would have compensated preceding changes of alkalinity.

4.3. Temporal and spatial variability of the inorganic carbon chemistry

Not much is known about the seasonal, interannual and regional variability of DIC and CO_2 in the North Sea. The available data will be discussed for the coastal zone within 20 km offshore between the river Rhine and the North Sea Channel. As the data originate from four expeditions in two different years, they only offer snapshots of the complex inorganic carbon chemistry.

Water of the rivers Rhine and the Scheldt (Fig. 1) is often undersaturated with oxygen (O_2), highly supersaturated with CO_2 and has high contents of alkalinity, inorganic and organic carbon relative to open North Sea water (Kempe, 1982). Freshwater input may induce high DIC, alkalinity and f_{CO_2} in the coastal zone relative to the open North Sea (Pegler and Kempe, 1988; Hoppema, 1990, 1991a,b; Kempe and Pegler, 1991). Water from the North Sea Channel with low salinity, high DIC and alkalinity, may reach the coastal zone near Noordwijk (from Hoppema, 1990, 1991a,b).

In March and April 1986 low contents of dissolved CO_2 and high contents of O_2 in surface water were attributed to primary production (Hoppema, 1991a,b; Table 1). DIC contents decreased from March to May 1986. Undersaturated CO_2 and high chlorophyll-*a* levels were observed in May (Pegler and Kempe, 1988). Probably algal blooms had depleted DIC and CO_2 . Warming of the water would have counteracted the decrease of f_{CO_2} .

Both f_{CO_2} and DIC were higher in September 1993 than in May 1986 (Pegler and Kempe, 1988;

Table 1). This combined increase of f_{CO_2} and DIC probably was the result of net mineralisation and air–sea exchange CO_2 , while warming further increased surface water f_{CO_2} .

The DIC content was somewhat higher in November 1986 than in September 1993, while average f_{CO_2} in September was close to the range indicated for November. The dissolved O_2 content was under-

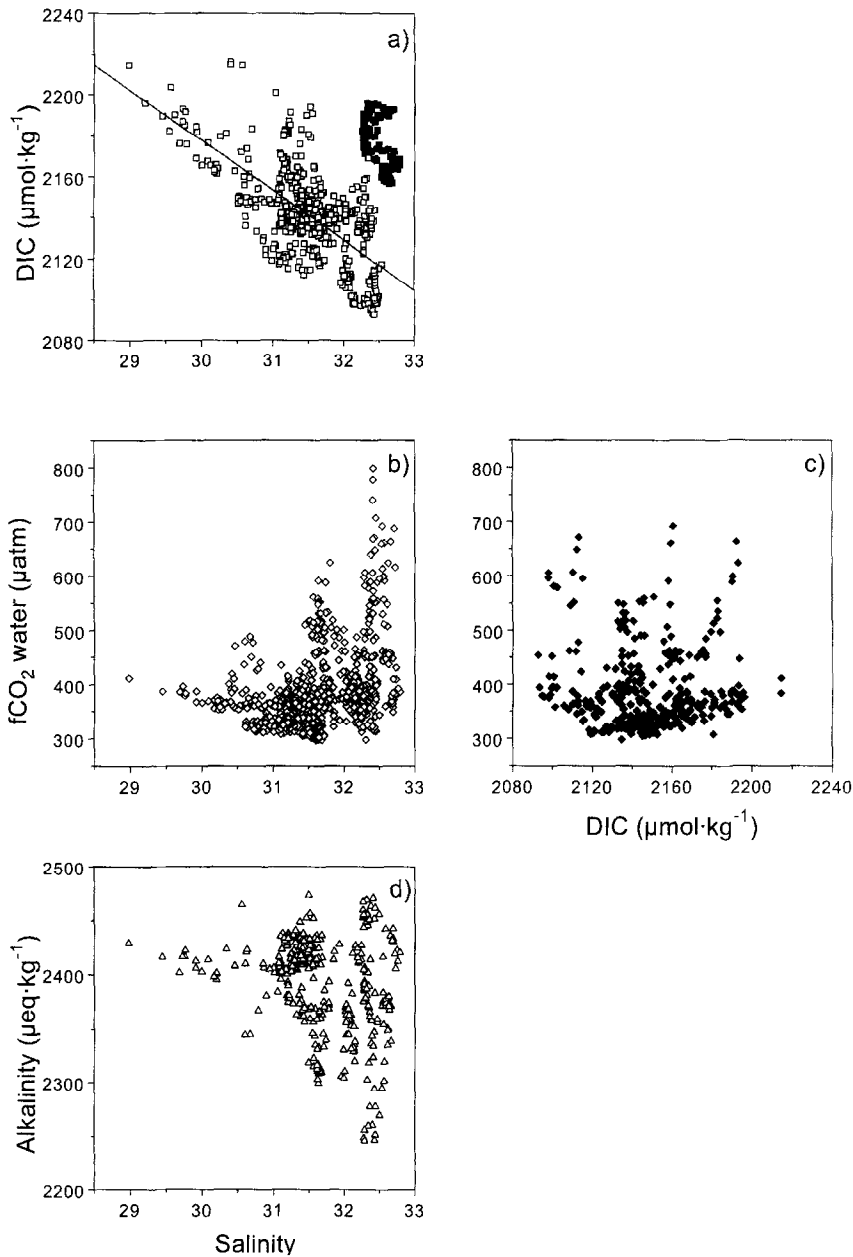


Fig. 8. Dissolved inorganic carbon (a), f_{CO_2} in water (b), and alkalinity (d) as a function of salinity of 8–30 September 1993 at Measuring Platform Noordwijk. Also indicated is f_{CO_2} in water as a function of DIC (c). The dotted line with the equation $\text{DIC} = 2909 - 24.4.5$ ($n = 653$, $r = -0.67$) results from linear regression for the white squares in (a). The 78 black squares, which represent water with high salinity and DIC from 7:50 U.T.C. on 15 September to 7:10 U.T.C. on 16 September, have been excluded from the regression.

Table 1

Surface water characteristics within 20 km offshore between the river Rhine and the North Sea Channel in 1986 (Hoppema, 1991a,b [1]; Pegler and Kempe, 1988 [2]) and at Measuring Platform Noordwijk in September 1993 [3]

	1986			1993	1986
	March [1]	April [1]	May [2]	September [3]	November [1]
Salinity	29–31	29–31	~ 31	29.0–32.8	27–31
Temperature (°C)	2.4	5.9	10	15.6–17.4	9.8
DIC (mmol kg ⁻¹)	> 2.10–2.15	> 2.05–2.10	1.90–2.00	2.09–2.22	> 2.15–2.25
Alkalinity (meq kg ⁻¹)	> 2.33–2.39	> 2.35–2.36	2.38	2.24–2.47	> 2.35–2.40
f_{CO_2} (μatm)	> 150–200	> 180–200	< 200	300–800	> 400–450
Chlorophyll- <i>a</i> (mg m ⁻³)	n.d.	n.d.	> 25	n.d.	n.d.
O ₂ saturation (%)	103–105	110–113	n.d.	n.d.	96–98

n.d. = no data available.

saturated in November (Table 1; Hoppema, 1991a,b). These observations could be explained by a combination of autumn cooling and continued mineralisation. Hoppema (1991a,b) suggested that the high DIC and f_{CO_2} levels in November 1986 partly resulted from decomposition in (suspended) sediments and ensuing fluxes of inorganic carbon into the water.

Apparently, biological uptake of CO₂ in spring and net mineralisation in summer and autumn largely determined the composition of the inorganic carbon system in the Dutch coastal zone. Seasonal temperature changes would be expected to have affected the solubility of f_{CO_2} strongly. The effects of air–sea exchange and precipitation and dissolution of calcareous material could not be discriminated in the CO₂ signal. The dissolved inorganic carbon chemistry in the coastal zone is complicated by mixing in of fresh water of variable composition, offshore gradients, stratification and coastal upwelling.

Values of 150–800 μatm for f_{CO_2} in surface water with large variations within a single tidal cycle have been observed in the coastal zone near Noordwijk. This wide range is in agreement with data for the mouth of the river Scheldt some 150 km towards the south (Fig. 1). In this area the f_{CO_2} of surface water varied from 100 μatm in May 1993 to 410 μatm in June 1992 and to 700 μatm in October 1993 (Frankignoulle et al., 1996a). In May strong CO₂ undersaturation was accompanied by high chlorophyll-*a* concentrations. In November 1993 large variability of f_{CO_2} from 350 to 600 μatm was related to the semi-diurnal tidal cycle, such that high

f_{CO_2} occurred during low tides and was ascribed to river influence (Frankignoulle et al., 1994).

4.4. The atmospheric CO₂ content and wind direction

The atmospheric contents of CO₂ had clearly been influenced by the nearby land, industry and population centres during the frequent offshore winds. The apparent inverse relationship between wind speed and mixing ratios of CO₂ reflected that offshore winds had a high and variable CO₂ content, while strong winds from the open sea had a more constant CO₂ content (Fig. 7a and b). A potential diurnal trend in the mixing ratio of CO₂ was overshadowed by the variability of anthropogenic emissions, wind speed and wind direction.

4.5. Sink or source for atmospheric CO₂?

The air–sea flux of CO₂ is insufficient to achieve equilibrium of CO₂ in these coastal waters relative to the atmosphere. Effects on f_{CO_2} in surface water of biological production, mineralisation, seasonal temperature changes, mixing in of river water, coastal upwelling and possibly calcification and dissolution of calcareous material by far exceed the stabilizing effect of air–sea exchange.

It is not possible to determine from this study, whether the Dutch coastal zone constitutes a net annual sink or source for atmospheric CO₂. During September 1993 the flux measurements had a momentary, local significance as a consequence of the

variable hydrography and dissolved inorganic carbon chemistry. The river Rhine and other freshwater sources add water with high contents of inorganic and organic carbon to the coastal zone. Part of the imported organic carbon is mineralised, increasing DIC and f_{CO_2} (S.V. Smith and Hollibaugh, 1993; Kempe, 1995). Sporadic upwelling adds water enriched in DIC to the coastal zone. On the other hand, river water introduces high contents of nutrients, which stimulate algal blooms and photosynthetic uptake of CO_2 (Hoppema and De Baar, 1991; Kempe, 1995). Dissolution or precipitation of carbonates and seasonal temperature changes also affect the carbon budget of the coastal zone.

Extensive study of the organic and inorganic carbon flows over all seasons, entering and leaving the coastal zone, would be necessary to quantify the role of the complex coastal zone in the global carbon budget. Simultaneous measurements of the in situ processes, affecting the dissolved inorganic carbon system, may yield a better understanding of the mechanisms behind it.

5. Summary

The observed, highly complex dissolved inorganic carbon chemistry resulted from variability of tidal mixing, wind speed, wind direction, freshwater input, coastal upwelling and biological processes. Consequently, it was impossible to completely unravel the individual endmembers and processes involved. Estimated air–sea exchange of CO_2 should be used with caution in the light of potential stratification.

Large variability of surface water f_{CO_2} was observed at short time scales. Very high CO_2 contents likely resulted from seasonal warming of the water and mineralisation of accumulated organic matter in water and sediments in combination with coastal upwelling. Undersaturated CO_2 values were ascribed to uptake of CO_2 by algal blooms. In all seasons rapid physical, chemical and biological processes prevented air–sea exchange from reaching equilibrium between f_{CO_2} in surface water and in the atmosphere. It cannot be ascertained from this study whether the Dutch coastal zone is a net sink or source for atmospheric CO_2 .

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